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Multi-Atom Resonant Photoemission and the Development of Next- Generation Software and High-Speed Detectors for Electron Spectroscopy

Alexander W. Kay

Materials Sciences Division

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Ph.D. Thesis

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Alexander William Kay
Ph.D. Thesis

Department of Physics
University of California, Davis

and

Materials Sciences Division
Ernest Orlando Lawrence Berkeley National Laboratory
University of California
Berkeley, CA 94720

September 2000

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Development of Next-Generation Software and
High-Speed Detectors for Electron Spectroscopy**

By

Alexander William Kay

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DISSERTATION

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Abstract

This dissertation has involved the exploration of a new effect in photoelectron emission, multi-atom resonant photoemission (MARPE), as well as the development of new software, data analysis techniques, and detectors of general use in such research.

We present experimental and theoretical results related to MARPE, in which the photoelectron intensity from a core level on one atom is influenced by a core-level absorption resonance on another. We point out that some of our and others prior experimental data has been strongly influenced by detector non-linearity and that the effects seen in new corrected data are smaller and of different form. Corrected data for the MnO(001) system with resonance between the O 1s and Mn 2p energy levels are found to be well described by an extension of well-known intraatomic resonant photoemission theory to the interatomic case, provided that interactions beyond the usual second-order Kramers-Heisenberg treatment are included. This theory is also found to simplify under certain conditions so as to yield results equivalent to a classical x-ray optical approach, with the latter providing an accurate and alternative, although less detailed and general, physical picture of these effects. Possible future applications of MARPE as a new probe of near-neighbor identities and bonding and its relationship to other known effects are also discussed.

We also consider in detail specially written data acquisition software that has been used for most of the measurements reported here. This software has been used with an existing experimental system to develop the method of detector characterization and then data correction required for the work described above.

The development of a next generation one-dimensional, high-speed, electron detector is also discussed. Our goal has been to design, build and test a prototype high-performance, one-dimensional pulse-counting detector that represents a significant advancement in detector technology and is well matched to modern high-brightness synchrotron radiation sources and high-transmission electron-energy analyzers as typically used in photoelectron spectroscopy experiments. The general design of the detector and the results of initial tests are discussed and the acquisition of photoelectron spectra with the first test detector is described.

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1 General Introduction

The advances in the production of intense tunable light sources in the extreme ultraviolet and soft x-ray regime using synchrotron radiation have allowed a broad range of scientific work to be pursued. The growth of scientific activities using these light sources also demonstrates the relationship between technological advances in scientific instrumentation and the natural progression of scientific knowledge and discoveries using these improved tools. Besides allowing well-developed experimental techniques to be performed more routinely and with higher precision, these instrumental advances open doors to the investigation of new physical processes and the development of new experimental techniques. It is in this spirit that we have performed a unique series of experimental studies involving interatomic multi-atom resonant photoemission. Although intraatomic single-atom resonant photoemission is well known, its interatomic counterpart could provide a powerful new technique for studying atomic identities and bonding. These studies are furthermore entirely dependent upon the tunable photon energy and high fluxes available at modern synchrotron radiation sources. This search for a new type of interatomic resonant photoemission effect is the focus of this dissertation and is more fully introduced later in this chapter.

Following this concept of a causal relationship between enhanced experimental capabilities and scientific advancement, we also have addressed the technological restrictions of the instrumentation presently used in conjunction with these radiation sources. Such a consideration is important in order to permit future scientific work to continue to prosper and to take full advantage of these light sources. With this in mind and with the performance of current electron detector systems being in fact a serious

limiting factor in many experiments, including our own, we have designed, constructed, and tested a prototype version for a new high-speed, one-dimensional electron detector appropriate for use in our own spectroscopy experiments and also of obvious use for many other similar experiments, even beyond synchrotron based work. In addition, noting that the software which controls a given experimental system can now be as important as the hardware in successfully carrying out a given experiment, we have written a versatile new software package for controlling the primary experimental end station used in this dissertation.

In this chapter, we will briefly introduce the related physical processes and experimental techniques relevant to the experimental and theoretical discussions in later chapters. First, we will discuss the most basic properties of synchrotron radiation sources and then consider the fundamental aspects of photoemission and other related processes that are especially relevant to our experimental work, including Auger electron emission and fluorescent x-ray emission, as well as x-ray absorption spectroscopy. We will then continue with a discussion of intra-atomic resonant photoemission (RPE) as a preface and motivation for our own investigations of an interatomic RPE process. After introducing the basic process involved in this interatomic resonance, we will relate the potential capabilities of this type of measurement to other independent but closely related experimental techniques. Concluding this chapter is a short outline of the contents of the remainder of this dissertation.

1.1 Synchrotron Radiation Sources

Synchrotron radiation sources have evolved from the first generation of parasitic use of the synchrotron radiation produced in electron or positron storage rings used for high-energy physics experiments. The centripetal acceleration of relativistic charged particles in these accelerators inherently results in particle energy loss in the form of radiation. Second-generation sources were specifically designed for and dedicated to the production of synchrotron radiation.

The first- and second-generation sources depended upon bending magnets to maintain the orbit in the storage ring of electrons or positrons at extreme-relativistic energies up to several GeV. The spectral distribution of the radiation produced in these bend magnets is quite broad, covering the infrared through hard x-ray energy ranges, depending upon the particle energy and the acceleration they experience in the magnetic field. With appropriate monochromatization via reflection from a grating for lower energies and from one or more single crystals for higher energies in a beamline, which also provides a high-vacuum path for the photons to reach an experimental station, a narrow range of photon energies can be selected over a very wide range of energy, and with easily variable resolving power or bandwidth. In addition, well known relativistic effects, understood by considering the Lorentz transform between the electron and laboratory reference frames of the orbiting electrons, cause the radiation emitted from the bend magnet to be highly forward focused into a narrow angular distribution centered in the plane of the ring orbit. This angular distribution is typically over only a fraction of a milliradian so that the normal flux losses of standard x-ray anode sources due to a high angular emittance are avoided. Thus, radiation with very high brightness can be achieved.

Finally, a natural polarization in the radiation (linear in the plane of the orbit and circular out of the plane) allows the experimentalist to take advantage of the differing selection rules for the photoexcitation of the energy levels in the atoms.

Rather than simply using the radiation produced by the magnets that maintain the orbit, the storage ring of third-generation light sources is built in a series of connected straight regions in which specialized linear arrays of magnets can be inserted. These magnetic devices are much more efficient in the production of photons than bend magnets, and by varying the gap between the magnets through which the storage ring current flows, the intensity of particular photon energies can be optimized, although monochromators are still usually used in the beamlines to obtain final sufficiently narrow bandwidths.

These arrays of magnets are collectively called insertion devices, and the extensive utilization of two types of these— wigglers and undulators— is a primary characteristic of third-generation sources. The principal difference between a wiggler and undulator is in the deflection experienced by the charged particles as they pass each magnet in the device. Undulators typically have smaller deflections that are designed to allow the photons generated in each period of the device to add coherently, while wigglers behave essentially like an incoherent array of bend magnets. While the simplest designs result in a fixed linear polarization of the photons that is similar to a bend magnet viewed in-plane,, more sophisticated arrangements of the magnets can create a variable elliptical or circular polarization, or even out-of-plane linear polarization. The experimental data in this dissertation were obtained using both a bend magnet and an elliptically polarized undulator capable of producing radiation of arbitrary polarization.

Both the production of synchrotron radiation and the wide range of experimental studies that may be performed using this radiation are more fully discussed in various sources, including those in Refs. [1,2].

All of the experimental research presented in this dissertation was performed at the Advanced Light Source in Berkeley, a third-generation facility that is optimized for high-brightness, low emittance operation in the vacuum ultraviolet (VUV)/soft x-ray energy regime, or from about 10 eV to 1000–2000 eV. Initial experiments were performed at the bend-magnet based beamline 9.3.2 while more recent work was done at the elliptical-polarization-undulator based beamline 4.0.2. The tunable energy and high fluxes available from these beamlines have been essential to the experimental work.

1.2 Photoelectron Emission and Spectroscopy

The field of photoemission has proven to be an extremely rich and productive one since its conception. An understanding of the photoelectric effect, due to Einstein [3] was of course one of the historical steps in the development of quantum theory and established the need to consider the discrete nature of the photon. The process is illustrated schematically in Fig. 1-1; here, the atom absorbs a photon of a given energy, with a transfer of the photon energy to an electron in a given energy level of the atom. The relationship between the photon energy, $h\nu$, and the kinetic energy, E_k , with which the electron is ejected in a photoemission process is given by Einstein's photoelectric equation,

$$E_k = h\nu - E_b^v(i), \quad [1-1]$$

where $E_b^v(i)$ is the binding energy of an electron in the i^{th} level of the atom, as referenced to the vacuum level.

Modern photoelectron spectroscopy (PES), which is also often simply called "photoemission", is by now a standard and well-developed technique of special importance in the fields of surface science and condensed-matter physics [4]. PES involves the measurement of the spectrum of emitted electrons as a function of kinetic energy or binding energy with Fig. 1-2 illustrating a typical broad PES spectrum emitted from an MnO(001) single crystal. Several fundamental aspects of the photoemission process warrant mention here. First, the photoemission process allows element specific information to be obtained for a given sample, due to the discrete set of strongly bound core-levels, $E_b^v(i)$, that uniquely characterize each element in the periodic table. Additionally, the chemical or structural environment of a given atom may result in observable changes to these $E_b^v(i)$ (sometimes referred to as chemical shifts) and the study of these further extends the sensitivity and utility of PES. Beyond this photoelectrons emitted from the weakly bound valence levels can also be studied, permitting the direct measurement of energy bands and other more complex properties related for example to magnetism and superconductivity [4]. Finally, for the photon energies considered here, the interaction of the radiation with the electrons can be treated rather accurately in the dipole approximation, with well-known selection rules and theoretical methodologies for determining intensities [4].

The suitability of PES to surface studies of materials is essentially due to the short inelastic attenuation length of the photoelectrons in the sample, as shown in Fig. 1-3,

where a “universal curve” for electron attenuation lengths in a large number of elemental samples as a function of electron kinetic energy is shown [5]. Although not really universal in value from one material to another, the general shape of this curve is universal, with theoretical expressions available for estimating it for a specific material [5b]. Since spectra such as that in Fig. 1-2 are analyzed primarily in terms of the unscattered or “no-loss” features, photoelectrons from far below the surface region of the sample are heavily attenuated through inelastic processes, and are either not emitted from the sample, or appear as a continuous inelastic background at kinetic energies less than predicted by Eq. 1-1. In Fig. 1-2, this type of background is clearly seen below the no-loss peaks, with a step in the background occurring on the low kinetic energy (high binding energy) side of each peak.

Secondary Effects: Auger Electron and Fluorescent X-ray Emission

The hole left in the final state of the photoemission process will eventually decay by one of two processes: Auger electron emission or fluorescent x-ray emission. These processes are diagrammed in Fig. 1-4.

Auger emission involves three energy levels (binding energies) in the atom. The binding energy to form the initial hole $E_b^v(1)$, the binding energy of the electron that fills the hole $E_b^v(2)$, and the binding energy of the electron to which the excess energy is finally transferred $E_b^v(3)$. The relevant energy conservation equation here is

$$E_k = E_b^v(1) - E_b^v(2) - \overline{E}_b^v(3) , \quad [1-2]$$

where the first two binding energies correspond to leaving the system with one hole (in level 1 or level 2), and the third $\bar{E}_b^v(3)$ to removing electron 3 with electron 2 already missing and thus leaving the system with two holes (in levels 2 and 3). If the energy difference $E_b^v(1) - E_b^v(2)$ is sufficient to promote the third electron into an unbound state (i.e., is greater than $\bar{E}_b^v(3)$), then an Auger electron can be emitted, and its kinetic energy will furthermore be characteristic of the available energy levels in the atom, again allowing element-specific detection. As in PES, Auger electron spectroscopy (AES) is a surface sensitive technique due to electron inelastic attenuation effects. Because the kinetic energies of the Auger electrons are similar to the kinetic energies of emitted photoelectrons, AES is generally performed simultaneously with PES, as illustrated by the presence of the specific oxygen and manganese Auger lines identified in the PE spectrum of Fig. 1-2.

In fluorescent x-ray emission spectroscopy (XES), the energy distribution of emitted photons is measured, again allowing element specificity in the same manner as with PES. The photons are emitted in a process conceptually the same as in AES, with Fig. 1-4 again illustrating the process. But here, the relevant energy conservation equation is simpler than for the Auger case, being

$$h\nu = E_b^v(1) - E_b^v(2), \quad [1-3]$$

where $h\nu$ is the emitted photon energy. However, the much longer attenuation lengths (absorption lengths) typical of the VUV and soft x-ray energy photons considered here

make this technique essentially a bulk technique, unless extreme grazing incidence geometries are utilized. The instrumentation required for XES experiments is significantly different from the PES/AES instrumentation, due to the need to detect and resolve in energy photons in the VUV to soft x-ray region.

While both possible channels are generally available for the secondary decay of the initial photoemission hole in some level 1, Auger decay dominates for typical core levels accessible with XPS photon energies (<2 keV) [6]. However, for filling of deep core holes (>10 keV), fluorescence decay dominates. The fraction of events resulting in x-ray production is termed the fluorescence yield.

Photoelectron Diffraction

Only a very small portion of our work concerns the subject of photoelectron diffraction (PD) [7], and so only the simplest consideration of this phenomenon is appropriate here. In the PES (or AES) process, an emitted electron wave function may involve scattered components from the atoms surrounding the emitter atom. Given local positional order in the sample, the superposition of the unscattered and scattered components can produce strong diffraction effects in a given core-level photoemission intensity as a function of either emission direction (by scanning direction over the hemisphere above the sample) or emission energy (by scanning the photon energy at a fixed emission direction). In either case, the relative phases of the summed direct and scattered waves at the detector are changed, producing modulations in the photoemission intensity, often as high as 50%. We will later show some data in which these modulations are present, and they have to be allowed for in order to clearly distinguish the interatomic resonant photoemission effects that are the primary focus of this work. In

general, analysis of the PD pattern can reveal the short-range geometric structure near the surface of the sample, making PD an extremely powerful probe of surface atomic structure [7].

1.3 X-ray Absorption Spectroscopy

When x-rays pass through any material, a fraction of them will be absorbed. In fact, a primary source of this absorption in the VUV/soft x-ray regime is just the photoelectric effect mentioned above, which produces a photoelectron in a free state above the vacuum level. Beyond this, absorption of a photon so as to excite an electron from a bound occupied state to a bound unoccupied state can also lead to strong absorption. This latter type of absorption occurs near what are called edges or resonances associated for example, with different core levels in a given atom. In this dissertation, we will pay special attention to the two edges in Mn associated with its $2p$ levels, which are split by the spin-orbit interaction into a $2p_{3/2}$ at lower binding energy and a $2p_{1/2}$ at higher binding energy. Measurement of the amount of absorption as a function of x-ray energy directly reveals these so-called edge structures, where the level of absorption suddenly increases. The relevant energy conservation equation near these edges is more complex, in that no electron leaves the system, but the system simply goes from its ground state with some level l occupied and level j unoccupied to an excited state with level l unoccupied and level j occupied

$$h\nu = E_{tot}^{exc}(\text{hole in } l, j \text{ occupied}) - E_{tot}^{gnd}(l \text{ occupied, hole in } j), \quad [1-4]$$

where the energies here are total electronic energies for the entire system. If the level j is above the vacuum level, then x-ray absorption reduces to the photoelectric effect.

While other well-known absorption mechanisms exist beyond the photoelectric effect and near-edge absorption, including Compton scattering, pair-production, and nuclear disintegration, they are entirely negligible for the photon energies considered in this work ($<1\text{keV}$).

X-ray absorption spectroscopy (XAS), in which the detailed form of the core-level absorption edges are recorded in a sample (e.g. by transmission through thin foils, reflection, or total/partial electron-yield measurements [8]), shares the element specificity seen in PES. An example of an XAS edge profile is shown in Fig. 1-5 for the case of the Mn $2p$ edges in an MnO(001) single crystal, which are here clearly split into a $j=3/2$ and $1/2$ doublet by the spin-orbit interaction. Because of the relatively deep penetration depths of the photons, XAS is generally considered a bulk technique; however, if inelastically scattered secondary electrons are used to detect the absorption, XAS in fact may only reach in to an average depth of 20-30 Å.

The absorption profile, $\mu(h\nu)$, is a measurement of the attenuation of light in the sample as a function of energy. This measured absorption coefficient can be related to the complex index of refraction $n_r = \sqrt{\epsilon} = 1 - \delta + i\beta$, via the relationship $\mu(h\nu) = 4\pi\beta(h\nu)/\lambda_x$. The two optical constants, δ and β , are in turn related through a simple Kramers-Kronig transform, so that measurement of only $\mu(h\nu)$ is in fact sufficient to obtain both optical constants and the total complex index of refraction or dielectric function. This will prove to be quite important to our work, as discussed in some detail in Ch. Four.

Also shown in Fig. 1-5 are two tabulated curves for β , as obtained from standard references on x-ray optics [9]. These represent the expected effects from photoelectron emission only, and do not accurately account for the special many-electron effects occurring near the absorption peaks. The more recent tabulation of Chantler includes the spin-orbit splitting of the $2p$ levels [9c]. Note that these two different curves asymptotically agree very well with one another on either side of the $2p$ resonances.

1.4 Single Atom Resonant Photoemission

Before introducing the specific physical process investigated in this work, it is beneficial to briefly consider the well-known phenomenon of intraatomic resonant photoemission [10,11,12], which we will refer to as *single-atom* resonant photoemission (SARPE) for reasons that will become clear.

A classic case of SARPE results due to Krause and co-workers [13] is shown in Figs. 1-6 and 1-7. Here, as shown in the energy-level diagram of Fig. 1-6, the excitation of a photoelectron from the Mn $3d$ level in a gas-phase Mn atom is followed as the photon energy is increased and reaches ~ 50 eV, an energy that is just sufficient to excite a deeper-lying Mn $3p$ electron in the same atom up to the first dipole-allowed bound excited state, which will also be of Mn $3d$ character. When this occurs, the very strong resonant Mn $3p$ -to-Mn $3d$ excitation can be considered to decay immediately so as to produce a free electron at the same energy as the photoelectron directly excited from Mn $3d$ at the same photon energy, as shown by the dashed arrows in Fig. 1-6. This resonant process, which is formally related to Auger electron emission, but more properly termed autoionization [14], is simultaneous with and coherent with the usual direct

excitation of the photoelectron, and it can lead to significant increases and decreases in intensity, depending on the relative phases of the direct and resonant channels. The variation of the intensity of the Mn $3d$ photoelectrons has been measured as photon energy passes over this particular resonance region and the resulting data [13a] are shown in Figs. 1-7(a)--a typical spectrum on resonance, and 1-7(b)--the energy dependence of just the Mn $3d$ intensity. Note the change in sign of the resonance effect as photon energy varies due to a change in phase between the direct and resonant channels, with the resonance curve generally following one possible manifestation of a Fano profile [14]. Simple one-electron Hartree-Fock (HF) theory is unable to predict this phenomenon, whereas many-body perturbation theory (MBPT) is [13b]. The peak intensity is increased by a maximum of a factor of about 7 for this case. As another overall measure of the strength of the resonance, the positive and negative effects of the resonance (darker grey-shaded areas) can be integrated over the full energy range over which the effect causes significant differences in intensity from the simple non-resonant Hartree-Fock (HF) theory [13b] and compared to the estimated non-resonant intensity (lighter grey-shaded areas); this leads to an overall effect of about 63%.

The strength of SARPE is strongly dependent upon orbital overlap of the two energy levels in the atom involved, without which, the coupling of the two channels via the Coulomb interaction vanishes. By considering such resonances between a valence and core level in an atom, SARPE is often used to study element specific contributions to photoemission from the valence band [4b]. That is, by tuning over the core level of a given atom, the portion of the valence emission associated with just the resonating energy level(s) strongly localized on that atom is enhanced and so is finally extractable from the

overall valence structure that may contain contributions from all atoms present. SARPE thus represents one type of element-specific probe of valence electronic structure.

1.5 Introduction to Multiple Atom Resonant Photoemission

The process studied in this dissertation is rooted in the same essential concept as SARPE, but distributes the two energy levels involved across two atoms. In this interatomic effect, a photoelectron is ejected from a given core level of a first atom " A " and the photon energy is tuned through an absorption edge or threshold for a core level on a neighboring atom " B ". Such a process is expected to involve the contribution of several of the atoms of type B around the A type atom and so is termed multi-atom resonant photoemission (MARPE). A diagrammatic model of the process is given in Fig. 1-8 for the case of interaction between only two atoms, with A = oxygen from which an O 1s photoelectron is being emitted on the left and B = manganese in which a Mn 2p electron is being excited to some unoccupied state on the right. An artist's conception of the effect is further shown in Fig. 1-9.

If such interatomic effects perturb the intensity of photoemission from the A atom significantly enough to be measurable, they would represent an interesting new aspect of the x-ray absorption process. But beyond this, a sufficiently short-range (nanometer or less) interaction would allow MARPE to be applied as a new probe of matter in which emission/excitation of one atom A could be directly used to sense the presence of other atoms B near to it, at least on the nanometer scale that is commonly discussed in many current materials science developments. Adding magnetic sensitivity via magnetic

circular or linear dichroism (as will be discussed below) should also permit selectively monitoring the magnetic order of those atoms B that are near to A .

As a further rationale for pursuing this topic further, this projected capability can be compared to several current characterization techniques based on x-rays, electrons, and nuclear transitions. Several methods presently permit determining the bulk atomic structures of solids, including x-ray diffraction and extended x-ray absorption fine structure (EXAFS) [15]. EXAFS is also element-specific via core-level electronic excitations, allowing the local structure around each atomic type to be determined, at least as to the radial positions of shells of neighboring atoms. If the atomic structure near solid surfaces is to be probed, one can add to this list low energy electron diffraction (LEED) [24], and photoelectron diffraction (PD) [7], with the latter (as introduced above) also being element-specific via core excitation. However, as powerful and widely used as the foregoing methods are, none of them permits directly determining the type of atom that neighbors a given atom. That is, some of these techniques (e.g. EXAFS and PD) may be element-specific for the central atom in the structure, but there is no simple way to determine the near-neighbor atomic identities (atomic numbers) from them. In some cases, use can be made of the differences in electron-atom scattering strengths between different atoms in these last two methods, and then comparing experiment with model calculations, but this is only unambiguous when atomic numbers are relatively far apart, and even then, this procedure often provides only a semi-quantitative distinction of atomic identity. From this brief overview, it thus appears that MARPE could add a significant new aspect to the array of x-ray based methods for characterizing matter. More broadly, the fact that all atoms beyond He have a core level that can be used as one

side of a MARPE experiment indicates that it could have broader applicability across the periodic table than two other powerful spectroscopic probes, Mössbauer spectroscopy and nuclear magnetic resonance, which require the use of certain nuclei or nuclear pairs.

In brief review of our own work on MARPE, initial experimental [16,17,18,19] and theoretical [18,20] work demonstrated evidence for strong and easily detectable MARPE effects throughout a range of materials and energy level combinations. These effects were measured not only in PES as indicated in Figs. 1-8 and 1-9 [16,17,18], but via secondary decay processes with AES and XES measurements as well [18,19]. Indeed, evidence of a nanometer length scale in the interaction [21] was found, in general agreement with similar independent measurements [22].

More recently, the identification of significant instrumental influences, in particular strong detector non-linearity with countrate, on the first set of measured data has shed new light on the effect [23]. New fully corrected experimental data, together with corrected microscopic theoretical calculations that were found to have had a small but important computational error in previous results [20] finally result in excellent agreement between experiment and theory. In later chapters we will consider in detail both the instrumental problems (Ch. Five) and the corrected experimental results (Ch. Four) for those systems that we have so far been able to more fully investigate, concentrating on the PES results. In addition, the corrected microscopic theory as well as a simpler macroscopic x-ray optical theory will be discussed and compared to the corrected experimental results.

1.6 Dissertation Outline

The remaining chapters of this dissertation are concerned with instrumentation and experimental results, and overall conclusions. Chapter Two consists of a short overview of the experimental systems and data manipulation schemes used for this work. Chapter Three describes data acquisition software designed and written by the author and used in the collection of the data for this dissertation, and so in some respects represents a continuation of the material in Chapter Two. However, because the software is quite complex and was developed as part of this dissertation, the discussion is somewhat more detailed and oriented towards documentation of the work.

Chapters Four and Five contain the experimental results and discussions relating to MARPE, with Chapter Four concentrating on both the past (briefly) and current understanding of the measured data as well as the theoretical treatment of the process. Chapter Five contains a detailed discussion of instrumental effects recently discovered in our measured data that are responsible for the recent reinterpretation of the data as contained in Chapter Four. This includes an analysis of the detector non-linearity and the application of this analysis to data correction, with specific attention given to the MARPE datasets. However, the correction procedure discussed here is generally applicable to any measurements made with the same or similar instrumentation, and in fact should be applied in any future use of this particular detector.

Chapter Six focuses on a unique and important instrumentation development project: a high-speed multichannel electron detector designed for use in electron and other related particle-counting spectroscopies. This detector is a significant improvement in technology compared to today's standard detector systems and represents a critical

need for synchrotron-based and even laboratory based experiments throughout the world where a combination of countrate, spatial resolution, and response characteristics often limit both the time required to collect and the final accuracy of experimental data. In fact, this detector directly addresses the instrumental difficulties encountered during the MARPE experiments carried out as part of this dissertation. If it had been developed beyond the testing stage and used in our experimental work, it would have negated the need for any correction procedure to the data and allowed us to avoid the initial conclusions drawn from the uncorrected data.

Finally, a brief conclusion is given in Chapter Seven where we return to the subject of MARPE and a discussion of several other independent experiments directly stimulated by our work [22,25,26]. We also consider possible directions of future studies in the field.

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Fig. 1-1 Simple model of the photoemission process, illustrating the excitation of a core level electron into the continuum by a sufficiently energetic photon. The binding energies are referenced to the vacuum level. Note that the final excited state atom contains a hole; the atom is now ionized.

Fig. 1-2 A photoemission spectrum of MnO over a large energy range obtained with a photon energy of 750eV, as generated by a synchrotron radiation source. A number of characteristic core-level photoemission lines from both Mn and O are clearly seen, together with those from the valence bands (V.B.). Several Auger electron emission lines are also visible (O *KLL* and Mn *LMM*).

Fig. 1-3 Illustration of the “universal curve” for electron attenuation in solid state materials as a function of electron (kinetic) energy (from [5]). For most of this range, the attenuation lengths are less than $20\text{\AA}$, leading to the extreme surface sensitivity characteristic of electron spectroscopies such as PES and AES.

Fig. 1-4 Simple model of the Auger electron emission (or fluorescent x-ray emission) process in which an excited or ionized atom fills a hole with an electron in a less deeply bound energy level. The hole is left after the photoemission process or may be created by other means (typically electron bombardment). Note that for Auger electron emission, there are three energy levels involved in the filling of the hole, E_1 , E_2 , and E_3 with the final Auger electron kinetic energy, E_k , being given by simple consideration of energy conservation (cf. Fig. 1-2). The fluorescence process involves only two energy levels E_1 , E_2 and a final fluorescent photon energy, $h\nu$.

Fig. 1-5 An example of absorption edges or resonances showing the detailed structure of experiment compared to the step structure of simple theoretical treatments based on one-electron theory. In this case, the Mn $2p_{3/2, 1/2}$ edges are shown as measured in an MnO(001) single crystal sample. The dashed and dotted curves represent the result of two simple theoretical models for the optical constant, β , (which is in turn proportional to the absorption coefficient, μ) and are shown for reference to the experimental data which has itself been slightly background adjusted to match the theory above and below the edge.

Fig. 1-6 Single-atom resonant photoemission (SARPE) for the case of Mn 3*d* emission from atomic Mn. The energy level diagram is shown, with the resonance occurring via the Mn 3*p* -to- Mn 3*d* excitation. The direct and resonant excitations are indicated by the solid arrows, and the dashed arrows indicate the autoionization decay via the Coulomb interaction.

Fig. 1-7 Single-atom resonant photoemission (SARPE) for the case of Mn 3d emission from atomic Mn [12a,12b]. (a) A photoelectron spectrum covering the Mn 3d region, with the photon energy set on resonance at about 50 eV. (b) The measured variation of the Mn 3d intensity with photon energy, together with two types of theoretical calculation: Hartree-Fock = HF and many-body perturbation theory = MBPT. The region shaded dark grey represents the effect of the resonance; the overlapping region shaded light grey underneath the smooth HF curve represents the estimated non-resonant intensity, with relative areas as integrated over energy indicated in percent.

Fig. 1-8 Diagram of the MARPE process for O 1s emission from MnO. Note the similarity to the SARPE diagram in Fig. 1-6, but with various energy levels distributed between two atoms. The interaction is still fundamentally Coulombic, involving the interaction of potentially many atoms in the sample.

Fig. 1-9 A conceptual view of the MARPE process between two atoms, illustrating the atomic orbitals and incident radiation for the case of O 1s emission from MnO, with resonance via the Mn 2*p*-to-Mn 3*d* excitation. The orbital charge densities and outgoing photoelectron wavelength are approximately to true scale, but the with the photon wavelength is significantly too small relative to the separation between the atoms.

2 Instrumentation and Experimental Methods

This chapter presents a detailed discussion of the instrumentation, experimental methods, and data analysis procedures used in the experimental work presented elsewhere within this dissertation. Some material contained within this chapter is repeated within chapters containing experimental discussions. In such cases, the information provided in these later experimental chapters is generally in a briefer form, and provided for the sake of the internal completeness and coherence of those chapters.

2.1 Experimental Geometry

The experimental geometry used throughout this dissertation is illustrated in Fig. 2-1. Three angles are sufficient to fully describe the geometry. In our convention, the polar angle, θ , is the angle between the surface plane and the propagation wave vector of the emitted electron, defined in the plane that includes this wave vector and the surface normal. θ is thus scanned by rotating about an axis perpendicular to this plane, as shown in the figure. In this same plane, the angle between the wave vector of the exciting radiation and the sample surface is denoted by θ_{hv} .

The azimuthal angle, ϕ , is scanned by rotating the sample about the sample normal and is usually measured relative to a particular low-index direction lying in the sample crystal. A fourth angle defining the spectrometer orientation, the included angle between θ_{hv} and θ , is denoted as θ_{sp} . Any two of these angles, θ_{hv} , θ , and θ_{sp} , in addition to the angle ϕ is thus sufficient to fully specify the experimental geometry available during the experimental work.

Determination of Crystal Orientation

Because the experiments in this dissertation all involved single crystals or films with a high degree of epitaxy, it was necessary initially to determine the precise orientation of the crystal in the experimental frame. Such crystal orientation was determined by performing x-ray photoelectron diffraction (XPD) scans using unmonochromatized AlK α radiation with a mean energy of 1486.6 eV and with θ_{sp} fixed at the so called “magic-angle” [1] of 54.74°. Both polar (θ) and azimuthal (ϕ) scans are used to orient the crystal in the polar and azimuthal directions, respectively.

For the high kinetic energies (>500 eV) of the emitted photoelectrons generally used in the AlK α scans, forward scattering dominates the diffraction signal and, by applying a knowledge of the known crystal structure and exposed surface orientation, the sample orientation can be trivially derived simply by direct examination of the diffraction pattern. For example, Mn 2*p* and W 4*f* photoelectrons used to orient MnO and W crystals, respectively, are emitted at about 820 eV and 1455 eV kinetic energies. Typical examples of azimuthal and polar angle scans for MnO(001) using the Mn 2*p* peak are shown in Fig. 2-2. The azimuthal scan for $\theta = \theta_{true}$ (to distinguish it from the manipulator setting) = 45° shows the fourfold periodicity expected of this surface, and the strongest forward scattering peaks are found to be along the dense $\langle 011 \rangle$ -type directions, providing one aspect of the orientation. The polar scan at $\phi = \phi_{true} = 60^\circ$ shows a strong symmetric peak that will lie along the [001] direction, and this permits determining the polar orientation to within about 0.5° or less.

2.2 Sample Preparation

MnO(001) Single Crystal

The MnO(001) single crystal sample cleaning was initially performed by a high temperature ($\sim 650^\circ\text{C}$) anneal of about 30 minutes, generally following the procedure given elsewhere [2]. Residual hydroxyl compounds observed as a shoulder in the primary O 1s peak did not appear to be reduced by this procedure however, so an argon-ion sputtering procedure was adopted instead. Sputtering appears to eliminate the hydroxyls as judged by the O 1s line shape, and the procedure was performed with Ar at 5×10^{-5} torr, a 0.5 kV ion gun potential, and a 20 mA gun emission current. The sample was continuously rotated in azimuth during the sputtering, which was performed for about 10 minutes, in an effort to sputter as evenly as possible over the crystal surface.

Sample heating was performed with a non-inductive "button" heater mounted below and in contact with the crystal. This heater required about 30 Watts to obtain a sample temperature of 650°C . Sample heating was also used during photoemission experiments to increase the conductivity of the MnO crystal (an insulator at room temperature) and hence decrease the amount of sample charging due to the extracted photocurrent [2]. The MnO crystal was typically maintained at 350°C during the experiments. Temperature readings were performed with a Wahl Model HSM-671 IR pyrometer with the sample emissivity set to 0.69.

W(110) Single Crystal and Fe/Cr Film Deposition

After exposure to atmosphere, the W(110) sample was first subjected to an oxygen-reduction procedure to remove carbon contaminants from the surface. This required maintaining the sample at approximately 1300°C in O_2 at a pressure of

5×10^{-7} torr (as read directly from the ion gauge, reading not adjusted for sensitivity to O_2). This was followed by several high-temperature flashes up to $\sim 1800^\circ\text{C}$, achieved by electron-bombardment of the back of the crystal. Clear, sharp (1×1) low-energy electron diffraction (LEED) patterns and x-ray photoelectron (XPS) spectra were used to confirm sample cleanliness. Temperature monitoring was performed with the IR pyrometer with the sample emissivity set to 0.30 and crosschecked with an optical pyrometer (Chino Model Ir-U).

Deposition of Fe and Cr films was performed *in situ* by means of molecular beam epitaxy (MBE) using custom-built Knudsen evaporation cells. The cells consist of a tungsten crucible containing the material to be sublimated surrounded by a filament for electron bombardment heating of the crucible. The crucible/filament assembly is surrounded by a water-cooled radiation shield to minimize unnecessary heating and degassing of the surrounding chamber walls. A chamber pressure of $< 5 \times 10^{-10}$ torr or better could be maintained throughout the deposition, with typical pressures being $1 - 2 \times 10^{-10}$ torr.

In order to monitor the deposition rate from the cells, an Inficon XTC/2 quartz crystal monitor (QCM) was used. The crystal monitor was placed at the identical position of the W substrate and the rate monitored until stable. The standard procedure used for film preparation required the substrate crystal to first be prepared by the repeated flashing procedure as discussed above. This flashing is sufficient to eliminate any previously deposited Fe/Cr film from the substrate. The cells were then activated and allowed to stabilize as indicated by the QCM. Shutters placed in front of the cell aperture allowed both cells to be calibrated independently, even when both were in use

simultaneously for alloy preparation. Once the rates were stabilized at an appropriate rate, the QCM was withdrawn, the crystal moved into position, and the cell shutter opened. Once the necessary film thickness was obtained, the shutter could again be closed, the sample moved away from the cell and the rate rechecked with the QCM to ensure stability was maintained through the deposition. Typical deposition rates were $\sim 1 \text{ \AA/min}$ and the alloy stoichiometries were confirmed through XPS quantitative analysis, including varied emission angle data that also confirmed the absence of significant surface segregation of either component of the alloy.

2.3 Photoemission Experiments

All photoemission work included in this dissertation was performed with the Advanced Photoelectron Spectrometer/Diffractometer (APSD) at the Advanced Light Source (ALS) in Berkeley. A brief overview of the features of the APSD and the beamlines used is given below.

2.3.1 Advanced Photoelectron Spectrometer/Diffractometer

The Advanced Photoelectron Spectrometer/Diffractometer (APSD) endstation [3] was built primarily for surface and interface science experiments, involving high-resolution, angle-resolved photoelectron spectroscopy, diffraction, and holography as excited by synchrotron radiation produced by the Advanced Light Source, and its main components are illustrated in the three panels of Fig. 2-3.

Sample Manipulator and Heating System

The APSD manipulator (shown at the top of all panels in Fig. 2-3, and in more detail in Fig. 2-4) allows *in situ* sample changes and storage of up to eight samples on a carousel attached to the manipulator. Any one of these samples may be mounted in the

primary sample position on the manipulator by means of an externally accessible “wobble-stick”. Each sample incorporates its own heating mechanism, of which three types have been built: non-inductive resistive heating (via a “button heater”, as for MnO), electron-beam bombardment heating (as for W), and direct ohmic heating by passing current through the sample. The last mechanism was not used in the work presented here.

The entire manipulator is mounted on an x-y stage shown in Fig. 2-4(b) allowing precise alignment between the sample, analyzer, and beamline to be maintained. A linear transfer bellows assembly allows the manipulator to be translated in the z-coordinate between the preparation chamber and main experimental chamber.

As can be seen in Fig. 2-4(a), the sample manipulator provides both polar (θ) and azimuthal (ϕ) angular degrees of freedom (with an estimated $\pm 0.3^\circ$ mechanical accuracy) while maintaining electrical contact to the sample holder for heating and/or sample grounding. There is also provision for liquid nitrogen cooling as well by bringing a detachable “cold-finger” into contact with the side of the sample holder. The cold-finger is connected to a liquid nitrogen cooled heat sink via a copper braid and can reduce the sample temperature to approximately 200°K but was not used during this research. It may be engaged *in situ* with the same wobble stick that is used to load the sample holders. Four electrical contacts are brought to the sample holder by means of sliding spring clips. The clips maintain contact for steady sample heating and grounding, while still allowing the sample to rotate freely in azimuth.

A sample loadlock that enables loading and unloading of up to five mounted samples at a time into the experimental preparation chamber without disturbing the

chamber vacuum was added during this research. The loadlock has a typical turn around time of 12-24 hours depending upon the heat sensitivity of the samples and resulting maximum tolerable bake-out temperature. Samples are transferred between the loadlock and the manipulator sample carousel by means of the wobble-stick. This loadlock was added during the course of this dissertation work and after the photos in Fig. 2-3 were taken, but is attached to the preparation chamber approximately perpendicular to the plane of Fig. 2-3(b).

Preparation Chamber

The preparation chamber includes an ion-sputtering gun (Perkin Elmer 04-161) for cleaning samples, a four-grid LEED optics for checking long-range surface atomic order and cleanliness (Princeton Research), and several electron bombardment MBE cells of Knudsen type for metal deposition, as described above. A large electromagnet has also been installed in the chamber that provides *in situ* sample magnetization. With the addition of appropriate optical components [4], this magnet could also be used to perform magneto-optical Kerr effect (MOKE) measurements although such measurements were not carried out in this research. Additional components mounted on the preparation chamber include the quartz microbalance, a number of gas inlet or “leak” valves, and the sample loadlock.

Main Experimental Chamber

The APSD is equipped with a 200mm mean radius hemispherical analyzer (Gammadata/Scienta Model ES-200). The detailed electron optical properties of the 300 mm predecessor of this analyzer are described elsewhere [5]. This analyzer has discretely variable resolving power by means of selectable entrance slits with various

widths and angular acceptances. The ultimate resolving power, $\frac{E_{pass}}{\Delta E}$, of $\sim 10^3$ thus corresponds to a maximum resolution of $\sim 2\text{meV}$ at a 2eV pass energy).

In all cases, the analyzer lens was configured for high transmission mode, which preserves linear kinetic energy dispersion across the radial direction of the detector plane while not attempting to preserve any information in the perpendicular plane. However, the curvature of the entrance slits used is designed to bring all electrons of a given kinetic energy out at the same radius. Under appropriate configuration, the lens can preserve either spatial or angular emission information from the sample, but at the expense of total transmission and hence count rate. The lens voltage-tables used for this work provide a $5\times$ magnification of the sample at the analyzer focal plane. The analyzer angular acceptance is about $\pm 5^\circ$ but can be reduced to $\pm 1^\circ$ by means of an external collimator that can be installed *in situ* immediately before the analyzer lens.

This analyzer may also be rotated relative to the beamline, allowing adjustment of θ_{sp} within a 60° range. This is accomplished by means of a pair of differentially pumped graphite-impregnated Teflon (Balseal) seals that allow the main chamber of the system to rotate relative to the rest of the chamber and the beamline. A large diameter ($13.75''$) bellows, as shown in Figs. 2-3(a) and 5, is required to connect the main chamber to the beamline to preserve the line-of-sight between the beamline and sample over the extent of the chamber rotation.

An unmonochromatized dual-anode ($\text{AlK}\alpha$ and $\text{MgK}\alpha$) x-ray source (Perkin Elmer 04-548) is installed in the main chamber with a fixed θ_{sp} of 54.74° ; this angle corresponds to the zero in $P_2(\cos\theta_{sp})$, thus yielding simpler interpretation of photoelectron

relative intensities [1]. The x-ray source has a power supply that allows adjustment of the x-ray power in 1 Watt increments, which proved quite useful in the calibration of the detector as referred to below.

Detector

The standard detector system in this Gammadata/Scienta analyzer is based finally on a charge-coupled device (CCD), and was used to collect all experimental data from the electron analyzer. The system consists of a chevron stacked microchannel plate (MCP) providing cascade multiplication of incident electrons passed by the analyzer. This MCP is mounted in front of a phosphor screen held at high accelerating potential (~ 3.5 kV) relative to the back of the MCP. The electron pulses emerging from the channel plates result in a visible light flash when they impact the screen. These flashes are recorded by the CCD and through appropriate binning electronics and software, a spectrum is recorded. The electronics that readout and interpret the CCD camera pixels can be run in one of two modes: pulse-counting “black-and-white” (BW) or analogue “gray-scale” (GS). The GS mode was used exclusively except for portions of a study of the detector behavior as discussed elsewhere [6]. This detector system is highly susceptible to saturation in BW mode and, as configured by manufacturer technicians, has proven to have a highly non-linear response function in both BW and GS modes [6].

The APSD chamber has been fitted with a custom built detector carousel that allows two detector systems for the Scienta analyzer to be loaded in the vacuum chamber simultaneously and swapped *in situ*. The purpose of the carousel is to allow both a multichannel (one or two dimensional) detector as used for standard photoemission studies and a spin-resolved “micro-Mott” style detector for more specialized magnetic

studies to be accessible to the experimentalist without opening the vacuum chamber. The standard detector (with appropriately altered mechanical mounting of the MCPs, phosphor screen, and voltage feedthroughs) has been installed in one port of the carousel and it was used throughout this dissertation work (with the exception of specific tests of a new high-speed detector to be discussed in Ch. Six).

As shown in Fig. 2-6, the carousel consists of a pair of bellows, each on an independent linear drive and a large differential-seal similar to those that allow the main chamber to rotate relative to rest of the chamber and beamline. To swap detectors, both detectors are driven to a fully withdrawn position (extended bellows) and then the entire assembly is rotated against the analyzer by 180°. The detector that is parked in front of the analyzer detector port can then be driven in to the proper operating depth near the analyzer focal plane. Chamber pressures as measured in the analyzer lens during rotation typical remain below 5×10^{-9} torr and recover immediately (within seconds) after ceasing rotation.

Vacuum System

The APSD vacuum system is schematically shown in Fig. 2-7. Ion pumps and titanium sublimation pumps (TSPs) provide the primary pumping. Turbomolecular pumps (turbo pumps) backed by second stage turbomolecular and then diaphragm pumps are available for primary evacuation from atmosphere and pumping during chamber bake-outs. Because of the three-stage pumping, the turbomolecular pumps may be used in addition to or as a substitute for the ion pumps even at UHV pressures and are used for recovery of UHV after the chamber is backfilled with gas for sample cleaning or preparation. Various ion pumps and a scroll pump provide continuous pumping for the

inner and outer stages, respectively, of the differential seals that allow the main chamber and detector carousel to rotate. Typical experimental pressures can reach $<1 \times 10^{-10}$ torr, with the base pressure typically limited by the beamline. The chamber, when closed to the beamline, can be easily maintained in the range of 5×10^{-10} to $<7 \times 10^{-11}$ torr.

2.3.2 Measurement of Absorption Profiles

The partial-electron-yield absorption profiles measured in this dissertation were collected with the Scienta ES-200 analyzer and the standard CCD detector. By tuning the excitation energy across the absorption edge of interest, the increased absorption at the edge corresponds to an increased photoelectron production. These electrons then contribute to the overall inelastic background at kinetic energies less than the photon energy, in proportion to the photoelectron current. We thus make a standard assumption that no significant changes take place in the ratio of Auger to fluorescence electron secondary processes in this photon energy range.

One way of using these inelastically scattered "secondary" electrons to measure the absorption profile is simply to derive the integrated background under a given photoelectron peak as the photon energy is scanned and the peak thus moves along in kinetic energy. This is the procedure used for the data on MnO to be reported here.

Similarly, by setting the electron energy analyzer to an appropriately chosen kinetic energy, the absorption profile may be extracted directly from the inelastic background intensity. In order to select an appropriate kinetic energy range to monitor, a couple of issues must be considered. First, the kinetic energy must obviously be less than the lowest excitation energy in the scan. Second, the kinetic energy must be placed so that no spectral features pass through it. At a constant kinetic energy, no-loss

photoelectron peaks may pass through the window as the photon energy is swept. If a fixed binding energy (“constant initial state”) scan is preferred, care must be taken to avoid Auger peaks, which could in that case sweep through the window. The software developed to perform these scans in the APSD is discussed elsewhere [7].

In practice, a usable energy window of at least several tens of eV can generally be located. In this case the integrated background intensity over a many eV window (simultaneously acquired due to the multichannel nature of the detector) may be recorded to improve statistics. For the APSD, this energy window is determined by the percentage of the detector being integrated over multiplied by about ten percent of the analyzer pass energy.

Simultaneous measurement collection of the incident photon flux as described above was important due to the presence of a significant amount of Cr in the beamline 9.3.2 mirrors, resulting in a decreased radiation flux as the Cr $2p$ edges were crossed. Without correction for this, the Cr $2p$ absorption profile will appear to have too low an intensity relative to the Fe $2p$ profile, introducing errors in the quantitative analysis of the profiles.

Once the absorption profile is measured, tabulated theoretical or experimental values for the absorption coefficient before and after the strong modulation at the edge can be used to adjust the overall background in the profile, as noted previously.

2.3.3 Light Sources

All experiments were performed at the Advanced Light Source of the Lawrence Berkeley National Laboratory in Berkeley, California. This is a third-generation synchrotron-radiation source that is optimized for high brightness in the VUV/soft x-ray

range, with general characteristics as described in Ch. One. This national user facility is discussed at length elsewhere [8, 9]. The APSD endstation has been stationed at beamline 9.3.2 of the ALS until a recent relocation to beamline 4.0.2 in March, 2000.

ALS Bend-Magnet Beamline 9.3.2

Although the ALS is built primarily for insertion device based beamlines, there is still the opportunity to use radiation generated at the bend magnets joining the straight insertion device sections. Beamline 9.3.2 [10, 11] is a bend magnet based beamline, capable of providing light in the range of approximately 30 to 1500eV, and its main components are illustrated in Fig. 2-8. It can produce both linear polarized and circular polarized light by taking advantage of the inherent polarization distribution of radiation emitted in the bend magnets. Radiation in the plane of the storage ring is linearly polarized while that emitted above/below the ring plane is increasingly right/left (or left/right depending upon the chosen convention) circularly polarized. All data presented with this dissertation were acquired with linear polarization and with a degree of polarization of about 90% according to previous beamline calibration [10, 11].

The beamline has a monochromator with three possible spherical gratings for use in varied energy ranges. During the collection of data for this dissertation, the high-energy grating (1000 line/mm) had been removed due to manufacturing defects, setting the practical upper limit of photon energy at about 850eV for first order diffraction from the mid-energy-range grating. A set of slits before and after the monochromator grating are translatable so as to maintain a Rowland circle geometry and hence optimally maintain the beamline resolving power as the monochromator energy is varied. In

addition, the slit widths are continuously variable at the micron scale to allow manual adjustment of the beamline resolving power, $\frac{E}{\Delta E}$, up to up to about 10^4 .

The monochromator entrance slit was maintained at a fixed position during this experimental work. This has been found to have little practical effect on the beamline resolution while optimizing the flux throughput to the sample.

When situated at beamline 9.3.2 of the ALS the APSD resides on one of two primary experimental platforms, as shown in Fig. 2-8(b). These platforms allow endstations to be rotated on/off-line without breaking the vacuum connection to the beamline, permitting more efficient sharing of the beamline among a number of users.

ALS EPU Beamline 4.0.2

Beamline 4.0.2 [12, 13] is the first of two planned beamlines that will use the light generated by a 5.0 cm elliptical polarization undulator (EPU) in straight section 4 of the ALS, and its components are illustrated in Fig. 2-9. By suitable relative longitudinal alignment (phase) of the 37 period undulator magnet quadrants, the EPU is capable of providing light in four polarization modes: circular, elliptical, horizontal linear, and vertical linear. The monochromator can work in an energy range of about 20 to 2000 eV. It is constructed with a single variable angle plane grating monochromator with varied grating groove depth used to achieve the full available energy range with maximum efficiency. The actual energy limits are imposed by the undulator and depend upon the storage ring energy: At 1.9 GeV storage-ring energy, the 2000 eV limit can be achieved, while a 1.3 GeV ring energy provides a 60 eV undulator imposed minimum. The resolving power can be set to as high as 10^4 at the lower energy range.

This beamline has been used in much of the work presented within this dissertation [6, 14]. Relocation of the APSD chamber to this beamline was a nontrivial effort. Work performed as part of this dissertation included disassembly and reassembly of the electronic subsystems and portions of the chamber, evaluating and recalibrating the analyzer/detector system, and writing an additional software component [7] to automate the monitoring and high-level control of the monochromator and undulator during APSD based experiments. The first photoemission spectrum recorded by any group at the EPU, shown in Fig. 2-10, was acquired with the APSD and this custom software.

2.3.4 Instrumentation Development

The primary enhancement to the APSD instrumentation during the course of the research presented here has been the design, writing, debugging, and extensive use of new data acquisition software by the author which is discussed in an independent chapter of this dissertation [7].

Additionally, a new high-speed multichannel detector prototype has for the first time been installed and operated in the APSD chamber [15]. Although the detector was not used in the collection of the experimental data discussed here, it represents a significant step forward in detector technology and the prototype is a very successful proof-of-principal for our adopted design. The successful operation of the detector in the APSD represents the culmination of considerable efforts by a number of people, and the project is quite dependent upon the software development already mentioned. This software permits successfully operating the detector both in a separate development chamber and in an integrated system such as the APSD where the computer must also

control the analyzer, manipulate and display data appropriately, and store the data for later analysis.

In the near future, additional testing of this high-speed detector, commissioning of an additional micro-Mott spin resolved detector, and the addition of a new commercial x-ray fluorescence spectrometer (as indicated in Fig. 2-3(c)) will continue to enhance the capabilities of the APSD endstation.

2.4 Data Analysis

The analysis of the photoemission spectra as discussed in this dissertation consists of several steps. Before discussing each step it should be remembered that we will be focusing primarily on sets of spectra acquired in sequence at photon energies that are tuned over an absorption edge of a core energy level of some atom "B" in the sample. The spectra that we are repeatedly acquiring will contain a photoemission peak from a second core level of some atom "A" and we will be interested in modulations to the photoemission intensity as a function of the photon energy when passing over the absorption edge of B.

The first step of the analysis is to correct the raw data for non-linear detector response. Failure to include this step results in false apparent effects [6, 14]. The response function correction converts the measured count rate of every data point in every spectrum into the actual true count rate (within an overall constant multiplier that is irrelevant to our studies).

With these instrumental artifacts removed from the spectra, curve fitting is performed using software distributed by Gammadata/Scienta (DOS based, ver.1.54 and a

16-bit Windows 3.1 based version) that is capable of simultaneously optimizing background levels as it performs non-linear least-squares fitting via the Levenberg-Marquardt method [16] over a user defined set of peaks. Linear or Shirley (integral) type backgrounds [17] and Gaussian or (approximate) Voigt line shapes were determined to accurately describe our various measured spectra.

After each spectrum is fit, the results may be interpreted in terms of our particular interests. The background level as a function of photon energy allows a convenient simultaneous measure of the absorption profile for the edge that the photon energy was tuned over, as described above. The peak area above background plotted against photon energy reveals the photoemission strength of interest to us. In both cases, however, the effect of photon flux changes throughout the experiment (e.g. due to the usual decay of the electron current in the ALS storage ring) is still included.

The final step, then, (which could be applied immediately after the detector response correction as well) is to simply normalize the various quantities (spectrum counts, areas, heights) to the incident photon flux, I_0 , that was recorded during all beamline based experimental work. The flux was measured by means of the photocurrent from a gold-coated high-transmission mesh placed in the path of the beam between the sample and the last optical element of the beamline. This step eliminates the effect of the countrate losses simply due to excitation strength losses. These losses arise both from the slow loss of stored current in the synchrotron storage ring and, in scanned photon energy experiments, photon absorption by the beamline optical components. For much of our work, the ALS was operating with four-hour fill periods, and a flux loss of approximately

50% was incurred over the fill, but the installation of third harmonic cavities at the ALS has led to more recent six-hour fills such that only ~30% losses are now typical.

There is an assumption that the I_0 measurement represents a true measure of the photon flux at the sample, which may not always be true due to changes in relative intensities of each diffraction order (all of which are included in the I_0 measurement) from the beamline monochromator as the photon energy is changed. In addition, any small changes in beam position over the course of the fill may result in a change in the amount of the grid generating the I_0 signal that is illuminated, and hence influence the reading. Beam position shifts may also cause the photon beam to strike the sample surface over an area that has more or less overlap with the area actually seen by the analyzer, and this could cause additional changes in the photoemission intensity. Regardless, the general success of the I_0 correction indicates that it does represent a reasonable measure of the photon flux.

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Fig. 2-1 The experimental configuration, with various key elements and parameters defined. The Berkeley Advanced Light Source beamlines 9.3.2 and 4.0.2 were used to provide photons ($h\nu$). All of the variables $h\nu$, θ_{hv} , θ_{sp} , θ , and ϕ could be varied independently subject only to $\theta_{hv} + \theta_{sp} + \theta = 180^\circ$.

Fig. 2-2 An example of x-ray photoelectron diffraction (XPD) from the MnO(001) single crystal: AlK α (unmonochromatized) excited Mn 2p intensity for (a) and azimuthal scan at $\theta_{\text{true}}=45^\circ$ and (b) a polar scan at $\phi_{\text{true}}=60^\circ$. Here, θ_{true} is defined relative to the surface, and ϕ_{true} relative to the [100] direction lying in the surface. The locations of the most prominent peak in the azimuthal scan correspond to $\langle 011 \rangle$ forward scattering centers and thus unambiguously reveal the crystal orientation and expected four-fold symmetry. The position of the strong peak in the polar scan reveals the normal emission or [001] direction with $\theta_{\text{true}}=90^\circ$.

Fig. 2-3 (a) The Advanced Photoelectron Spectrometer/Diffractometer (APSD) endstation while located at beamline 9.3.2 of the Advanced Light Source. Note the large bellows to the right of the analyzer, needed to allow the main chamber to rotate relative to the beamline. (continued on next page)

(cont.) (b) Another perspective of the APSD. The beamline is behind the chamber, with the analyzer to the right (hidden by the electronics rack). (continued next page)

(cont.) (c) Additional view of the APSD with more components labeled above. The large viewport in the main (bottom) chamber looks into the analyzer lens. The beamline is to the back, left hand side of the chamber in this perspective.

Fig. 2-4 (a) The sample goniometer of the APSD manipulator. Polar and azimuthal angles are variable while maintaining electrical contacts (sample ground/ heating) and cooling. A customized “wobble stick”(not shown) allows the primary sample to be swapped with any sample in the carousel *in situ*.
(continued next page)

(cont.) (b) The entire APSD sample manipulator. The goniometer is attached to the end of a long z-stage mechanism and bellows used for vertical movement of the sample between the preparation and main chambers. A precision x-y stage for movement in the horizontal plane allows for alignment of the sample to the beamline and analyzer. The top of the z-stage contains the goniometer as well as mechanical, electrical, and liquid nitrogen feedthroughs.

Fig. 2-5 APSD schematic illustrating the rotatable analyzer geometry relative to the beamline exit port. Note the large flexible bellows required to maintain the line-of-sight between beamline and sample during the extent of the 60° of rotation. The detector carousel is shown here only in a conceptual manner.

Fig. 2-6 A drawing of the detector carousel mounted on the APSD chamber. The carousel contains two separate detector ports, with each consisting of bellows on linear motion drives. Either detector may be rotated in front of the Scienta ES200 analyzer detector port and then moved to the proper operating distance relative to the analyzer focal plane is reached. The rotation mechanism is a differentially pumped seal as described in the text.

Fig. 2-8 (a) A scale drawing the overall layout of beamline 9.3.2 of the ALS and (b) the optical components of the beamline .

Fig. 2-9 Schematics of beamline 4.0.2 at the ALS indicating the general layout of the beamline and the experimental location of the APSD endstation.

Fig. 2-10 The first photoelectron spectrum acquired at beamline 4.0.2 of the ALS. The APSD endstation was used to acquire this spectrum after relocation from beamline 9.3.2. The spectrum, of an uncleaned MnO(001) single crystal was obtained as part of the sample preparation and instrument alignment procedure, with other later data obtained on this beamline to be presented in Ch. Four and Five.

3 Software Development for Data Acquisition

Instrumentation software plays an ever-increasingly important role in the experimental systems used in modern scientific endeavors. The quality and capabilities of the software used to control an experimental system can greatly influence the degree to which the experimentalist can reliably automate tedious tasks, thus enhancing the efficiency and accuracy of data taking. In addition, software itself is increasingly an integral component of the instrumentation itself providing the sole means of hardware control and data readout, display, and storage.

Predictably, the experimental work presented in this dissertation was entirely acquired through the use of specialized software for data collection. In order to automate the acquisition of datasets to the highest practical degree, a major project undertaken during this dissertation was to develop custom software permitting simultaneous control of the various components of the Advanced Photoelectron Spectrometer/Diffractometer (APSD) [1,2] at the Advanced Light Source (ALS), the primary synchrotron radiation research facility of our group. This system includes the Gammadata Scienta hemispherical analyzer with its electrostatic lens, the synchrotron radiation beamline, the sample manipulator, and a number of detector systems. This software has now replaced the vendor-supplied software for the analyzer that was not able to control beamlines for automated photon energy scanning and also offered only limited control of the manipulator as well as a restrictive data-file scheme. Most importantly, this previous software package could not control new detectors under development in the research group.

The development of the software discussed in this chapter was a significant portion of the work done for this dissertation and represents a significant advance in the collection of our experimental data and an important part of the development of a next-generation high-speed detector, as discussed elsewhere [3]. This chapter will discuss the various components or modules of the software control, as well as the requirements (support files and hardware) of each component. Generally, no attempt is made here to describe the implementation details such as the internal data structures, routines, and library compiling/usage instructions. For these details, the reader is referred to the source code [4] and comments therein for each component as tabulated throughout the chapter.

The software has been designed to be as modular as possible. The essential attributes and functionality of each module are constructed in a standard manner, so that by using the same model, a new analyzer, light source, or manipulator system can be integrated into the experiment and spectrum collection components with minimal effort. For example, the software has already successfully operated with two different beamlines (bend-magnet 9.3.2 and undulator 4.0.2 at the ALS) and two different detectors (the standard Gammadata Scienta CCD-based detector and the next-generation high-speed detector), and is now being used routinely by other members of our group. A block-diagram indicating the overall structure of the program is shown in Fig. 3-1.

3.1 Development Environment and Tools

The popularity of x86 based personal computers running Microsoft Windows dictated the choice of target system for the software. The primary development tool environment used is National Instruments LabWindows CVI, ver. 4.0.1p2 for Win32. The software should recompile without modification under version 5.x as well as other

environments, provided the appropriate National Instruments libraries (included with LabWindows) are available for linking. The LabWindows package is based on a 32-bit ANSI C compiler, and all code has been written in C. A graphical user interface (GUI) editor and library that is independent of the standard MS Windows libraries allows simplified layout and code generation for the various interfaces available in LabWindows, with reasonably minimal effects on overall program performance.

LabWindows CVI has been used in one prior software system for controlling a Gammadata Scienta ES-200 analyzer, as written by G. Reisfeld in the Johnson group at Brookhaven National Laboratory, and we benefited from early discussions with him. However, no actual code, data constructs, or program structure/design from that software is present in our final version.

The complexity of the overall project and desire to maintain maximum portability of the final source code dictated the choice of LabWindows over the popular LabView development environment (a related product of National Instruments). The nonstandard graphical programming of LabView was determined to be more prone to poor in-code documentation, and to result in essentially non-portable code compared to the standard C-language used within the LabWindows environment.

For miscellaneous data manipulation tools (i.e. file format converters), Borland C++ Builder (version 4.0) has also been used [6].

3.2 I/O Hardware

The various instruments that are controlled by the assorted software modules require a number of input/output (I/O) boards and communication protocols. For a listing of the currently used hardware and various configuration information, see Table 3-1. In

future modifications or improvements of this hardware system, we note that many of these boards could be eliminated by purchasing equipment that can be controlled using the GPIB, VXI/VME, or Ethernet protocol, thus allowing multiple items to be controlled through a single common connection to the computer.

The majority of the boards used are built for the PC ISA bus, an architecture that is by now actively being phased out of personal computers. To physically accommodate all of the required ISA boards, a bus expansion chassis has been purchased (Industrial Components), but the resource configuration (bus addresses, interrupt assignments) of all the boards requires care to prevent conflicts between boards and preexisting computer hardware.

A discussion of the hardware used is contained below in the discussion of each module. When an opportunity for improvement in the I/O hardware exists or special consideration are required for the current hardware this will be mentioned.

3.3 Instrument Control Modules

This section will briefly describe the primary instrument control and modules development for the system. An overview of the capabilities, the required source code files, support files for initialization, and the required I/O hardware are tabulated and discussed. In addition, any dependence on third-party libraries (other than National Instruments provided LabWindows libraries) will be noted. Note that while each module will have a unique GUI to allow, for example, manual control, or status reporting, a few typical interfaces along with the primary program window may be seen in Fig. 3-2.

3.3.1 Gammadata Scienta ES-200 Analyzer

A driver and graphical interface utility for the Gammadata Scienta ES-200 hemispherical electron energy analyzer [7] has been written. Additional analyzers from Scienta should be able to be operated from this driver by simply updating the initialization files with the appropriate lens voltage tables for the particular analyzer. The analyzer is equipped with a GPIB (IEEE 488.2) hardware interface to control the power supplies. Newer versions of the analyzer have migrated to a fiber-optic interface, and would require an appropriate I/O card and driver to be installed. This represents a very minor change to the overall software module, involving a modification of only a handful of functions that currently call GPIB library functions to instead call equivalent optical card I/O functions.

This analyzer is fairly sophisticated, with each electrostatic element (as well as the standard detector channel plates and phosphor screen) determined by a specific node on a network of stacked power supplies [8]. Each power supply must be set by software according to a set of voltages tables that vary with the operation modes: lens transmission mode and hemisphere pass energy. Each change in analyzer kinetic energy, pass energy, or lens mode requires a table lookup and, in some cases, a cubic spline interpolation [9] to a sub-table for each “element” of the analyzer, which in turn corresponds to a given power supply. The software naturally decomposes into two portions. The first is the control of the power supplies, including the I/O system management. The second is the portion that manages the current analyzer settings and performs the calculation of the needed voltages to obtain these settings.

Power Supply Submodule

The power supply module is responsible for managing individual power supplies and “supply sets”. A supply set is a labeled group of individually labeled power supplies, with the associated address settings, calibration parameters, and allowed limits for each supply in the set. There are two standard sets consisting of “high pass energies” and “low pass energies” that represent distinct changes in which of the available power supplies are in use in the system. The software cannot detect the presence of the power supplies and so cannot automatically determine the correct supply set to use. The user is responsible for selecting (in the graphical user interface) the current set whenever it is changed in hardware.

The module GUI allows the user to select the current supply set and view a list of the supplies in that set. Each power supply can be accessed independently in order to examine the calibration settings or set the supply to automatic, manual, or shutdown mode. In manual mode, the voltage requests by the user are sent immediately to the power supply, a feature useful for troubleshooting. In shutdown mode, the power supply is sent a zero voltage request. For either of these modes, the module ignores external requests (from the element module normally) that refer to that supply while the automatic mode exclusively obeys these requests (within the voltage limits set for that supply).

The module accepts external voltage requests in array form so that multiple settings may be requested at once. When a voltage request is made, the software checks that the supply is available (has not been set to manual or shutdown mode) and then if the voltage differs from the last requested voltage, the command is queued for transmission

to the supply. Once the entire set of requests has been processed, the entire command is sent, minimizing the communications overhead.

The supplies are controlled by means of an integer setting, which is calculated by means of the supply calibration parameters. Whenever a supply is physically replaced, care must be taken to note the new calibration parameters and update the initialization file (*SES_supp.ini*) accordingly. Failure to do this will result in incorrect voltage settings, although these should be only slight if the supply is replaced with an identical model from the vendor.

Analyzer Element Submodule

With a set of power supplies defined, the main function of the analyzer software is to simply determine what voltages the supplies need to be set to for a particular analyzer setting. The analyzer setting is determined by the *mode* and the *kinetic energy*. A list of modes is provided in the input file with each of the three modes defining the lens operation (high transmission, spatial, or angular) and the pass energy setting of the analyzer, although additional modes could easily be added that are distinguished by lens magnification or other discrete operational settings. For our purposes, only high-transmission modes are used, as the others require two-dimensional detection electronics that are not currently installed in the system. Each mode consists of a list of attributes, voltage tables, and calculation schemes, generally following the model taken by the manufacturer in their own program in order to make comparison between the tables as easy as possible. The calculation scheme provides the information for combining the lens tables to obtain a voltage for each power supply.

Control of the analyzer by external modules allows setting of the mode and energy (an approximate settling time is returned after each update). Although great effort has been made to optimize the setting routines, the module also allows the user to preset the next desired settings [8] (that is, to calculate the voltages and send pending commands) while waiting for detector data or otherwise in a known state of low processor activity. When the actual settings are required, a fast “set” command is transmitted. The ability to send delayed commands to the power supplies is a feature of the electronics system that was simply taken advantage of in the software.

Both the element and supply module graphical interfaces may remain open during scanning of the analyzer by external routines, however a detectable delay is introduced at high refresh rates of the current voltage listing. For this reason, the windows should remain closed when not needed. See Table 3-2 for a complete listing of source files, needed supporting files, and hardware.

3.3.2 Light Sources

A light source module is required to expose at least three pieces of information: a label, energy, and whether or not it is a variable energy light source. If the source is variable, then it is required to allow energy requests, a ready status flag (to indicate the light source is in a well defined condition), and energy request limits. Several light source modules have been created.

Fixed Energy Light Sources

The fixed energy source module, as appropriate, for example, when using a standard laboratory x-ray source, simply maintains a list of labels and energies (in eV) in

the initialization file. The user selects the appropriate source from a list of label/energy value pairs displayed in the GUI. Any number of pairs may be added by simply editing the input file. See Table 3-3 for the related source and support files.

ALS Beamline 4.0.2 Module

For communication with the ALS undulator beamline 4.0.2 [10,11], a Simple Channel Access (SCA) library has been used which communicates via a subset of the EPICS control system that is used throughout the ALS. This library was obtained from ALS websites [11]. The version used is compiled as a Win32 DLL and requires an appropriate version of WinSock to be installed on the computer, as well as several support DLLs that are used by the SCA library. The system requires the computer to be installed on the local network to be granted access to the beamline control and ALS monitoring channels. See Table 3-4 for all the related source code and support files.

Because the network interface is too slow to allow rapid polling and averaging of the photon flux reading (usually referred to as the I_0 or "I-zero" monitor), an additional analog I/O based flux monitor was incorporated in the module using an analog input channel on a National Instruments Lab-PC+ board. Information regarding this submodule is also given in Table 3-4.

ALS Beamline 9.3.2 Module

The interface to the ALS beamline 9.3.2 (actually the first to be completed and used) is accomplished through a serial (RS-232) connection using any available 9 or 25-pin COM port on the computer. This allows the program to control the photon energy collect photon flux (I-zero) readings. The RS-232 interface provides a direct access line into the main VME crate that controls the beamline, using only the send and transmit

lines (Rx/D, Tx/D) of the 25-pin VME port. The cabling does not require a null modem between the PC and VME ports. Further details regarding the VME crate and definition or the serial commands are given in the source code (Table 3-5) and in beamline documentation [12,13].

It would also be possible here to use the SCA interface as used in the BL4.0.2 software (with appropriately modified commands), but because of the network communication overhead inherent to the SCA/EPICS system, this is a relatively slow connection compared to the serial line and so has not been adopted.

3.3.3 Sample Manipulator

The sample manipulator of the APSD endstation is a custom built two-axis goniometer, allowing full control over polar and azimuthal sample angles, as shown in Fig. 3-3. Here, the polar rotation axis is always perpendicular to the plane containing the photon incidence and electron exit directions. These angular motions permit varying the electron emission direction with respect to the sample axes, as for example, in photoelectron diffraction and holography, and in angle-resolved photoemission studies of valence bands. These motions are provided by a Compumotor [14] AT6400 Controller and a pair of LN series drivers attached to micro-stepping motors (Compumotor LN57) whose fine step (50000 steps/rev) eliminates need for any gear reduction. The AT6400 controller requires a full-sized ISA bus slot in the PC. Although a working version of the low-level interface code for this board was initially written as part of this project, an equivalent vendor-distributed dynamic link library (*wn956000.dll*) has subsequently been released and then adopted for our use. Use of this DLL requires related virtual device-driver files (*wrtdev*.vxd*, *=0,1,2,3,4) to be copied to the “\windows\system\mmm32\”

directory when using MS Windows 95. A separate DLL is also distributed for NT systems, with equivalent functionality, but has not been tested. Regardless of the library, an additional file containing the AT6400 “operating system” (firmware) normally named “*at6400.ops*” is also needed and is uploaded to the controller by the PC software over the ISA bus.

The board control library allows commands to be given to the controller in the Compumotor 6000 series motion programming language through the PC. This ASCII-command based programming language and the board interface library are described in full detail in Compumotor documentation [14]. Refer to Table 3-9 for a listing of all required source code and support files in addition to the hardware for the module.

As of this writing, there is a product, the Compumotor 6K controller, that could in the future replace the ISA bus based AT6400 board and which uses Ethernet (or serial) communications and therefore simply requires a standard network connection in the computer. To accommodate this in the software, the same controller commands (in the 6000 series language) would be used in the software. The required change in the software would be replacement of the Compumotor DLL and device driver files and function calls with the equivalent hardware library and function calls supplied with the new controller. This library is currently implemented as a 32-bit OLE automation server, which should be accessible using libraries included in newer versions of LabWindows.

The mechanics of the sample manipulator, of which several similar ones are in use in our group, result in the polar motion being coupled to the phi motion; thus, an

advance of the polar axis must be combined with an equal advance of the azimuthal axis to result in a zero net azimuthal motion of the sample. The motion axes have not been equipped with indexers and the current position is simply determined by a visual reading of mechanical indicators followed by input of these “mechanical angles” via the software graphical interface. In addition, these angles will generally not correspond to standard “true” or experimental angles as defined in Fig. 3-3. Tracking between mechanical and “true” or experiment angles is maintained within the software, including compensation for the polar-azimuthal coupling and mechanical backlash compensation.

The primary APSD chamber includes a standard x-ray excitation source with two anodes providing Al $K\alpha$ and Mg $K\alpha$ radiation, in addition to a beamline port providing synchrotron radiation. These two sources are oriented symmetrically about a plane including the sample manipulator and the analyzer symmetry plane. Our standard definition of the true polar angle (Fig. 3-3) is measured relative to the sample surface plane so that a true polar angle of 90° represents the “normal emission” geometry with the sample normal aligned to the analyzer. In order to unambiguously assign true angles in an experiment, a choice in the handedness of the polar angle was made so that increasing mechanical angle values (as read off the rotary indicator) also corresponds to increasing polar angle values. This means that the true polar angle will be $<90^\circ$ when oriented toward the x-ray anode side of the analyzer, and $>90^\circ$ when oriented toward the beamline, again, as illustrated in Fig. 3-3.

For operation with the standard x-ray source, the angle θ_{spec} between the source and the analyzer is fixed at the so-called “magic angle” of 57.74° for which the Legendre polynomial $P_2(\cos(\theta_{\text{spec}})) = 0$; this implies that atomic cross sections do not depend on the

asymmetry parameter β , thus simplifying quantitative analysis of peak relative intensities. However, the APSD chamber also allows the angle, θ_{spec} , between the beamline and analyzer to be manually varied. Care should be taken to remember that, while the x-ray source remains fixed relative to the analyzer, the manipulator does not. This means that a rotation of the analyzer will require an adjustment of the current reference angles (i.e. redefinition of the offset between mechanical and true angles) in the user interface. This is a simple operation in the graphical user interface, where the user is expected to ensure that the mechanical angle corresponding to normal emission is correctly assigned. Failure to make this adjustment will result in the manipulator responding to motion requests as if the analyzer remained at the old position.

3.3.4 Gammadata Scienta CCD Detector

A significant motivation for creating this software package was the integration of new detectors into the APSD. However, we have also integrated the standard CCD camera based detector system that is delivered with the Gammadata Scienta ES-200 [7,8] into the software. All detector modules are built in two parts. The first module consists of low-level interface and control routines for the detector. The second module contains the spectrum acquisition, or “scanning” routines applicable to the detector. The acquisition module requires the integration of the several modules in the software: analyzer control, light source control, data file management, and the low-level detector commands. The module must also conform to a well-defined structure for external control by the primary experiment control module.

The Scienta detector interface is relatively simple, and the control signals consist of documented [8] ASCII commands over the same GPIB interface used to control the

Scienta analyzer power supplies. The version of the detector electronics that we own only allows one-dimensional information to be read from the detector. When performing standard swept/dithered mode scans, the slow speed of the hardware interface prevents continual readout of the entire data array for each frame of the scan and so we have adopted built-in hardware binning and addition of subsequent frames.

3.3.5 Micro-Mott Spin Resolving Detector

A MicroMott detector permitting the detection of electron spin polarization after energy analysis [16] has four data channels, each producing a TTL pulse for each counting event at the corresponding detector channel. The channels are denoted as Left, Right, Up, and Down and correspond to measuring different spin orientations of the electrons that enter the analyzer. The Left/Right pair measures spin perpendicular to the plane of x-ray incidence and electron exit in Fig. 3-3, whereas the Up/Down pair measures spin lying in that plane, and perpendicular to the direction of electron propagation. This detector was built by D.M Lind and K. Shaw at Florida State University, but has had both its mechanical and electronic components modified considerably since first delivery to us. Its use was not critical to the measurements in this dissertation, and it is just now undergoing final testing in a genuine experimental environment. It will be used in subsequent work in our group on magnetic systems.

In terms of data processing, this detector is quite simple. The four independent detection channels are driven by micro-sphere plates (MSPs) used for cascade multiplication of electron events in much the same way as micro-channel plates (MCPs). The MSPs are attached via shielded wiring to external preamplifiers and discriminators, and finally interfaced to the computer as TTL pulses. A portion of the software

development involved configuring the counter board and additional power supply control I/O hardware and this will be discussed in some detail.

Mott Channel Counters

In order to integrate (count) the pulses over a given dwell time, we use a National Instruments PCTIO-10 DAQ board and the National Instruments NIDAQ driver software for Win32. The board occupies one ISA bus expansion port in the PC and requires that the user properly configure the board using the National Instruments NIDAQ software [5]. The board requires bus address space and (if one is available) an IRQ line that does not conflict with other hardware in the system. See the PCTIO-10 and NIDAQ manuals [5] for information about configuring these values on the board and in the driver configuration.

The PCTIO-10 card contains 10 16-bit timer/counters on two chips (5 on each). In order to ensure that the detector can be left to integrate for relatively large amounts of time (a few seconds) without any chance of overflowing the 16 bit counters, pairs of them have been cascaded to form effective 32-bit counters. According to the National Instruments documentation, there is a slight (and in fact not detectable during testing) latency in performing operations on the counters (i.e. starting and stopping counting). In the interest of providing identical counting hardware for each of the 4 detector channels, the cascaded counter pairs all consist of one counter on each chip, with the low 16-bits on a chip1 counter and the high 16-bits on a chip2 counter, as indicated in Table 3-13.

All counters are software configured to count events on the rising edge of the pulse, with high level gating. Low 16-bit counters are set to have pulsed, positive polarity output. This creates a low-high-low pulse on counter overflow which is passed

on (through connector pin jumpers) to the correct high bit counter. During counting, the counters are set to continuous count mode so that they roll over to 0 and continue counting on overflow and allow the counter cascading to work.

High 16-bit counters are set to toggled, positive polarity output and single counting mode. This allows us to use the output state of the counters as an overflow indicator (overflow is active high). The gate pin of each counter must be jumpered to the Integration Gate Timer output pin (see below). The source pin for each high 16-bit counter must be jumpered to the output pin of its matched low 16-bit counter. The source pins of the low 16-bit counters each accept the corresponding MicroMott event pulses (counts).

Integration Gate Timer

Because the data acquisition will be done from a Win32 based application, accurate integration times can only be guaranteed through the use of hardware that is independent of the PC bus and processor. The PCTIO-10 card has two counter/timers left after using the 8 counters needed for the Mott Channel Counters. The board can be configured so that either of these 2 extra timers creates a low-high-low TTL pulse of a given duration. This pulse can be used to gate the detector counter channels. That is, the Mott Channel Counters can be configured to count only when their gate (jumpered to the output of the pulse timer) is logic level high (5V).

Internal timebases on the board allow software selection of the accuracy of the pulse length. When the pulse length is selected to have an accuracy of 0.1 milliseconds (corresponding to a 100 kHz timebase), the total length of the pulse can be up to $(2^{16} - 1) * 0.1 \text{ milliseconds} = 65535 * 0.1 \text{ milliseconds} = 6.5535 \text{ seconds}$. Integration

time is software selectable in 0.1 millisecond increments from 0.1 milliseconds to this maximum value. This configuration allows us to count up to $2^{32} - 1$ pulses on the cascaded counters in about 6.5 seconds or more that 660 MHz with 0.1 millisecond integration resolution. The timer is set to toggled, positive-polarity output via the software so that the output of this timer is logic-level high during the entire pulse and can be used as the gate signal on the Mott Channel Counters.

When the pulse is finished, the timed integration is complete and the software can read the values on the counters. It is possible to detect the end of the pulse by two distinct mechanisms in the software. If an IRQ (interrupt request) port was available during the board installation, the acquisition process can be alerted to a high-low transition on the gate output via an interrupt service routine. This is implemented through a standard Windows message posting and servicing. To enable the IRQ, the gate output must have an additional jumper to one of the two External Interrupt pins in the PCTIO-10. I have tested that both work and use EXTIRQ1.

If no IRQ is available, the software can poll the status of the gate output until it sees it go low. This requires more work for the PC processor, but should be acceptable in all realistic situations. The primary limitation of the polling method is that the polling must not be allowed to begin for a brief amount of time (3 timebase periods = 0.3 millisecond in this case) after the gate pulse is requested. This is because the board takes 2 or 3 periods to synchronize to the timebase before actually starting the pulse. The software could therefore read a low output simply because the pulse has not yet begun rather than because it has completed. The PC software driver written for the Micro-Mott waits a one millisecond before polling begins to prevent such a problem.

See Tables 3-13 and 3-14 for a full listing of the signal connections and jumper placements required to implement these counting schemes.

Detector Elements and Power Supplies

The Micro-Mott detector includes several electrostatic lenses in order to focus electrons emitted from the analyzer onto a high-potential (20-30kV) gold scattering foil. The precise voltages necessary for this have been optimized relative to the original design using electron trajectory calculations by B.S. Mun and G. Fecher, also working in our group. The detector power supplies remain referenced to chamber ground even as the analyzer to which it is attached is floating at up to $\pm 1500\text{V}$ (the analyzer retardation potential). In order to maintain focusing conditions within the detector and not introduce problematic acceleration or retardation of electrons between the analyzer and detector as the analyzer potential is changed, the detector lens voltages must be appropriately adjusted for the analyzer settings. By following a scheme similar to that used in the Scienta Analyzer Module the voltages may be controlled from the software. An “element” submodule is responsible for cubic-spline fitting to voltage tables depending upon the analyzer setting for each lens element. A power supply sub-module is responsible for sending the appropriate signals to hardware to obtain these voltages. The detector is equipped with power supplies that are programmed by an analog voltage input, and so a National Instruments AT-AO-10 board has been used to set the voltages from the PC. By choosing to use either additional Scienta power supplies (as used with the ES-200 analyzer module) or purchasing other GPIB controllable power supplies, this board could have been eliminated and possible analog programming signal problems

(noise, ground loops) avoided. However, all tests to date indicate that the system as presently configured should perform adequately.

All Micro-Mott counter attributes, spline tables, power supply attributes and other information required by the software are found in the input file named *mott.ini*. See Table 3-7 for a complete listing of all source files, support files, and hardware.

3.3.6 LBNL Highspeed Detector

The LBNL Highspeed detector is a new prototype detector designed to dramatically increase the dynamic counting range available in high spatial resolution, multichannel electron detection. The detector is controlled by a digital signal processor (DSP), as described elsewhere [3]. Because the multichannel nature of the detector is similar to that of the Scienta CCD detector, substantial reuse of scan acquisition code could be achieved, with the appropriate changes made in the details of the hardware commands and data handling. See Table 3-8 for the listing of source code files, support files, and hardware.

The most specialized board used in all of the current software is the customized AT&T 32C DSP board [15], which requires an ISA slot in the PC. Because the DSP runs real-time software that controls the behavior of the detector, replacing it with a non-ISA bus I/O hardware represents a significant effort. A different DSP board could be purchased, but would require significant changes to be made to the current detector software (PC side) and a rewrite of the DSP code to match the internal architecture of the new DSP. Attention should be paid to this issue as the second-prototype stage of the project is begun.

3.4 Data Storage Module (File Format)

With relatively complicated data acquisition modes available, in which a large number of different datasets can be collected in various orders, the storage of the data to disk as it is acquired can become rather complicated. The ability to add new types of experiments without major modifications to the file structure has also been considered when selecting the file format.

Data storage/retrieval demands proved to require a more elaborate file format than simple appending to an ASCII (text) file as new data was acquired. This is primarily due to the fact that the data acquisition program is capable of acquiring datasets much larger than can practically be held in memory during the experiment, particularly if dynamic memory allocation is used. Even if data were stored in memory throughout the entire experiment, it would still be desirable to flush the data to disk periodically to protect against accidental data loss due to computer or software problems. Continuous storage of the data as it is acquired required simultaneous maintenance of a parsing routine that could reorder the final data file into the correct logical order and grouping for analysis and so added needless programming complexity to a conceptually simple problem.

File Format Library

As a solution to this problem, a decision was made to use the Hierarchical Data Format (HDF) that is distributed by the National Center for Supercomputing Applications (NCSA) [17]. This format provides an assortment of data storage and grouping mechanisms within a system file from which a standard file structure may be built. Several considerations contributed to the choice of this format. First, it is a freely distributed, open source code library that is widely supported among many commercial

software packages [18]. Second, the library is available on multiple platforms (Win32, various Unix distributions, Linux, Macintosh, etc.) with an identical interface. The file format itself is also bitwise identical regardless of the platform the file was created on, so files can be easily transferred and used across platforms. Finally, the format is “self-documenting”: the format specifies a set of components or objects that the developer assembles into the desired standardized application format. Because the format is assembled from standard building blocks, another application can find and access the stored information in a general manner simply by iterating through the objects contained in the file. Finally, the format is binary, saving both disk space and optimizing read/write times.

The objects in the file can be quickly and arbitrarily accessed without parsing of the file as would be needed with an ASCII file. This allows portions of the file to be created and then continually reaccessed and modified as portions of the data within an experiment are acquired. This completely eliminates the need to flush large amounts of data at once and to maintain all data in memory.

At the time of development, the library version that was in full release was HDF ver.4.1.2. However, NCSA had published detailed information regarding the implementation of HDF ver.5 [17]. In the interest of future upgrades, only portions of the 4.1.2 library that have equivalent structures within the new format were used: tree level grouping; generalized data arrays, and attribute objects. Actual migration to the ver.5 library has not been pursued due to the still evolving status of the new release and the lack of free and commercial software that have so far migrated to the new version.

The NCSA HDF ver. 4.x library requires a special procedure to be followed in order to link properly under LabWindows CVI 4.0.1 due primarily to variable-type definition conflicts between the HDF and LabWindows library header files. See the source code for details regarding the problems and the solution. All required files used with the HDF library are listed in Table 3-10.

Internal File Structure

The HDF library provides a well-defined interface to a set of objects that may be placed in a file. The file is composed of various objects of two basic types: grouping objects (with the HDF vGroup interface) and data objects (either named variables with HDF vGroup Attributes or data arrays with the HDF Scientific Data Set (SDS) interface). The grouping objects allow a tree structure analogous to a common file directory structure to be built within the file. Data objects can then be used to populate the grouping tree in a meaningful manner.

The tree and data structures chosen for experimental data are diagramed in Fig. 3-4. Note that an *experiment* begins as a top level or *root* object in the file. This allows multiple independent experiments to be added to the file by simply adding additional root level objects to the file. In other words, the file can be opened, an experiment acquired, and the file closed. At any later time, the file may be reopened, and additional experiments added as new root level objects without affecting the existing experiment data in any manner. This allows closely related experiments to be stored together or for a batch of experiments to be acquired in sequence while only requiring a single filename to be specified by the user.

Within an *experiment* object, an arbitrary number of named attribute strings may be appended, describing the experiment as needed. Also, an *experiment parameters* grouping object is attached. This group contains attributes and data arrays describing the experiment scan variables such as sample angles, beamline settings, etc. Finally, an arbitrary number of *dataset* objects are added.

A *dataset* object is defined as a group containing a set of named attribute strings and data arrays along with a “type” identifier. This is where the actual spectra are stored. The types currently used are “XPS” and “XAS”, representing either a set of photo/Auger emission spectra (as counts vs. binding or kinetic energy) or a set of absorption spectra (counts vs excitation energy). The primary data arrays in both these cases are two-dimensional: energies in one dimension and the experiment parameter index (corresponding to specific angle(s), time, radiation polarization, etc.) in the other. Additional dataset types could easily be added by simply defining a consistent set of data arrays and required attributes and a “type” name and using this to build the objects stored within the standard *dataset* object. For instance, if a full frame grabber were used with the CCD detector, so that a two-dimensional image was available, a new type of dataset to store this in may be referred to as “XPS2D” with a three dimensional data array allowing multiple two-dimensional images to be stored in the standard looped scan experiment as a function of the experiment parameter. We note that this mode is in fact implemented in versions of the Scienta vendor software in which photoemission spectra at different polar emission angles are imaged successively along the detector axis perpendicular to energy (based on a so-called “angle-resolving” mode of the electrostatic lens that is not yet implemented in our analyzer), but our new software could also easily

be made to accommodate this mode of operation with the above-mentioned hardware modifications.

Note that the HDF file format is very convenient in terms of allowing additional data to be stored after initial creation and storage. For instance, if an analysis (curve fitting, etc.) routine were written to read and work from an HDF file, then the results for each dataset could easily be stored in a new analysis group added within the dataset with any required data stored within. This sort of addition will not effect the operation of programs that access the original structure, as the still-existing original objects are not effected by the additional objects.

Currently, no data analysis package for dealing directly with the HDF files has been written or purchased, and a search over various options during the course of this dissertation did not in fact discover any package with all the desirable characteristics. Thus, data analysis at present depends on a legacy spectrum-fitting package distributed by Scienta [8] with the original software for the ES-200. In order to continue to use this software, which still has several good features for the kinds of analysis we do, it was thus required to write a format converter between HDF format and the Scienta binary format. Using the Scienta format as the primary storage format for the software was considered, but a large number of limitations in this format made it an undesirable long-term solution. This converter was written partially in Borland C++ Builder [6] due to the availability from Scienta of portions of file I/O code written in Pascal. The Borland compiler has an integrated Pascal compiler that could compile this code, wrapping it in C code that could in turn be linked into LabWindows code. An additional HDF-to-ASCII converter has

also been written for importing of data into most commercial graphics or analysis packages.

3.5 Experiment and Scan Modules

The experiment module contains routines for acquiring an experiment including the instrument control, user interface, and data storage. An experiment is defined as a series of loops over a set of datasets/scan regions. Each loop generally corresponds to a different set of instrument parameters, such as sample geometry or excitation energy, and in the future, perhaps also radiation polarization. The experiment module uses the scan module associated with each detector to acquire the set of scan regions.

The type of experiment determines the conditions under which these regions are looped over. For example, a polar, azimuthal, or hologram (solid angle) scan will vary the sample geometry in between repeated collection of the set of electron kinetic/binding-energy scan regions. A photon scan will vary the excitation energy or wavelength in equal steps. A timed scan will simply wait a defined amount of time between consecutive sets of scan regions. If the requested time has already passed when the scan is ready to begin, then it starts immediately. The data file stores the actual elapsed time since the experiment began.

The experiment module uses the HDF data file module to save the experiment information and determines where the scan modules will save acquired spectra. In addition, access to the appropriate instrument module for controlling the loop parameters is required (e.g., sample manipulation module or light source module).

Detector-Specific Scan Modules

Each detector must have a set of scanning routines (defined in the source code [4]) in order to be integrated into the experiment module, although significant amounts of code can be reused from one detector scan module to another. The general model requires the scanning function to accept a file pathname containing the scan definition, a reference to the position (group) in the HDF data file (as well as access handles for the file) where the scan is to be placed, and a number of loops (times the scan will be repeated in the experiment) in a “load” function. This allows the load function to allocate an appropriate amount of data space in the file to hold all data that is to be acquired. The loading function must return a “handle” (an integer whose meaning is private to the scan module) that is then passed to the scan module in an “acquire” function along with a loop number. The loop number may be out of sequence, and no assumption should be made to the contrary by the scan routines. With the information passed by the load function, the scan module is expected to maintain any required information about the scan until an “unload” call is made to the handle representing the scan. The maintenance of scan handles throughout the lifetime of the experiment allows the scan module to allocate any required memory for the scan (i.e. data arrays used to buffer the file data) only once, providing optimum immunity to poor allocator library performance, as well as simplifying the storage of per-scan changes (i.e. acquisition time changes) throughout the experiment.

Any instrument settings to which the scan module is sensitive (e.g., excitation energy for spectra defined via binding energy) should be checked at each “acquire” call and not the “load” call since it may be changed by the experiment routine, other scan

routines, or user intervention between each “acquire” call. In addition, the module is expected to maintain a GUI display with the appropriate information (plot of current spectrum, status, etc.) in a window that is independent of the experiment module status window. Examples of typical GUI windows for both the experiment and scan modules are shown in Fig. 3-5.

Experiment Setup Modules

This module contains routines for editing and managing experiment and scan definitions. These are simply file editors with a graphical interface that ensures valid data values are stored for each attribute. Currently, the experiment and scan files are edited in separate modules. The experiment setup interface allows the user to select the type of experiment (single scan, polar angle scan, etc.) and the variables required to define this experiment (for a polar scan, the beginning, ending and step angle along with the fixed azimuthal angle). In addition, the user selects any number of scan regions to be included in the experiment. These are separate files and so the user selects the filenames and stores only these filenames in the experiment definition. Independent editing of the scan regions defined in these files results in a change to the experiment. The entire list of scan regions is performed at each step of the experiment loop in the order defined in the list. Thus, for example, one can measure several distinct photoelectron spectra over both core and valence levels at each emission direction or each photon energy in a series of measurements. Several additional options and attributes are also settable in the interface.

The scan region files are edited in a separate module, allowing the user to select the type (e.g., XPS: fixed kinetic energy or binding energy; XAS with measurement usually of a flat secondary electron spectral region) and various values to define the scan.

These values include the analyzer mode, scanned energy range/step (in kinetic or binding energy), acquisition time, and detector settings, among others.

Note that the experiment and scan region files are simple ASCII formats that could be edited by hand, but knowledge of the appropriate entries is required. Once an experiment acquisition is begun, the files may be reedited (if desired) without affecting the acquisition; all file information is loaded into memory for the duration of the experiment.

The source code files and required support files for both the experiment setup and acquisition modules are listed in Tables 3-11. The code for each detector scan module code is listed with the corresponding detector control module code as discussed earlier.

3.6 Continued Development Directions

Several portions of this program have the potential for future enhancement. The most obvious software issues involve simply recompiling the code as new versions of various vendor libraries become available. Third party libraries likely to require attention, especially in the event of an operating system upgrade, are the Compumotor libraries and National Instruments NIDAQ/GPIB drivers.

In view of the large number of current boards and interface protocols used in this project, all future instruments should be, as much as possible, purchased with either a network (Ethernet and TCP/IP) or GPIB interface to eliminate the need for additional boards dependent on PC architecture. Such measures also make porting of the interface software to new operating systems transparent at the hardware level.

Finally, it should be noted that a compromise was made relative to what might be considered the optimal design in the final versions of the software. That is, because the

LabWindows CVI v.4.x compiler cannot debug into dynamic link libraries, many of the modules that were originally intended to be built into DLLs were in fact compiled directly (statically linked) into the primary executable. Upgrading to LabWindows CVI ver.5.5 or higher would eliminate this debugging problem. However, for users of the software, the only real benefit of this would be faster loading times of the software, as DLL based modules could remain completely unloaded until needed.

3.7 Final Remarks

A complete data acquisition system for the Advanced Photoelectron Spectrometer/Diffractometer endstation at the Advanced Light Source has been developed and put into operation on two distinct beamlines. The basic features of the software modules, including the current state of the software libraries and hardware setup have been discussed, with sufficient documentation to permit future developers and users to understand their operation and if necessary also modify them. Finally, recommendations have been given for future improvements or upgrades of both the hardware and software.

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Hardware	Module	Configuration and Interface Information
National Instruments AT-GPIB/TNT	Scienta ES-200 analyzer	-GPIB (IEEE 488.2) bus controller. -Configured in National Instruments GPIB driver and initialization file <i>SES_comm.ini</i> .
	Scienta CCD detector	-Connects to Scienta Interface Electronics.
Ethernet Card	ALS BL 4.0.2	-Configured in Windows [®] . -Connects to ALS local network.
National Instruments Lab-PC+ Board	ALS BL 4.0.2 flux meter	-Configured in National Instruments NIDAQ and initialization file <i>fluxmeter.ini</i> . -Connects to voltage output of beamline I_0 current amplifier.
Serial (RS-232) Port	ALS BL 9.3.2 serial interface	-Configured in Windows [®] and initialization file <i>ALS_bl932.ini</i> . -Connects to BL9.3.2 VME Crate (ALS cabinet BL0930), and Port 2 (25-pin connector using only TX and RX and <i>without</i> a NULL modem).
Compumotor AT6400 Indexer	APSD manipulator	- Configured with on-board DIP switches and initialization file <i>manip_apsd.ini</i> . -Connects to external AT6400 indexer which connects to Compumotor LN drives. -ISA Bus.
National Instruments PC-TIO-10	Micro-Mott detector counters	-Configured in National Instruments NIDAQ, on-board DIP switches, and initialization file <i>mott.ini</i> . -Connects to detector pulse discriminator outputs with appropriate pin jumpers (see Tables 3-13, 14). -ISA Bus.
National Instruments AT-AO-10 Board	Micro-Mott power supplies	-Configured in National Instruments NIDAQ, on-board DIP switches, and initialization file <i>mott.ini</i> . -Provides analog voltage I/O and each line connects to a power supply programming input. -ISA Bus.
Spectrum Signal Processing, AT&T DSP32C	LBNL HS Detector Control	-Digital Signal Processor Board. -Configured with on-board DIP switches and initialization file, <i>lbnlhs_det.ini</i> . -ISA Bus.

Table 3-1 Hardware Settings: Note these settings represent a successful configuration in a particular PC. For any other PC, many settings will require changes due to conflicts with OEM hardware (video drivers, etc.). When the hardware settings (especially bus addresses) are changed, software initialization files will also have to be updated.

Scientia ES Series Analyzer Module	
Source Files	
\\ses\\SES_analyzer.c	Primary analyzer element module routines and code interface, and GUI handling
\\ses\\SES_analyzer.h	header for above
\\ses\\SES_analyzer_common.c	Additional misc. analyzer module routines
\\ses\\SES_analyzer_common.h	header for above
\\ses\\SES_hardware.c	I/O hardware control
\\ses\\SES_hardware.h	header for above
\\ses\\SES_supplies.c	Primary power supply module routines and data
\\ses\\SES_supplies.h	header for above
\\ses\\SES_supplies_common.c	Internally shared routines and data for the power supply module
\\ses\\SES_supplies_common.h	header for above
\\ses\\SES_supplies_util.c	GUI routines for the power supply module
\\ses\\SES_supplies_util.h	header for above
\\ses\\SES_win.h	Definitions for module GUI
Support Files	
\\alexESCA\\ini\\ses_hemi.ini	Voltage element tables and analyzer definitions
\\alexESCA\\ini\\ses_supp.ini	Power supply definitions and hardware configuration
\\alexESCA\\uir\\SES_PS_win.uir	LabWindows GUI definition for power supplies
\\alexESCA\\uir\\SES_win.uir	LabWindows GUI definition for analyzer interface
NI GPIB Driver for Windows	Required to enable GPIB communication (see Nat. Inst. documentation)
Hardware	
NI GPIB TNT (PCI Bus) Card	GPIB (IEEE 488.2) Protocol. Scientia interface is <u>hardwired</u> as Device 1, so any other equipment sharing the bus must not use this address.

Table 3-2 Listing of the required files and hardware for the Scientia ES Control Module.

Lab (Fixed Energy) Light Source Module	
Source Files	
\\lab_source\\light_labsource.c	Primary module routines and interface
\\lab_source\\light_labsource.h	header for above
Support Files	
\\alexESCA\\ini\\light_lab.ini	Hardware and software configuration information
Hardware	
None	

Table 3-3 Listing of the required files and hardware for the fixed energy light source module.

ALS Beamline 4.0.2 Light Source Module	
Source Files	
\\als_b1401\\alsbl401.c	Primary module routines and interface
\\als_b1401\\alsbl401.h	header for above
\\als_b1401\\alsbl401_common.c	Additional module routines and data
\\als_b1401\\alsbl401_common.h	header for above
\\als_b1401\\alsbl401_win.h	Definitions for module GUI
\\fluxmeter\\fluxmeter.c	Simple analog board configuration and reading
\\fluxmeter\\fluxmeter.h	header for above
\\sca_library\\scalib.h	Definitions for the SCA library
\\sca_library\\scalib_shared.h	Definitions for the SCA library
\\sca_library\\sca_library.c	Dynamic binding to the SCA dll, below
\\sca_library\\sca_library.h	header for above
Support Files	
\\alexESCA\\ini\\alsbl401.ini	Hardware and software configuration information
\\alexESCA\\uir\\alsbl401_win.uir	LabWindows GUI definitions for all module interfaces
\\alexESCA\\ini\\fluxmeter.ini	Hardware and software configuration information
ca.dll †	Channel access library, the part of EPICS we are using (file must be in the system path) Requires autoexec.bat file to have the following line in it (it should also be possible to add this to the environment settings programmatically via Windows [®] SDK calls, but this is simpler): "SET EPICS_CA_ADDR_LIST=131.243.71.255"
caRepeater.exe †	Channel access repeater. (file must be in the system path)
sca3.dll †	Simple Channel Access, ver. 3 library (file must be in the system path)
msvc60.dll †	Microsoft C/CPP library, needed by ca.dll (file must be in the system path)
msvcrt.dll †	Microsoft C runtime engine, needed by ca.dll (file must be in the system path)
Winsock 2, 32 bit †	Must be installed on the system.
Hardware	
Any standard Ethernet network card configured for TCP/IP protocol.	PC must be connected to the local network in order to be granted EPICS access.
Any Nat. Inst. Board Analog Input Channel Currently NI PC-Lab+ Board (Channel 0)	Requires that <i>fluxmeter.ini</i> has the correct values for NIDAQ board and channel.

Table 3-4 Listing of the required files and hardware for the ALS Beamline 4.0.1 Light Source Module.

Marked files (†) may be found online [11] with instructions and documentation.

ALS Beamline 9.3.2 Light Source Module	
Source Files	
\\als_b1932\\BI932.c	Communication and GUI management routines
\\als_b1932\\BI932.h	header for above
Support Files	
\\alexESCA\\ini\\ALS_b1932.ini	Hardware and software configuration information
\\alexESCA\\uir\\bl932_monitor.uir	LabWindows GUI definitions for all module interfaces
Hardware	
Any available standard serial I/O (COM) port	Ensure the PC port used is correctly identified in <i>ALS_b1932.ini</i> Do NOT use a NULL modem in the serial cable. Connect "CABLE A2 TO BL093020 FRM BL0933" (ALS Cabinet BL0930) into Serial Port 2 on the back of the VME Crate. Connect the opposite end of the cable (Cabinet BL0933) to the PC serial port.

Table 3-5 Listing of the required files and hardware for the ALS Beamline 9.3.2 Control Module.

Scientia CCD Detector Module	
Source Files	
\\scientia\\scientia_det.c	Primary module routines and interface
\\scientia\\scientia_det.h	header for above
\\scientia\\scientia_det_common.c	Code and data shared throughout the module
\\scientia\\scientia_det_common.h	header for above
\\scientia\\scientia_det_ect.c	Calibration table handling
\\scientia\\scientia_det_ect.h	header for above
\\scientia\\scientia_det_par.c	Detector parameter handling
\\scientia\\scientia_det_par.h	header for above
\\scientia\\scientia_det_ratemeter.c	Simple detector control and GUI for testing and setup of the detector
\\scientia\\scientia_det_ratemeter.h	header for above
\\scientia\\scientia_det_sen.c	Sensitivity table handling (not currently used)
\\scientia\\scientia_det_sen.h	header for above
\\scientia\\scientia_det_set.c	Detector settings handling (settings are adjustable parameters)
\\scientia\\scientia_det_set.h	header for above
\\scientia\\scientia_scan.c	Main spectrum scanning code. Requires access to the entire detector module, the analyzer and light source modules, and the data storage module. This is the most complicated module in terms of external library usage.
\\scientia\\scientia_scan.h	header for above
\\scientia\\scientia_scan_display.c	GUI code for the scan module
\\scientia\\scientia_scan_instance.h	Definition the scan data structure
Support Files	
\\alexESCA\\ini\\SES_det.ini	Hardware and software configuration information
\\alexESCA\\ui\\scientia_det_win.uir	LabWindows GUI definitions for all module interfaces
NI GPIB Driver for Windows	
Hardware	
NI GPIB TNT (PCI Bus) Card	GPIB (IEEE 488.2) Protocol. Scientia interface is <u>hardwired</u> as Device 1, so any other equipment sharing the bus must not use this address. Board settings must match listings in <i>SES_det.ini</i> .

Table 3-6 Listing of the required files and hardware for the Scientia CCD Detector Module.

Micro-Mott Detector Module	
Source Files	
\mott\mott_common.c	Routines and data shared by subcomponents
\mott\mott_common.h	header for above
\mott\mott_count.c	Counter routines for managing hardware,
\mott\mott_count.h	header for above
\mott\mott_det.c	Primary module routines and interface
\mott\mott_det.h	header for above
\mott\mott_det_win.h	Definitions for module GUI
\mott\mott_element.c	Maintains and uses tables to determine correct voltage element settings
\mott\mott_element.h	header for above
\mott\mott_monitor.c	GUI countrate display
\mott\mott_monitor.h	header for above
\mott\mott_power.c	Controls the available power supplies
\mott\mott_power.h	header for above
\mott\mott_scan.c	Main spectrum scanning code. Requires access to the entire detector module, the analyzer and light source modules, and the data storage module. This is the most complicated module in terms of external library usage.
\mott\mott_scan.h	header for above
\mott\mott_scan_display.c	GUI code for the scan module
\mott\mott_scan_display.h	header for above
\mott\mott_scan_instance.h	Definition the scan data structure
\mott\mott_settings.c	Detector settings handling (not currently used)
\mott\mott_settings.h	header for above
Support Files	
\alexESCA\ini\mott_det.ini	Hardware and software configuration information
\alexESCA\ini\mott_det_win.uir	LabWindows GUI definitions for all module interfaces
NIDAQ Driver for Windows	When installed and configured, provides low level driver for Nat. Inst. I/O Boards.
Hardware	
Nat. Inst PC-TIO-10 (ISA Bus)	Digital Timer/Counter card used for data collection. Must be jumpered according to Table 3-14. Board settings must match listings in <i>mott_det.ini</i> .
Nat. Inst AT-AO-10 (ISA Bus)	Analog I/O Board for programming the detector power supplies. Board settings must match listings in <i>mott_det.ini</i> .

Table 3-7 Listing of the required files and hardware for the Micro-Mott Detector Module.

LBNL Highspeed Detector Module	
Source Files	
\\bnl_hs\\bnlhs_det.c	Primary module routines and interface
\\bnl_hs\\bnlhs_det.h	header for above
\\bnl_hs\\bnlhs_det_common.c	Code and data shared throughout the module
\\bnl_hs\\bnlhs_det_common.h	header for above
\\bnl_hs\\bnlhs_det_ect.c	Calibration table handling
\\bnl_hs\\bnlhs_det_ect.h	header for above
\\bnl_hs\\bnlhs_det_par.c	Detector parameter handling
\\bnl_hs\\bnlhs_det_par.h	header for above
\\bnl_hs\\bnlhs_det_ratemeter.c	Simple detector control and GUI for testing and setup of the detector.
\\bnl_hs\\bnlhs_det_ratemeter.h	header for above
\\bnl_hs\\bnlhs_det_set.c	Detector settings handling (settings are adjustable parameters)
\\bnl_hs\\bnlhs_det_set.h	header for above
\\bnl_hs\\bnlhs_scan.c	Main spectrum scanning code. Requires access to the entire detector module, the analyzer and light source modules, and the data storage module. This is the most complicated module in terms of external library usage.
\\bnl_hs\\bnlhs_scan.h	header for above
\\bnl_hs\\bnlhs_scan_display.c	GUI code for the scan module
\\bnl_hs\\bnlhs_scan_display.h	header for above
\\bnl_hs\\bnlhs_scan_instance.h	Definition the scan data structure
\\bnl_hs\\spectrum_dsp\\32librar.c	Low level DSP control library provided by Spectrum Signal Processing
\\bnl_hs\\spectrum_dsp\\dsp32.h	header for above
\\bnl_hs\\dsp_defi.h	Defines memory locations used by the DSP code (allows control of DSP code by the PC)
\\bnl_hs\\dsp_io_a.c	High level control of the detector through DSP library calls (32librar.c)
\\bnl_hs\\dsp_io.h	header for above
Support Files	
\\alexESCA\\ini\\bnlhs_det.ini	Hardware and software configuration information
\\alexESCA\\ini\\bnlhsdet_sp.map	Data readout order to physical order mapping array for the detector
\\alexESCA\\uir\\bnlhs_det_win.uir	LabWindows GUI definitions for all module interfaces
\\alexESCA\\bin\\dsp.out	Compiled DSP software, loaded on DSP by module
Hardware	
AT&T DSP32C Card (ISA Bus)	Digital Signal Processor Board Address (dip switches) must match listing in <i>bnlhs_det.ini</i>

Table 3-8 Listing of the required files and hardware for the LBNL Highspeed Detector Module. This listing does not include the DSP code that is compiled and linked by DSP specific tools provided by the vendor [15]. The *\\bin\\dsp.out* support file is the compiled and linked object code that is run on the DSP.

APSD Sample Manipulator Module	
Source Files	
\\manip_APSD\\manip_APSD.c	Primary module routines and interface
\\manip_APSD\\manip_APSD.h	header for above
\\manip_APSD\\manip_APSD_utility.c	GUI routines
\\manip_APSD\\manip_APSD_utility.h	header for above
\\manip_APSD\\manip_APSD_utility_win.h	Definitions for module GUI
\\manip_APSD\\Wn956000.c	Dynamic binding to the Compumotor dll
\\manip_APSD\\Wn956000.h	header for above
\\manip_APSD\\Compumotor.h	Definitions for using the Compumotor <i>wn956000.dll</i> (below)
Support Files	
\\alexESCA\\ini\\manip_apsd.ini	Hardware and software configuration information
\\alexESCA\\uir\\manip_APSD_utility_win.uir	LabWindows GUI definitions for all module interfaces
\\alexESCA\\bin\\at6400.ops	Compumotor distributed AT6400 firmware
\\alexESCA\\bin\\meter.dll	Compumotor distributed dynamic link library for win95
\\alexESCA\\bin\\wn956000.dll	Compumotor distributed dynamic link library for win95
\\windows\\system\\vmm32\\wrtdev*.vxd	*= 0,1,2,3,4; Compumotor distributed virtual device drivers required by dll
Hardware	
Compumotor AT6400 Mult-Axis Controller (ISA Bus)	Board address (dip switches) must match listing in <i>manip_apsd.ini</i> . Software Assumes Axis 1= Polar (θ), Axis 2= Azimuthal (ϕ) of Axis 1-4

Table 3-9 Listing of the required files and hardware for the APSD sample manipulator module.

Data File I/O (NSCA HDF Library Based) Module	
Source Files	
\\data\\hdf412_lib\\hd412m.lib	NSCA import library
\\data\\hdf412_lib\\headers\\mfhdf.h	Primary header for library. Several additional subheaders are included in the <i>hdf412_lib\\headers\\</i> directory
\\data\\hdf412_lib\\hm412m.lib	NSCA import library
\\data\\hdf412_lib\\mfhdf.lib	NSCA import library
\\data\\hdf_expt.c	Experiment Storage in the HDF format
	header for above
\\data\\hdf_regions.c	Region (Scan) Storage in the HDF format
	header for above
\\data\\hdf_tools.c	Misc. tools for accessing HDF files
\\data\\hdf_tools.h	header for above
Support Files	
\\alexESCA\\hd412m.dll	NSCA dynamic link library
\\alexESCA\\hm412m.dll	NSCA dynamic link library

Table 3-10 Listing of the required files for using the pre-compiled HDF library as available from NSCA [17] and related utility routines .

Experiment Acquisition Module	
Source Files	
expmnt\expt_instance.c	Experiment collection routines
expmnt\expt_instance.h	header for above
expmnt\expt_instance_display.c	Experiment collection GUI routines
expmnt\expt_inst_win.h	Definitions for experiment. scanning GUI
expmnt\expt_done.c	Experiment completion routines
expmnt\expt_done.h	header for above
exptDefine\expt_acq_param.c	Experiment mode routine handling (see <i>exptmode\</i> files below)
exptDefine\expt_acq_param.h	header for above
exptDefine\expt_attr_define.c	Experiment attribute handling
exptDefine\expt_attr_define.h	header for above
exptDefine\expt_define_win.h	Definitions for experiment. GUI
exptDefine\expt_def_define.c	Primary experiment. definition handling
exptDefine\expt_def_define.h	header for above
exptDefine\expt_def_utility.c	Experiment. definition utility (GUI)
exptDefine\expt_def_utility.h	header for above
exptDefine\expt_define_win.h	Definitions for experiment. definition GUI
exptDefine\expt_option_define.c	Experiment option handling
exptDefine\expt_option_define.h	header for above
exptDefine\queue_define.c	Experiment. queue (currently unused)
exptDefine\queue_define.h	header for above
exptDefine\region_define.c	Primary scan(region). definition handling
exptDefine\region_define.h	header for above
exptDefine\region_utility.c	Scan(region) definition utility (GUI)
exptDefine\region_utility.h	header for above
exptDefine\scan_define_win.h	Definitions for scan definition. GUI
exptmode\em_azimuthal.c	Azimuthal expt. definition and implementation: requires Sample Manip. Module
exptmode\em_azimuthal.h	header for above
exptmode\em_common.h	Shared definitions for all experiment modes
exptmode\em_excitation.c	Excitation expt. definition and implementation: requires Light Source Module
exptmode\em_excitation.h	header for above
exptmode\em_holo.c	Hologram expt. definition and implementation: requires Sample Manip. Module
exptmode\em_holo.h	header for above
exptmode\em_polar.c	Polar expt. definition and implementation: requires Sample Manip. Module
exptmode\em_polar.h	header for above
exptmode\em_timed.c	Timed expt. definition and implementation
exptmode\em_timed.h	header for above
Support Files	
\alexESCA\ini\expt.ini	Experiment acquisition initialization
\alexESCA\ini\exptspec.ini	Experiment definition initialization
\alexESCA\uir\expt_inst_win.uir	Experiment acquisition GUI initialization
\alexESCA\uir\expt_define_win.uir	Experiment definition GUI initialization
\alexESCA\uir\scan_define_win.uir	Scan/Region definition GUI initialization

Table 3-11 Required files listing for the experiment and scan definition utilities as well as the experiment acquisition routines.

Miscellaneous Utility Libraries	
Source Files	
alexesca_main.c	contains the initial entry point (WinMain) and primary library loading and unloading routines.
toolbox/inifile.c	Section/tag/value file reading utilities (modified from National Instruments library)
toolbox/inifile.h	header for above
toolbox/time_to_go.c	Simple time calculations
toolbox/time_to_go.h	header for above
toolbox/toolbox.c	Unmodified National Instruments library for lists and misc.
toolbox/toolbox.h	header for above
alexmisc/alexmisc.c	Simple function s for misc. tasks
alexmisc/alexmisc.h	header for above
Utilities/Convert/convert.c	Conversions related (primarily) to physical values (i.e. photon wavelength to energy)
Utilities/Convert/convert.h	header for above
Utilities/macros.h	Useful definitions for the precompiler
Utilities/pathlists/pathnames.c	Maintains and sorts, etc arrays of strings (used for pathname lists)
Utilities/pathlists/pathnames.h	header for above
Manip/manip.c	Loading and linking code for manipulator modules †
Manip/manip.h	header for above
manip_msg.c	Windows message registering for manipulator modules
manip_msg.h	header for above
manip_win.h	
light.c	Loading and linking code for light source modules †
light.h	header for above
light_msg.c	Windows message registering for light source modules
light_msg.h	header for above
frontend/frontend.c	Handles creation and maintenance of the AlexESCA front end display
frontend/frontend.h	header for above
frontend/frontend_window.h	Definitions for frontend GUI
frontend/frontend_wndproc.c	Redefinition of the default WinProc for the frontend window for custom window behavior
detector.c	Loading and linking code for detector modules †
detector.h	header for above
detector_msg.c	Windows message registering for detector modules
detector_msg.h	header for above
scan.c	Loading and linking code for detector spectrum collection modules †
scan.h	header for above
analyzer.c	Loading and linking code for analyzer modules †
analyzer.h	header for above
analyzer_msg.c	Windows message registering for analyzer modules
analyzer_msg.h	header for above

Table 3-12 Listing of miscellaneous files including several used throughout most modules.

†The various “Loading and linking code for *X* modules” entries currently use “switch-case” based function calling due to the use of statically linked libraries (due to debugger limitations). When using dynamic link libraries, alternate versions of these files will dynamically load and obtain function entry points for that library.

Mott Detector Channel	High Order Counter (chip 2)	Low Order Counter (chip 1)
Left	6	1
Right	7	2
Up	8	3
Down	9	4

Table 3-13 Micro-Mott detector counter assignments on the National Instruments PC-TIO-10. Pairs of 16 bit counters are cascaded into 32 bit counters for each detector channel of the detector, designated as Left, Right, Up, Down. The low order counter input is connected to the corresponding detector channel signal while the high order bit is connected to the rollover signal of the low order counter.

Signal		Source	Connection
Data Signal (TTL) -or- Test Signal	Left Right Up Down	Corresponding pulse discriminator outputs (external electronics) -or- Pin 29	Pin 1 Pin 4 Pin 7 Pin 10
Counter Cascading (Implements Table 3-13)	Left Right Up Down	Pin 3 Pin 6 Pin 9 Pin 12	Pin 15 Pin 18 Pin 21 Pin 24
Counter Gating		Pin 28	Pins 2, 5, 8, 11, 16, 19, 22, 25
Counter Gate IRQ service		Pin 28	Pin 32

Table 3-14 Micro-Mott detector counter interface jumper and wiring connections for the National Instruments PC-TIO-10 counter board. This listing must be followed in order for the software to work properly. For PC-TIO-10 pin positions and descriptions, refer to National Instruments product documentation [5].

Fig. 3-1 Application Module Block Diagram for *AlexESCA*. Solid Lines indicate hardware level control and telemetry links. Dashed lines indicate simple status queries and menu level control (i.e. “open the module manual control utility”), but no direct hardware control.

Fig. 3-2 Screen image showing the typical style of the module GUIs in the AlexESCA software. This image includes windows displaying lens tables for the Scienta analyzer, the analyzer power supply list, and the manual control window for the sample manipulator.

Fig. 3-3 (a) True azimuthal (ϕ) and polar (θ) angle definitions as used in the APSD sample manipulator software. The true azimuthal angle is defined relative to some reference direction lying in the sample surface, usually some low-index direction $[hkl]$ for a single-crystal sample. The polar angle is always measured with respect to the surface, and can be $>90^\circ$ as dealt with in the software, although it is common in final data treatment to express it always as an acute angle. (b) The angle between photon incidence and electron exit (θ_{spec}) is fixed at 57.74° when using the x-ray source, but not with (c) the beamline due to the unique construction of the APSD chamber, which permits rotating the analyzer in the plane of the electron storage ring. From the geometry shown, valid experimental angles capable of yielding non-zero photoelectron intensities before either the excitation source or the analyzer line-of-sight to the sample surface is lost (given ideal system alignment and sample mounting) are clearly $0^\circ \leq \theta_{true} \leq \theta_{spec} + 90^\circ$ for the standard x-ray source and $\theta_{spec} \leq \theta_{true} \leq 180^\circ$ for the beamline. The azimuthal angle is always free to rotate to any position.

Fig. 3-4 Internal tree structure of the data files. The structure is implemented under the NCSA HDF ver. 4.1.x library. Note an analogy between a standard file directory structure, with directories becoming “groups” and files becoming “attributes” and data arrays. Under such a system, complicated and easily extensible data structures can be stored and logically assembled within the file.

Fig. 3-5 Screen image of the acquisition routine while using the Scienta CCD detector in the *AlexESCA* software. The bottom window contains the current spectrum as it is acquired and allows the user limited control during acquisition through the menu bar (add acquisition time, stop, start over, change graphing style) The center window maintains a listing of the overall experiment related actions: parameter status, current scan in progress, approximate time to go, etc. It also allows similar control of the experiment during acquisition through the menu bar.

4 Investigations of Multiple Atom Resonant Photoemission

4.1 Introduction

In several recent papers by our group that were completed as part of this thesis research [1-5], it has been suggested that photoemission associated with a certain core electronic level of a given atom "A" can be significantly enhanced in intensity by tuning the photon energy through core-level absorption edges of a near-neighbor atom "B". The apparent enhancements seen in experimental data for several metal oxides (e.g. MnO, Fe₂O₃, and La_{0.7}Sr_{0.3}MnO₃ [1,2]), as well as in a series of Cr/Fe alloys and bilayers [3] were very large, ranging up to 40-100% of the non-resonant intensity, and they were furthermore observed to follow closely the x-ray absorption coefficient of atom B in shape [1-3]. The effects observed have been termed multi-atom resonant photoemission (MARPE) to distinguish them from the better-known intraatomic single-atom resonant photoemission (SARPE). Similar effects have also been reported in other transition metal compounds [6] and in an adsorbate [7] by other groups. Analogous and presumed related enhancements also appeared to be present in the secondary decay processes of Auger electron and fluorescent x-ray emission, again tracking very closely the x-ray absorption coefficient in form [4]. A theoretical model based on an extension of normal SARPE theory has also been presented to describe these results, and first comparisons of calculations based on it yielded encouraging agreement with experiment [5]. The potential utility of such effects for studying near-neighbor atom identities and bonding have also been pointed out [1-4]. Independent of this work on core-core multi-atom resonant photoemission, other groups have reported the enhancement of valence

photoemission intensities primarily associated with emission from a certain atom A upon tuning the photon energy through the core-level absorption edges of a nearby atom B, with this work including measurements near solid-solid interfaces [8,9] and on a free molecule [10]. No attempts have as yet been made to theoretically model this latter type of valence-core MARPE effect.

In this chapter, we first briefly review the primary experimental results of the core-core multi-atom resonant photoemission effects as presented in our earlier work [1-4]. We then point out that these measurements (or indeed any resonant- or non-resonant- photoemission effect) must be carried out with extreme care to avoid nonlinearities in the electron detector response, and illustrate these effects by carrying out corrections on a few representative data sets for O 1s emission from MnO in resonance with the Mn 2p excitations. The corrected results are found to show significantly smaller MARPE effects on photoelectron intensities, with shapes now considerably different from the x-ray absorption coefficient. In addition, theoretical calculations based on the previously-discussed microscopic model [5], and on a simpler macroscopic classical theory of x-ray optics [11] are presented and found to yield excellent agreement with the remaining experimental effects, thus clarifying the physics involved. We also comment on the implications of this work for other recent core-core and valence-core MARPE measurements [6-10], as well as for x-ray emission and x-ray scattering experiments. Potential future uses of MARPE as a new method for studying near-neighbor atoms are also considered.

4.2 Experimental Procedure and Data Analysis

As noted earlier in this dissertation, all photoelectrons were analyzed in energy and detected with a Scienta ES200 electron spectrometer system [13], as situated either on a bend-magnet beamline (9.3.2) [13b] or an undulator beamline (4.0.2) at the Berkeley Advanced Light Source. The high brightness of the ALS (a third-generation synchrotron radiation source), coupled with the high transmission and resolution of the rotateable Scienta ES200 electron spectrometer used to measure photoelectron spectra, permits determining photoelectron intensities rapidly enough to study any resonant effects observed as a function of the key experimental parameters of photon energy $h\nu$, photon incidence angle ($\theta_{h\nu}$), and photoelectron emission direction (θ, ϕ). The ability to rotate the electron spectrometer over approximately 60° in the plane of the storage ring, together with the polar (θ) rotation of the sample goniometer, also permits varying θ and $\theta_{h\nu}$ independently, a feature of significant importance to this work.

The multichannel detection system used is that provided as part of the standard equipment by the manufacturer of the analyzer: a microchannel plate multiplier followed by a phosphor screen at high voltage in vacuum, and a CCD video camera outside of vacuum to finally convert light pulses into counts, as introduced in more detail in an earlier chapter. We have operated this detector in the "grayscale" or "analogue" mode in which integrated CCD charge is used for counting, rather than in the alternate "black-and-white" or "digital mode" in which individual pulses are counted. This grayscale mode has been developed by the manufacturer in order to permit counting at somewhat higher rates than available with the easily saturatable black-and-white mode. The

detector has in addition been used as delivered and installed by the manufacturer. This spectrometer and detector system is furthermore the same as that used by some other groups attempting to measure multi-atom resonant photoemission effects [6,7]. We have in the present study calibrated our detector system in both grayscale and black-and-white modes by using a standard x-ray tube with continuously-variable emission current at fixed high voltage. We verified initially that the total electron current from the sample (as measured with a picoammeter) tracked linearly with the emission current while at a fixed high voltage between cathode and anode: thus, we can assume that the emission current is directly proportional to the x-ray flux incident on the sample. For an ideal detector, the number of counts recorded in a given spectrum would thus track the supply emission current in a linear fashion, and it is the deviation from this behavior that we wish to quantify here. The general methodology for this calibration and the final correction of spectra is discussed in more detail elsewhere [14,15], in one case together with previous data for a similar electron detection system [14], and in the another for data acquired as part of this work in our own experimental system [15].

The nature of the MARPE measurements require scanning photon energy continuously over absorption thresholds, and then making a careful determination of the elastic or no-loss peak intensities above a suitably subtracted inelastic background. A variable-energy synchrotron radiation source is thus required. All intensities were normalized to allow for the time-dependent decay of the electron current in the Advanced Light Source storage ring at which all measurements were performed; the time between fills during these measurements was 4-6 hours, with current dropping to about 40-50% of its initial value just before a refill.

Most of the experimental work presented here was performed with a polished MnO(001) single crystal. During photoemission experiments on MnO, the sample was maintained at a temperature of approximately 630°C to increase the sample conductivity and hence reduce both the shifting of photoelectron emission energy and the broadening of peak widths due to charging effects on the sample. These charging shifts can be significant because of the large changes in countrate (sample photocurrent) during the experiment that arise from both the nature of the measurement and the decay of the photon flux during the course of a storage ring fill. The initial angular orientation of the sample was accomplished by means of x-ray photoelectron diffraction (XPD) scans, as described in Chs. One and Two.

Additional work with Cr/Fe bilayers and alloys was also performed before the full extent of the detector calibration corrections was realized [31], and this will be briefly considered. In this work, photoemission experiments and partial electron yield measurements of the x-ray absorption coefficient were performed on bending-magnet beamline 9.3.2 of the Advanced Light Source. The angle of light incidence, θ_{hv} , was 20° with respect to the sample surface and the photoelectrons were collected in normal emission. Cr/Fe bilayer films were prepared by vapor deposition of Fe and then Cr at a rate of about 1 monolayer per minute and a pressure of $1-2 \times 10^{-10}$ Torr onto a clean W(110) substrate at near 300 K. $\text{Cr}_x\text{Fe}_{1-x}$ alloy films 150 Å thick and with the Cr concentration, x , in the range from 7% to 100% were grown on W(110) under similar conditions by varying the relative Cr and Fe deposition rates to achieve the desired alloy composition. Deposition rates were determined with a quartz microbalance and checked

before and after deposition. Cr and Fe layer thicknesses, as well as alloy compositions, were confirmed after deposition using quantitative angle-dependent photoelectron spectroscopy and x-ray absorption spectroscopy. No indications of surface segregation of Cr or Fe were found in the alloy films.

4.3 Results and Discussion

MnO(001), O 1s–Mn 2p Resonance– Initial Analysis

In reviewing our initial work, we will consider the case of an MnO(001) sample, in which we investigate the MARPE modulation of the O 1s photoemission intensity (with oxygen thus as atom “A”) as the photon energy as the photon energy is scanned through the Mn $2_{3/2}$ and $2p_{1/2}$ absorption thresholds (with manganese then as atom “B”), as illustrated in the energy level diagram in Fig. 4-1.

We show in Figs. 4-2(a)-(c) various aspects of the spectral features involved and the interatomic enhancement of O 1s emission from MnO observed, as the photon energy crosses the Mn 2p thresholds. The O 1s level is a deep-lying core electron with approximately 532 eV binding energy (cf. Fig. 4-2(a)). The deeper-lying Mn $2p_{3/2}$ and $2p_{1/2}$ thresholds that lead to the strong so-called “white-line” peaks in the x-ray absorption curve occur at approximately 640 and 652 eV, respectively (as also seen in the broad binding energy scan in Fig. 4-2(a)), which was obtained with a photon energy of 750 eV well above these resonances). Tuning the photon energy across these 2p thresholds thus results in photoelectron kinetic energies in the range of 110-120 eV. The autoionization decay that would occur for the Mn $2p_{3/2}$ resonance is indicated by the dashed arrows in Fig. 4-1: it involves the simultaneous deexcitation of Mn 3d to Mn $2p_{3/2}$

and excitation of O 1s to a free-electron state at the photoelectron energy. The coupling between the two atoms is via the Coulomb interaction.

From an experimental point of view, we also note that the peak intensity has to be measured carefully via inelastic background subtraction, since the background increases substantially as the photon energy goes above the 2p thresholds, primarily due to inelastic scattering of Auger electrons that are produced in the decay of the Mn $2p_{3/2} \rightarrow 3d$ excitations via secondary Auger processes that are different from the resonant autoionization channel. The Mn LMM Auger series that turns on in crossing the Mn 2p thresholds and is primarily responsible for this enhanced background is also shown in Fig. 4-2(a). We have in fact used the photon-energy dependence of this inelastic background intensity underlying the O 1s peak to measure the x-ray absorption coefficient of MnO in our experiment, and its behavior as a function of photon energy is shown in Fig. 4-2(b). After background subtraction and curve fitting using methods described in Ch. Two, the final O 1s intensity data (as peak areas above a Shirley-type background) for a 20° x-ray incidence angle is given in Fig. 4-2(c). This plot shows a clear enhancement of the O 1s signal in crossing the Mn $2p_{3/2}$ and $2p_{1/2}$ absorption peaks: the peak intensity increases by about 42% at the $2p_{3/2}$ peak, and the effect as integrated relative to a smooth background over the $2p_{3/2}$ region is about 11%. Thus, although the overall enhancement in peak intensity is about an order of magnitude less than seen in the example case of intraatomic Mn 3d emission from atomic Mn with a Mn3p-to-Mn3d resonance discussed in Ch. One, it is still pronounced and easily measurable. We have also noted that the energy-integrated effect is only reduced by a factor of 1/5-1/6 compared to this more dramatic intraatomic case.

The form of the MARPE intensity enhancement as judged from these first measurements is also found to be rather closely linked to the normal x-ray absorption coefficient. To see this more clearly, in past work [1-4] we have normalized the O 1s data by subtracting off the smooth non-resonant background seen in Fig. 4-2(c) and setting its value equal to unity. This permits a more direct comparison with the x-ray absorption coefficient. This curve also is shown in Fig. 4-2(c), and there is an obvious strong degree of similarity between the normalized MARPE enhancement and the x-ray absorption coefficient. This attribute is observed to be common in nearly all early measurements by our group in several metal oxides [1-4,31], and metallic alloys and bilayers [3,31], and then in similar measurements by two other groups [6,7].

MnO(001), O 1s–Mn 2p Resonance– Corrected Results

We now consider the same type of measurement, but with a careful allowance for possible non-linear behavior in the detector system utilized. In Fig. 4-3 and its inset, we show the measured (dashed curve) vs. ideal or "true" (straight line) response of this detector as used in analogue mode over a countrate range spanning zero to 500 Hz in one of the approximately 70,000 x-y pixels of the CCD camera used in normal operation. The inset, covering a very broad countrate range, makes it clear that there is curvature in the response, with falloff and incipient saturation being seen as countrate increases. Although one might then expect linearity for the lowest countrates, the blowup of the 0-20 Hz region (the maximum used in all of our measurements specifically to avoid falloff and saturation) shown in the main figure makes it clear that there is still significant non-linearity, including what is found to be a predominantly quadratic component as compared to an ideal detector with linear response. The behavior of the ideal detector we

define to be equal to that of the real detector in the limit of zero countrate (solid line of unit slope in figure and inset), although none of our subsequent corrections or conclusions depend on this particular choice of the ideal reference. For reference, the 20 Hz per pixel rate would correspond to a global countrate of ~ 1.4 MHz (before a “multiple counting” divisor introduced by the manufacturer’s software is applied) for the entire useable portion of the detector phosphor, provided that the phosphor were evenly illuminated via electron pulses from the analyzer.

Thus, although measured and true rates can be conveniently defined to yield the same unit slope as countrates go to zero, the measured rates deviate significantly from linearity, showing quadratic overcounting over the full range of our measurements. Similar quadratic effects were also found in the black-and-white mode, although this mode was not used in our measurements [15]. An additional effect of such quadratic overcounting expected is the narrowing or broadening of photoelectron peaks in energy as a high-intensity resonance is passed, depending on which portion of the non-linear response a given photon energy scan occupies. For example, if the low-intensity portion of a photon-energy scan occupies the bottom of the curve in Fig. 4-3(a), and the high-intensity on-resonance portion of the scan occupies the top of this curve, then the peak area will be enhanced artificially on resonance, and in being so enhanced, may also have exhibit changes in the full width at half maximum (FWHM) intensity, depending upon the exact portion of the detector response profile used in the measurements. In view of this kind of peak width consideration, we have in prior work [1-4] also used the additional criterion of constant peak width over an energy scan to try to minimize nonlinearities. However, this criterion of constant peak width proves to be inadequate for

avoiding spurious effects on peak intensity measurements. It is in fact found to be necessary to carry out a fully quantitative correction for these non-linearities, using methods described in detail elsewhere [14,15]. Briefly, the detector response curve in Fig. 4-3 can be turned into an efficiency, and the inverse of this efficiency then used to correct individual spectra in a point-by-point fashion.

Both uncorrected (as-measured) and corrected ("true") spectra are shown in Fig. 4-4 for O 1s emission from MnO, where the photon energies of 637.6 eV and 640.2 eV have been chosen to be just below the strong Mn $2p_{3/2}$ resonance and just on this resonance, respectively [1]. Because of the significantly increased background level associated with secondary decay processes and inelastically scattered electrons arising from the Mn $2p_{3/2}$ absorption, which in turn forces the detector countrate further up its non-linear response curve, the correction procedure acts to a greater degree on resonance, as expected. Thus, the intensity on resonance is artificially enhanced. In fact, in order to decrease these non-linear correction effects to negligibly low levels, we have found in data not shown here that the countrates had to be lowered by another order of magnitude from our prior typical operating points, or to about 2 Hz per pixel [15].

In Figs. 4-5(a)-(d), we now show uncorrected and corrected O 1s intensities measured as areas by fitting analytical peak shapes plus Shirley-type backgrounds to spectra such as those in Fig. 4-4, as a function of photon energy and for four different x-ray incidence angles of $\theta_{hv} = 30^\circ$, 20° , 10° , and 5° . Uncorrected curves such as these have been discussed previously in terms of multi-atom resonant photoemission [1-4]. It is first clear that the uncorrected MARPE scans in Fig. 4-5(a) for $\theta_{hv} = 30^\circ$ and in Fig. 4-5(b) for $\theta_{hv} = 20^\circ$ follow very closely the previously published x-ray absorption

curve for MnO in the Mn $2p_{3/2}$ region [1-3], which we also show in the bottom portions of these figures as derived from the inelastic electron background under the O $1s$ spectra [1]. These O $1s$ intensity profiles exhibit about a 17% enhancement for $\theta_{hv}=30^\circ$ and about a 32% enhancement for $\theta_{hv}=20^\circ$ of intensity at the Mn $2p_{3/2}$ absorption peak [1-4]. However, the corrected MARPE scans show much smaller effects of about 10% and 12% in overall excursion, respectively, and also of much different form, being negative just below the resonance and then going positive. The data obtained at lower x-ray incidence angles of 10° and 5° shown in Figs. 4-5(c) and (d) exhibit the negative-positive excursions both before and after correction. Fig. 4-5 thus makes it clear that the corrected effects are strongly dependent on angle, being largest for more grazing x-ray incidence angles. For example, the corrected results for 10° shown in Fig. 4-5(c) have about a 37% overall excursion and those for 5° have about a 64% excursion. It is also evident that the effects remaining in the corrected data quickly decay in magnitude as θ_{hv} is increased.

It is thus clear that detector non-linearity can have a dramatic effect on such measurements, with the solid curves in Figs. 4-4, and 4-5 now representing much more accurately any effects beyond a simple one-electron intraatomic picture of O $1s$ emission from MnO in which the Mn $2p$ excitation would be completely decoupled from the O $1s$ excitation. Without such interatomic effects, one should observe a simple smooth curve of negative slope over this region in energy due to a combination of subshell cross section and electron inelastic attenuation length variation with energy [11,16], as perhaps also modulated by energy-dependent photoelectron diffraction (PD) [17].

That photoelectron diffraction must be considered in quantitatively analyzing such data is clearly demonstrated in the scan of O 1s intensity over a wider photon energy range shown in Fig. 4-6 and it is responsible for the strong overall slope superimposed on the MARPE signals in Figs. 4-4 and 4-5. Full multiple-scattering PD calculations [29] confirm that this general oscillatory form of diffraction is expected for this system.

As an additional point, we note the differences that persist even after detector correction in the inelastic background-derived absorption profiles between Figs. 4-5(a)-(e). The variation is due to well-known [30] self-absorption effects occurring when the incoming photon attenuation length perpendicular to the surface becomes comparable to the inelastic electron mean free path in the sample, as is the case over the Mn 2p absorption edge considered here, especially as the x-ray incidence angle is decreased. The predicted changes in the background-derived (electron yield) absorption profiles as a function of θ_{hv} for normal emission are shown in Fig. 4-7. Here, the 30° experimental data is adjusted for self-absorption effects using the energy-dependent x-ray absorption coefficient μ , which is in turn related to the imaginary part of the optical constant as introduced in Fig. 1-5, via $\mu = 4\pi\beta/\lambda_x$. The predicted results for angles below 30° are in excellent agreement with the experimental results (Figs. 4-5(a)-(e)) if we assume a reasonable secondary electron attenuation length of 4.7 Å, indicating that this phenomenon is properly understood. The small difference between 30° experiment and 90° predicted x-ray absorption coefficient measurements does however indicate that the 30° data by themselves are not a fully accurate representation of the x-ray absorption coefficient.

While the PD effects with scanned photon energy mentioned above simply represent a secondary effect beneath the MARPE profile of interest, we have also attempted to determine the effect of MARPE on azimuthal angle PD scans. The azimuthal scans were performed both on ($h\nu = 640.2$ eV) and off ($h\nu = 637.2$ eV) resonance with the Mn $2p_{3/2}$ edge in MnO as shown in Fig. 4-8. Again, the O $1s$ photoemission has been monitored, on a sample containing a strong surface hydroxyl component that can be easily eliminated if desired by ion sputtering of the surface. The correction for detector non-linearity was applied to all O $1s$ spectra before background subtraction and fitting to derive intensities, just as with the energy-scan MARPE data. By comparing the on and off resonance scans (Fig. 4-8(a) and (b), respectively) for both the bulk and hydroxyl components (seen clearly in Fig. 4-8(c)), we note subtle differences between profiles. Especially interesting is the hydroxyl component, shown in an amplified format both on an off resonance in Fig. 4-8(d). Because the hydroxyl species is situated at the surface, effects due simply to a change of photon attenuation length in the sample from off to on resonance are unlikely to influence the diffraction. The small change in photon energy of only 3 eV also makes it unlikely that the hydroxyl diffraction pattern would change as strongly as indicated in Fig. 4-8 simply due to normal photoelectron diffraction and so these results indicate that MARPE may be influencing the final diffraction results. Further investigation is needed however to clarify the extent to which these differences may be associated with the 3 eV difference in the kinetic energies of the emitted photoelectrons, which will influence the diffraction at least slightly [17]. For example, the diffraction-produced modulations of the hydroxyl+bulk

O 1s intensity in the scanned-energy curve of Fig. 4-6 show maximum changes of about 10% over an energy interval of 3 eV.

Cr_xFe_{1-x} Alloys and Bilayers

With the dramatic changes in the measured data for MnO after correction, it is a reasonable assumption that other data presented or obtained in previous work has been similarly affected. As discussed elsewhere [15], there are practical difficulties with correcting older datasets acquired before the detector correction was known to be necessary. By contrast, the data presented above in the corrected MnO results have been acquired with appropriate steps taken to ensure maximum effectiveness of the correction [15]. The only exception in the MnO data is the azimuthal data in Fig. 4-7, which represent a recently-derived correction function applied to data obtained previously.

However, we can expect some degree of success with the correction of older data, for other systems and so as a further example, we will consider the case of Fe/Cr alloys grown on a W(100) substrate. These measurements, mentioned in our previous work [3,4] but not yet published, involve the investigation of a MARPE enhancement in the Cr 2p (Cr = atom "A") photoemission as the Fe 2p (Fe = atom "B") thresholds are crossed with the photon energy.

The promising results seen in the first analysis of the MnO data as described above, lead to the conclusion that a MARPE effect could in fact easily be observed and reproducibly measured. The proposed enhancement was furthermore assumed to involve a characteristic interaction length over which multiple neighboring atoms contribute to the MARPE-enhanced emission from the B-atom resonator energy level. However, the

metal-oxide results [1-3] provided no direct means to extract either the interaction length or its functional form. To make a first estimate of the sensing length, a number of Cr/Fe bilayer and $\text{Cr}_x\text{Fe}_{1-x}$ alloy thin films were studied, and the systematic changes in the MARPE enhancement as a function of varying film thicknesses and compositions were measured. The spirit of this is similar to that in the work of Ref. 7 in which the adsorbate system $\text{N}_2/\text{N}(100)$ was used to attempt to identify distance dependence in the MARPE process by differences in the MARPE enhancement of the N $1s$ core level photoemission over the Ni $L_{3,2}$ edges, for each of the two inequivalent atoms in the adsorbed N_2 .

In our work, we have studied the dependence of the Cr $2p$ intensity enhancement induced at the Fe $2p_{3/2,1/2}$ edges in Cr/Fe bilayers of varying Cr and Fe thicknesses, as well as in $\text{Cr}_x\text{Fe}_{1-x}$ alloy thin films of varying composition. All data shown were acquired in normal emission ($\theta = 90^\circ$) and with θ_{hv} at 20° . An initial analysis of the experimental results indicated a substantial enhancement of up to $\sim 40\%$ that appeared to vary with the sample composition in a manner consistent with an approximate sensing range in the MARPE interaction of $20 \text{ \AA}$ [3,31]. However, a more recent analysis in which the detector non-linearity effects introduced earlier are removed from the measured data have demonstrated significant reduction in any MARPE enhancement in these systems, as we now illustrate.

A MARPE scan typical of the results seen in both the alloy and the bilayer systems before correction is shown in Fig. 4-9(a), along with a pair of corrections to the same profile. Note that this data is not uniquely correctable since the exact conditions of detector use (e.g. the fraction of the detector pixels that were actually seeing electron pulses) were not recorded in these earlier experiments [15], and so a range of reasonable

correction factors is applied to simply indicate the best apparent correction. As is typical before correction, this MARPE profile in Fig. 4-9(a) (dashed line) closely follows the Fe $L_{3,2}$ absorption edge profile shown in Fig. 4-9(b). The strength of the MARPE profiles (before correction) was also seen to exhibit behavior as a function of the sample composition that was consistent with a 20–25 Å effective interaction length in the MARPE process.

However, once the data are corrected for the detector response, as shown for two reasonable detector filling factors [15] in Fig. 4-9(a), we see that the MARPE profiles essentially disappears, with only a very weak modulation of a few percent left near the maximum of the Fe $2p_{3/2}$ absorption resonance. These weak modulations, which e.g. look like a negative dip just before the Fe $2p_{3/2}$ absorption maximum, may well be due to MARPE effects like those seen in Fig. 4-5(a), or they may be related to small residual errors in the final correction. Further experiments with more precise detector correction will be necessary to resolve this.

Note in addition that the Cr $2p$ peak widths shown in Fig. 4-9(c) reflect the correction process very strongly. Before correction, the widths are seen to be much less stable over the Fe $2p$ absorption region, with the FWHM varying by more than 7% and being strongly peaked at the primary Fe $2p_{3/2}$ absorption peak. After correction, the widths are seen to broaden over the entire edge (due to the removal of the peak stretching effects mentioned previously), but to be much more stable, with only a few percent change overall. The peak in the FWHM near the Fe $2p_{3/2}$ position is almost gone after correction, and the two filling factors shown actually turn it from a slight dip to a slight

peak, suggesting that they bracket the optimum correction of no change in FWHM for this data.

Data from another alloy sample after correction is compared to data before and after correction from a pure Cr film in Fig. 4-9(d) and (e). Since all of our alloy and pure-component films exhibited some epitaxy and short-range crystalline order, photoelectron diffraction effects were always present, with the alloy patterns being very similar to those of the two pure components. Note that in this case, the peak widths in either case did not exhibit strong modulation over the absorption edge, but the correction procedure still results in a reduction in the distribution of widths and an overall width variation very similar to those in the corrected data of Fig. 4-9(c).

The correction effect for the pure Cr film for which no MARPE can occur is seen in Fig. 4-9(d) to be simply a matter of reducing the general negative slope of the individual curves for the Cr $2p_{3/2}$ and Cr $2p_{1/2}$ intensities, as well as their sum. Because of the ~ 13 eV kinetic energy difference between the Cr $2p_{3/2}$ and Cr $2p_{1/2}$ photoelectrons, and the ~ 17 eV difference in peak positions in the diffraction modulations in both peaks, the sum represents a nearly out of phase superposition of the two diffraction curves, and the resultant modulation is strongly suppressed in it.

In order to finally estimate an upper limit on MARPE enhancements in the Cr/Fe systems in this data, we in Fig. 4-9(e) compare the corrected $\text{Cr}_{0.49}\text{Fe}_{0.51}$ alloy data to the case of a pure Cr film in which there is no opportunity at all for resonance with Fe atoms. In this comparison, we see a very similar overall behavior of the alloy and pure Cr data over the Fe $2p$ edges, especially for the $2p_{1/2}$ peak. In both cases, we expect that the primary modulations are due to photoelectron diffraction effects. This assignment is

confirmed by the observation of XPD patterns from these samples for azimuthal angle scans using $\text{AlK}\alpha$ as the excitation source that indicate at least short range order in the films [31]. However, closer inspection of the alloy data reveals that both the $\text{Cr } 2p_{3/2}$ and summed curves show a weak dip of a few percent just before the $\text{Fe } 2p_{3/2}$ absorption maximum that could be residual MARPE effects like that suggested in Fig. 4-9(a), and seen more clearly for $\text{O } 1s$ emission from MnO at the same incidence angle in Fig. 4-5(b).

Because the correction procedure in the Cr/Fe data may be somewhat inaccurate, additional work will be needed to quantitatively determine the existence of MARPE in this system, but effects of a few percent appear to still be present for the two alloys shown here. In addition, all work shown here was acquired in normal emission with θ_{hv} at 20° and, as already seen in the case of the MnO results, decreasing θ_{hv} may make any effect more easily measurable.

MARPE in Secondary Effects

We also note that, in addition to affecting photoemission results, prior measurements by our group of secondary Auger and x-ray emission effects [4] also appear to have been strongly influenced by such detector non-linearities. For the former, this occurs just as for the photoelectron case due to the identical instrumentation, and for the latter via an x-ray absorption coefficient necessary for a self-absorption correction that was measured via secondary electrons in the same electron spectrometer and with the same detector. These measurements are of interest as alternate methods of observing the MARPE process. That is, the MARPE process in photoemission represents a negative-then-positive modulation in the number of core holes created, which must be filled by

these secondary mechanisms. Thus, while one would still expect secondary processes to exhibit modulations due to MARPE, we have not yet had the opportunity to repeat the measurements under appropriate correctable conditions. A preliminary correction of data previously published [3,4] indicates that the effects observed in secondary processes are significantly reduced once the detector correction is applied to an x-ray absorption coefficient that is necessary for correcting the data for sample self-absorption.

Beyond the particular case of MARPE considered here, we also point out that such detector non-linearities need to be corrected for and/or minimized in any use of this detector system for quantitative peak intensity analysis, as any comparison of intensities obtained over a range of countrates, even in a single spectrum, can be significantly altered by these effects.

4.4 Theory and Discussion

4.4.1 Interatomic Resonant Photoemission Model

We now consider several levels of theory in order to explain the remaining effects which link the O 1s intensity to the Mn 2p absorption process as seen in Figs. 4-5(a)-(d), first considering these effects via a prior microscopic many-body theoretical treatment of MARPE based on a resonant photoemission model [5], and then showing that this approach can be successively simplified for the case at hand to yield results essentially identical to those from classical x-ray optical theory. Focusing still on the case of O 1s photoemission from MnO(001) and the system initially prepared in its many-body ground state $|g\rangle$, the contribution of the direct or unscattered wave function to the photoelectron intensity can be written

$$I(\mathbf{k}) \propto |\phi_{\mathbf{k}}^0(\mathbf{r})|^2 \propto \left| \sum_{l\mu} Y_{l\mu}(\hat{\mathbf{k}}) i^l h_l^{(+)}(kr) M_{El\mu} \right|^2, \quad [4-1]$$

where $\mathbf{k}$ is the photoelectron wave vector, $\phi_{\mathbf{k}}^0(\mathbf{r})$ is the wave function at the detector, $Y_{l\mu}$ is a spherical harmonic, $h_l^{(+)}(kr)$ is a spherical Hankel function, and

$$M_{El\mu} = \langle El\mu, \underline{O1s} | T | g \rangle \quad [4-2]$$

is the matrix element describing the transition to the final state with a photoelectron $|El\mu\rangle$ of energy $E = \hbar^2 k^2 / 2m$ and an O 1s hole. Final-state photoelectron diffraction effects can also be incorporated in this model by using $M_{El\mu}$ as input for self-consistent multiple-electron-scattering equations [18].

The transition matrix T can be conveniently expanded in a power series with respect to the perturbation of the radiation field V . One then has [19]

$$T = V + VG_0V + VG_0VG_0V + \dots, \quad [4-3]$$

where G_0 is the Green function of the unperturbed solid. If we keep only terms up to second order in V , the part of Eq. 4-3 that makes a non-zero contribution to Eq. 4-2 reduces to the well-known Kramers-Heisenberg formula for resonant photoemission [20]

$$T = V_{\text{rad}}^0 + \sum_{j,m} V_{\text{Al}}^j \frac{|m,j\rangle\langle m,j|}{\hbar\omega + E_g - E_m + i\Gamma_m/2} V_{\text{rad}}^j, \quad [4-4]$$

where V_{rad}^0 is the interaction of the radiation with the emitter, V_{rad}^j is the interaction with the resonating atom j , V_{Al}^j is the autoionizing Coulomb interaction between the emitter and atom j , E_g is the ground state energy, and the sums are over both Mn atoms j and

their intermediate many-body states $|m, j\rangle$ of energy E_m and width Γ_m . We now note two special points that have been considered previously [5]:

–Because of the large distances that may be involved to certain resonating atoms, as compared to the $\sim 19 \text{ \AA}$ wavelength of the exciting radiation, retardation effects are important both in the autoionization interaction and in the interaction with the external radiation [5]. In particular, the latter takes the form

$$V_{\text{rad}}^j = A \mathbf{r} \cdot \boldsymbol{\varepsilon} e^{ik_{h\nu} \cdot \mathbf{R}_j} = A r \sum_{\lambda} Y_{1\lambda}(\hat{\mathbf{r}}) \varepsilon_{\lambda} e^{ik_{h\nu} \cdot \mathbf{R}_j},$$

where $\mathbf{R}_j$ is the position of atom j relative to the emitter, $\mathbf{k}_{h\nu}$ is the wave vector of the incoming light, $\boldsymbol{\varepsilon}$ is its polarization vector with components ε_{λ} , $\mathbf{r}$ is the coordinate relative to the atom nucleus, and A is a normalization constant.

–Similarly, the autoionization interaction requires going beyond the usual e^2/R description used in SARPE [5,20]. The fully-relativistic Møller formula used previously in high-energy Auger theory [21,22] has been adopted here [5], so that

$$V_{\text{AI}}^j(\mathbf{r}_1, \mathbf{r}_2) = \frac{e^2}{|\mathbf{R}_j + \mathbf{r}_2 - \mathbf{r}_1|} e^{ik_{h\nu} |\mathbf{R}_j + \mathbf{r}_2 - \mathbf{r}_1|} (1 - k_{h\nu}^2 \mathbf{r}_1 \cdot \mathbf{r}_2),$$

describes the interaction between electron 1 of coordinate $\mathbf{r}_1$ relative to the O emitter and electron 2 of coordinate $\mathbf{r}_2$ relative to the j^{th} resonating Mn atom. The first term inside the parenthesis describes the retarded interaction of the two electron densities, whereas the second one accounts for the retarded interaction of the two currents associated with the transition [5,21,22].

At this level, the treatment should be capable of describing all many-electron interactions up to second order in the perturbation via Eq. 4-4, or up to arbitrary order via Eq. 4-3 including those for nearest-neighbors with the greatest overlap and thus enhanced many-electron interactions with the emitting atom.

If we now sacrifice some accuracy in describing nearest-neighbor behavior, the autoionization interaction can be conveniently expanded in multipoles that should be valid for resonator distances from the emitter $R_j \gg r_1, r_2$, where r_1 and r_2 are electron-nuclear distances and are of the order of the relevant dimensions of the two core orbitals involved (here O $1s$ and Mn $2p$). With these assumptions, and the further neglect of multipoles higher than dipoles, the effective interaction can be reduced to the following, in which several quantities are written out more explicitly than in prior work [5]:

$$V'_{AI} \approx e^2 r_1 r_2 \sum_{\mu_1 \mu_2} F_{\mu_1 \mu_2}^{R_j} Y_{1\mu_1}(\hat{\mathbf{r}}_1) Y_{1\mu_2}^*(\hat{\mathbf{r}}_2), \quad [4-5]$$

where

$$F_{\mu_1 \mu_2}^R = \frac{-4\pi k^3}{3} \left[\frac{\delta_{\mu_1 \mu_2}}{2\pi} h_0^{(+)}(kR) + h_2^{(+)}(kR) Y_{2\mu_2-\mu_1}(\hat{\mathbf{R}}) \langle Y_{1\mu_2} | Y_{2\mu_2-\mu_1} Y_{1\mu_1} \rangle \right] \quad [4-6]$$

and the bracket represents a Gaunt integral. Eqs. 4-5 and 4-6 can be also derived in a more rigorous way using non-relativistic quantum electrodynamics [18,23,24], where Eq. 4-6 is found to be simply proportional to the Green function of the photon field in the transverse gauge [23], and the remaining short-range longitudinal Coulomb coupling is neglected [24].

Combining results, we now find, in slightly different notation from, but equivalent meaning to, that in Ref. 5

$$M_{El\mu} = A \langle E1|r|O1s \rangle \delta_{l,1} \sum_{\lambda} \varepsilon_{\lambda}^{\text{eff}} \langle Y_{1\mu} | Y_{1\lambda} Y_{00} \rangle = A \langle E1|r|O1s \rangle \delta_{l,1} \varepsilon_{\mu}^{\text{eff}} / \sqrt{4\pi}, \quad [4-7]$$

where A is a light-intensity normalization constant,

$$\varepsilon_{\lambda}^{\text{eff}} = \varepsilon_{\lambda} - \sum_{\lambda'\mu_2} F_{\lambda\mu_2} \alpha_{\mu_2\lambda'} \varepsilon_{\lambda'}, \quad [4-8]$$

is now the effective polarization vector that includes the effect of x-ray scattering at the Mn sites, and the magnitude of the resonance is controlled by a product of a structure-factor type of sum over Mn sites

$$F_{\lambda\mu_2} = \sum_j F_{\lambda\mu_2}^{\text{R}_j} e^{ik_{hv} \cdot \text{R}_j}, \quad [4-9]$$

and the Mn^{2+} polarizability tensor,

$$\alpha_{\mu_2\lambda'} = -\frac{4\pi e^2}{3} \sum_m \frac{\langle g|rY_{1\mu_2}^*|m \rangle \langle m|rY_{1\lambda'}|g \rangle}{\hbar\omega + E_g - E_m + i\Gamma_m/2}. \quad [4-10]$$

The form for the polarizability given here makes it clear that it is directly related to the usual description of resonant photoemission in Eq. 4-4 and Ref. 20.

The polarizability has been calculated using a configuration interaction scheme for a central Mn^{2+} ion surrounded by six O^{2-} ions in an octahedral cluster [5,20], with interaction parameters derived previously from fits to both SARPE and x-ray absorption data, and an average over orientations of Mn magnetic moments. since the experiments have been performed above the MnO Néel temperature. In addition, $\alpha_{\mu_2\lambda'}$ can be well approximated by a quantity averaged over diagonal elements, as $\bar{\alpha}\delta_{\mu_2\lambda'}$, where $\bar{\alpha} = (\alpha_{-1-1} + \alpha_{00} + \alpha_{11})/3$ [5]. The above equations were used in Ref. 5 to calculate O 1s

intensities. However, all resonant contributions to the O 1s intensities (i.e., the second term in Eq. 4-4) were incorrectly multiplied by an extra factor of -4 in the computer calculations. Here, we present corrected theoretical results from this model, as well as results going beyond the earlier approximations used by considering higher order interactions in Eq. 4-3, and also compare these two sets of results to a theoretical approach based on more standard x-ray optical theory.

In Fig. 4-11(a) we compare experimental and theoretical results for the O 1s intensity as a function of photon energy and for light incident at an angle of 10° with respect to the surface. The connected points represent the corrected experimental results from Fig. 4-5(c) and the thin solid curve the theoretical results based on Eq. 4-3 above. The experimental data show a steeper negative slope than theory as energy is increased that we have verified by measurements and calculations to be due to a combination of decreasing photoelectric cross section and strong modulations due to photoelectron diffraction (as mentioned above), both well understood effects [16,17]. If this difference in slope is allowed for, the agreement between experiment and theory is qualitatively good, although the amplitude of the intensity modulations is too small by a factor of 2-3 in theory. Now going beyond this level of microscopic theory, we note that the remaining terms in the series expansion [4-3] describe processes in which an incoming photon is scattered by more than one Mn atom before it reaches the O emitter. In particular, they incorporate higher-order Mn-Mn interactions via the Møller formula [5,21,22]. This gives rise to extra terms in the effective polarizability of Eq. 4-7, which now becomes

$$\varepsilon_{\lambda}^{\text{eff}} = \varepsilon_{\lambda} - \bar{\alpha} \sum_{\lambda', j} \mathbf{F}_{\lambda\lambda'}^{R_j} e^{ik_{\lambda\nu} \cdot \mathbf{R}_j} \varepsilon_{\lambda'} + \bar{\alpha}^2 \sum_{\lambda', \lambda'', jj'} \mathbf{F}_{\lambda\lambda'}^{R_j} \mathbf{F}_{\lambda'\lambda''}^{R_{j'}} e^{ik_{\lambda\nu} \cdot \mathbf{R}_{j'}} \varepsilon_{\lambda''} + \dots, \quad [4-11]$$

where the first two terms are the same as in Eq. 4-8 after approximating the polarizability by the average scalar $\bar{\alpha}$. This series can be summed up to an infinite order for a slab formed by a finite set of atomic planes [18], and a semi-infinite medium can be simulated by using a sufficiently large number of layers. The result obtained in that case for the O 1s intensity is shown in Fig. 4-11(a) as a solid curve. The new terms in Eq. 4-11 bring the theoretical result much closer to the experimental one, making it evident that it is essential to include what is in effect multiple scattering of the incoming radiation in order to accurately describe such strong soft x-ray resonances. To our knowledge, this point has not been made before in discussing such resonances.

4.4.2 Relationship to an X-Ray Optical (Dielectric) Model

We now consider the relationship of this microscopic many-body theory to another related theoretical method for dealing with such effects: an x-ray optical approach based on Maxwell's and Fresnel's equations, as described in detail elsewhere [11,25]. Eq. 4-11 involves sums over Mn positions in the MnO crystal. However, the details of the atomic structure of the Mn sublattice should be irrelevant in the limit of long radiation wavelengths λ_x for which phase shifts along the scattered paths can be neglected. In this limit, Eq. 4-11 can be shown to reduce to the polarization vector derived from a macroscopic dielectric description based upon Maxwell's equations, in which the solid is represented by a local frequency-dependent dielectric function ε that is related to the atomic polarizability as $\varepsilon = 1 + 4\pi n_{Mn} \bar{\alpha}$, where n_{Mn} is the density of Mn atoms. More specifically for the case of the Mn 2p resonance in MnO, the ratio of the

wavelength to the Mn-Mn nearest-neighbor distance is ≈ 6.1 . Therefore one would expect reasonable results to come out of the macroscopic description. We here have also implicitly assumed that the O atoms contribute only a small amount to the total polarizability in the vicinity of the Mn $2p$ resonances [5,18,25b,27].

Thus, an alternative, although more empirically-oriented, approach for calculating such effects is to first derive the energy-dependent x-ray optical constants $\delta(h\nu)$ and $\beta(h\nu)$ in the index of refraction $n_r = \sqrt{\epsilon} = 1 - \delta + i\beta$ [26] by measuring the absorption coefficient $\mu(h\nu) = 4\pi\beta(h\nu)/\lambda_x$ over the edges in question (here Mn $2p$), matching it in the non-resonant region to accurate theoretical and/or experimental data [25b, 27], and then using a Kramers-Kronig analysis to derive δ . We note here also that the measurement of the absorption coefficient has to be done with extreme care in view of distortions that can arise due to either detector non-linearities or the finite penetration depths of the x-rays compared to the secondary electrons used to measure absorption for certain experimental geometries, as illustrated in Figs. 4-5 and 4-7, respectively.

The basic elements of the Kramers-Kronig analysis as performed in this work are illustrated in Fig. 4-10. As shown in Fig. 4-10(a), the process begins with a measured absorption profile that includes an anomalous or resonant region corresponding to an absorption edge. This profile is proportional to the optical constant, β . In this case, the Mn $2p$ edges in MnO are shown. The initial step is to subtract the non-resonant portion of the absorption curve that can be obtained from one-electron theory and extracted from tabulated results [25b,27]. We have here used a relativistic tabulation due to Chantler and available from the National Institute of Standards and Technology (NIST) [27] and

this represents a stepped background under the resonant profile, as shown in Fig. 4-10(b). Because these calculations were relativistic, they include two steps for the Mn $2p_{3/2}$ and $2p_{1/2}$ absorption edges, by contrast with an earlier tabulation which was non-relativistic and included only one for Mn $2p$ as a whole [25b]. With only the resonant portion of β as shown in Fig. 4-10(c) remaining, the resonant portion of the dispersion, δ , is obtained through a standard Kramers-Kronig transformation: that is, the transform of the curve in Fig. 4-10(c) produces the resonant contribution to δ in Fig. 4-10(d). Now, the final total δ must have the non-resonant portion of δ added back in. These values can again be obtained from tabulated sources [25b,27] and are shown for our example as derived again from Chantler [27] in Fig. 4-10(e). Finally, the sum of these resonant and non-resonant contributions to δ yields the total δ as shown in Fig. 4-10(f).

Implicit in being able to carry out the above analysis is that the Kramers-Kronig transform is a linear operation, which allows us to decompose the resonant and non-resonant portions of β and δ . It is most useful to perform this decomposition because of the sensitivity of the transform of the non-resonant component to the extended values of the absorption profile far from the resonance, with values of the profile down to 10eV and up to 10000eV influencing the final result. The availability of the accurately transformed and tabulated values [25b,27] for this sensitive non-resonant component makes the decomposition both convenient and accurate in its final results. The only slight source of uncertainty in this method is in the positioning of the energy steps in the tabulated values relative to the energy scale of the experimental curves. Ideally, the steps in β should occur at the threshold for photoelectron emission, which cannot be directly

determined from the absorption coefficient curve alone. However, within ± 1 eV, we find that the results for δ are insensitive to this choice.

The two final parameters, β and δ , as derived experimentally in this study for the case of $\theta_{hv}=10^\circ$ are shown as a function of photon energy in Fig. 4-11(c) (solid curves), where they are compared also to the same parameters as derived from the parameterized many-body model discussed previously (dashed curves). The agreement between experiment and theory for these x-ray optical constants is very good, with more fine structure in experiment, as expected. Note also that the variation in the experimental O 1s intensity in Fig. 4-11(a) about a mean value follows very closely the behavior of δ , a point to which we return below.

Proceeding now via the Fresnel Equations to calculate the photoemission intensity as a function of photon energy, it can be shown that, for p-polarized radiation as used in this work (cf. inset of Fig. 4-4 for polarization geometry) incident on a planar surface from vacuum with $n = 1$, and for a conducting or non-conducting, but non-magnetic, reflective medium, the ratio of the complex electric field magnitude just below the surface ($E(z = 0+)$) to the incident complex field magnitude just above the surface in vacuum ($E_{vac}^{inc}(z = 0-)$) is given by

$$t \equiv \frac{E(0+)}{E_{vac}^{inc}(0-)} = \frac{2 \sin \theta_{hv}}{\sin \theta_{hv} + n_r \sin \theta_{hv}'} \quad , \quad [4-12]$$

where z is the coordinate perpendicular to the surface and θ_{hv}' is the complex angle of propagation below the surface, again measured relative to the surface. θ_{hv}' is further related to θ_{hv} via Snell's Law: $\cos \theta_{hv} = n_r \cos \theta_{hv}'$, with θ_{hv} real. The complex character of

n_r also implies that E attenuates with z only according to $\exp[-\text{Im}(k'z\sin\theta_{hv})]$, where k' is the complex propagation wave vector inside the medium and equal to $2\pi n_r/\lambda_x$, and λ_x is the wavelength of the radiation. Normalizing the electric field inside the medium to the incident field just above the surface then gives for the electric field strength at depth z relevant for photoemission

$$|E(z)|^2 = |t|^2 \exp(-\text{Im}\{4\pi n_r z \sin\theta_{hv}' / \lambda_x\}). \quad [4-13]$$

The photoemission intensity $I(h\nu)$ can now be obtained by introducing the energy-dependent differential photoelectron cross section $d\sigma/d\Omega$ appropriate to the experimental geometry (which may also include the effects of photoelectron diffraction), the energy-dependent inelastic attenuation length for electrons Λ_e , and integrating over z as

$$I(h\nu) \propto \frac{d\sigma}{d\Omega} \int_0^\infty |E(z)|^2 \exp(-\frac{z}{\Lambda_e \sin\theta}) dz, \quad [4-14]$$

where we have not included factors of atomic density and solid angle acceptance of the analyzer that will be constant over a given energy scan. Substituting Eq. 4-13 into Eq. 4-14 and integrating then yields finally

$$I(h\nu) \propto \frac{d\sigma}{d\Omega}(h\nu) \frac{|t(h\nu)|^2}{\frac{\text{Im}\{4\pi n_r(h\nu) \sin\theta_{hv}'(h\nu)\}}{\lambda_x(h\nu)} + \frac{1}{\Lambda_e(h\nu) \sin\theta}}, \quad [4-15]$$

which is a completely general formula for photoemission intensity from a conducting or non-conduction, non-magnetic, semi-infinite substrate, with all dependences on energy explicitly indicated. Making use of Eq. 4-15 and the experimental values for δ and β in Fig. 4-11(c), we arrive at the dashed curves shown in Fig. 4-11(a), and (b) for incidence

angles of 10° and 5° , respectively which are in excellent agreement with experiment, including all aspects of the fine structure. A similar degree of agreement is also found for other incidence angles θ_{hv} .

This x-ray optical approach furthermore exhibits only small differences in fine structure with respect to the microscopic description based upon Eq. 4-11, with these being due to differences in δ and β between theory and measurement (cf. Fig. 4-11(c)) and perhaps also the fact that only the Mn polarizability has been considered in the microscopic theory, thus neglecting the small contributions from non-resonant O scattering and other continuum processes over this energy range [25b,27]. In addition, we find that, if the infinite-order microscopic Eq. 4-11 is used together with the experimental x-ray optical constants to derive the polarizability, the calculated curve is essentially indistinguishable from that of Eq. 4-15. We thus verify the accuracy of the microscopic approach and its exact reduction to the x-ray optical model, provided that multiple scattering effects are included and certain conditions mentioned above are met.

In Fig. 4-11(d), we finally show normalized curves of the multi-atom effect on the O 1s intensity as a function of x-ray incidence angle, as calculated using the x-ray optical approach of Eq. 4-15. These curves make our earlier conclusion even more clear: the effects are strongly sensitive to x-ray incidence angle, being much smaller for angles greater than about 20-30 degrees. However, they are very similar in shape for all angles, being first negative-going, and then positive-going as an absorption peak is approached from the low-energy side. The calculated normalized +/- excursion of the effect as a function of incidence angle is further shown in the inset of Fig. 4-11(d), where it is compared to experimental results at four incidence angles. There is excellent agreement

between experiment and theory, and theory furthermore predicts an asymptotic value of about 4.5% for the excursion at normal incidence. These results thus further confirm the accuracy of the x-ray optical analysis as compared to experiment, and also imply that such effects should be observable on crossing strong core-level resonances for all angles of x-ray incidence, although with greater difficulty of observation as θ_{hv} goes above about 20°-30°.

It is now useful to compare these theoretical results with those from prior work by Henke on calculating photoelectron intensities via x-ray optics [25a]. We first note that he was interested in scanning the incidence angle θ_{hv} only, in which case δ , β , λ_x , and Λ_e all remain constant, and he was thus able to make certain approximations that we cannot due to the strong variation of both δ and β over a scan in photon energy. Nonetheless, if $|\delta|$, $\beta \ll 1$ over the energy scan, which Fig. 4-11(c) makes clear is an excellent assumption, our Eq. 4-15 can be simplified to

$$I(h\nu) \approx \frac{d\sigma}{d\Omega}(h\nu) \frac{|t(h\nu)|^2}{\frac{4\pi\beta(h\nu)\sin\theta_{hv}(h\nu)}{\lambda_x(h\nu)} + \frac{1}{\Lambda_e(h\nu)\sin\theta}}, \quad [4-16]$$

which permits more direct comparison with this prior work. In particular, our use of $|t|^2$ to represent the strength of the electric field squared below the surface is inherently more accurate and versatile in application than the factor $[1-R][\sin\theta_{hv}/\sin\theta_{hv}']$ used in this prior analysis (with θ_{hv}' there treated as real), and it can be shown that a more accurate expression related to this earlier formalism is a factor $[1-R][\sin\theta_{hv}/(\text{Re}\{n_r\sin\theta_{hv}'\})]$ (with θ_{hv}' here treated as complex). In addition, the inverse x-ray attenuation length perpendicular to the surface in this prior work and appearing here as the first term in the

denominator of Eq. 4-16 was further simplified by Henke, and finally is different from ours by a factor of $1/[\sin\theta_{h\nu}]^2$. In describing scanned-energy resonant data however, we find it essential to use the form in Eq. 4-15, or with some loss of accuracy, that in Eq. 4-16.

To gain additional insight into the relationship of photoemission intensity to δ and β , we can further approximate Eq. 4-15 to the conditions of the measurements shown here, for which δ and β are both much less than unity (cf. Fig. 4-11(c)) and the reflectivity R is also small (with a maximum value for all cases considered here of 0.18 at $\theta_{h\nu} = 5^\circ$). This finally yields, after suppressing the obvious dependences on photon energy

$$I(h\nu) \approx \frac{d\sigma}{d\Omega} \cdot \frac{1 + \delta}{\frac{4\pi\beta \sin\theta_{h\nu}}{\lambda_x} + \frac{1}{\Lambda_e \sin\theta}}. \quad [4-17]$$

From this expression, it is clear that the variation of intensity with photon energy as normalized to the values on either side of a resonance should qualitatively follow δ , just as observed. The magnitude of this variation is also enhanced by the change in β , whose increase over the resonance generally acts to decrease intensity over the same region. The negative excursion of δ just before the resonance, together with the increase in β , thus produces the strong dips in intensity seen at about 639.5 eV in Figs. 4-11(a) and (d).

Although the microscopic model embodied in Eqs. 4-1 through 4-11 can be reduced to an x-ray optical picture, provided we include higher-order effects representing multiple light scattering, it should nonetheless permit future calculations of such interatomic resonant photoemission effects from first principles, including in particular an allowance for nearest-neighbor many-body interactions that are only effectively

included in the optical approach. Beyond this, the excellent numerical agreement between the microscopic and macroscopic dielectric descriptions presented above is expected to break down when the wavelength of the radiation is of the order of, or smaller than, the interatomic distances. Thus, if the resonating atoms do not form a compact enough lattice (as Mn does in MnO), the dielectric treatment is not appropriate. Some possible examples of this are atoms situated inside the cages of fullerenes or zeolites, and/or resonant excitation with shorter-wavelength radiation. The dielectric model also is not appropriate for calculating such effects in nanometer-scale objects in which the detailed atomic positions are to be allowed for, nor in free molecules, in which core-core interatomic resonance effects appear to have recently been observed in photoelectron angular distributions for the specific case of S $2p$ emission from SF_6 as photon energy passes through the F $1s$ threshold [12].

Regardless of the theoretical model that is most appropriate to use, such interatomic resonance effects (even though generally smaller and of different form than discussed previously) still represent an experimental probe that should be able for various situations to provide unique information on the near-neighbor identities and bonding of atoms B that surround a given emitter A, as suggested in prior work [1-4].

Finally, we note that both of the theoretical models discussed above can be extended to describe fluorescent x-ray emission. For the x-ray optical model, and for the case of a fluorescent energy that is far from any resonance and at a fluorescence exit angle θ^F that is large enough to minimize refraction and reflection at the surface, this would involve simply replacing $\Lambda_e \sin\theta$ with $\Lambda_x^F \sin\theta^F$ in Eqs. 4-15 to 4-17, with Λ_x^F equal to the fluorescent x-ray attenuation length along path length or $\lambda_x^F/[4\pi\beta^F]$ in

obvious notation. The microscopic model could also be similarly extended to predict fluorescence intensities, but we will not present these details here.

4.4.3 Relationship of MARPE to Other Measurements and Processes

The presence of the interatomic core-valence resonances already mentioned [8-10] raised the question of the suitability of SARPE measurements for the extraction of element specific information from the valence bands in photoemission. That is, the assumption in standard SARPE measurements has been that the resonance is strictly intra-atomic and thus that the valence enhancements are unambiguously element specific. However, with the possibility of a second interatomic channel in which the resonance can occur, this element specificity may not be as rigidly adhered to as normally assumed. While no theoretical treatment of these core-valence resonant processes has so far been pursued, the microscopic theory discussed here should be able to treat them as well and so clarify the conditions under which standard assumptions about the SARPE process may or may not be expected to be valid.

As a final comment on the theoretical interpretation of MARPE, we contrast it with the well-known type of intermolecular or interatomic energy transfer involved in the Förster effect [32,33,34], which is also directly related to what has been described as sensitized luminescence [35]. In this effect, a low-energy excitation of the order of 1 eV that is very long-lived with respect to the core decay involved in MARPE is produced on one atom/molecule. This excitation then propagates from the "donor" atom or molecule to an "acceptor" atom or molecule with a matching energy-level system, with the propagation time being much shorter than the lifetime of the initial excited state. The

relationship of these times dictates that coherent quantum interference effects can be neglected, and the process is well described by a transfer rate equation in which energy diffuses from one site to another via real photons in multiple-step cascades. The interaction is again fundamentally Coulombic, and it reduces due to the long wavelength of the excitation to a non-retarded $1/r^3$ for typical donor/acceptor distances of the order of 10 nm. The final transition rates scale as the square of the potential or $1/r^6$.

MARPE is thus fundamentally different from the Förster effect and sensitized luminescence in several respects. It involves much higher excitation energies of 100–1000 eV, much shorter relaxation times leading to coherent interference effects, and much shorter wavelengths that can require considering retardation effects at the high end of the energy scale given above. A rate equation like that in the Förster effect is thus not appropriate, and the relevant interaction is, via interference with the direct process in the cross term of a squared amplitude, proportional to a perturbation associated with the autoionization process or V_{AI} . MARPE thus involves virtual photons and a single-step process, compared to real photons and a multiple-step process in the Förster effect/sensitized luminescence.. Both processes can however be considered to involve multiple scattering of photons, whether real or virtual, and inclusion of this in MARPE theory has been considered and, as already discussed, found to be important.

4.5 Conclusions

In summary, we have pointed out that a proper allowance for detector non-linearity is essential for accurately measuring multi-atom resonant photoemission effects, with the magnitude and form of the corrected results being significantly different from previous reports [1-4,6,7]. A microscopic theoretical model proposed previously for

describing these results [5] is found to accurately reproduce the observed effects, and confirms via agreement with experiment that they can be considered as interatomic resonance phenomenon. For the specific case of O 1s emission from MnO in the vicinity of the Mn 2p resonances treated here, this microscopic model, with the inclusion of higher-order interactions not considered previously, is also found to be reducible to a classical x-ray optical treatment using experimental optical constants. The x-ray optical model is furthermore found to describe well the observed intensity profiles as a function of both photon energy and x-ray incidence angle. Previously obtained photoelectron diffraction data for O 1s emission from a hydroxide surface species on MnO also may exhibit some multi-atom resonant effects in angular distributions of intensity. Previously obtained data for Cr/Fe alloys of about 50:50 composition in which Cr 2p could resonate with Fe 2p are found after detector correction to show at most very small MARPE effects of a few percent, with further experimental work being needed to confirm this.

It is thus of interest in future studies to explore the degree to which such effects, particularly with the expected enhancement of nearest-neighbor interactions, for more spatially dispersed resonating atoms and/or shorter x-ray wavelengths so as to go beyond the simple x-ray optical picture, in nanometer-scale objects, and/or in free molecules, can provide an element-specific probe of near-neighbor properties and many-electron interactions. Adding magnetic specificity via circular or linear dichroism measurements and/or spin-resolved photoemission is also suggested. The experimental and theoretical approaches outlined here should provide a sound framework for such work, both for photoelectron and fluorescent x-ray emission. The microscopic theoretical model outlined here should also be capable of describing such core-core interatomic resonance

effects in the intensities and angular distributions in photoemission from free molecules [12], as well as with straightforward generalization the valence-core interatomic resonance effects mentioned previously [8-10]. Finally, we point out that the demonstrated importance of multiple scattering of soft x-ray radiation in the vicinity of strong core-level resonances should be of relevance in the analysis of resonant elastic and inelastic x-ray scattering, other topics of high current interest [28].

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Fig. 4-1 The energy-level diagram of the multi-atom resonant photoemission process between O 1s and the deeper lying Mn 2p_{3,2,1/2} (Mn L_{3,2}) edges with the resonance occurring via the Mn 2p-to-Mn 3d (valence) excitation

Fig. 4-2 (a) A broad-range survey spectrum of MnO(001) with an exciting photon energy of 750 eV that is about 100 eV above the Mn 2*p* thresholds.. The O 1*s* and Mn 2*p* peaks are clearly seen, as are other labeled photoelectron and Auger spectral features. (continued next page).

(Fig. 4-2 cont.) (b) The Mn $2p$ absorption profile derived from the O $1s$ inelastic background intensity, for an x-ray incidence angle $\theta_{hv} = 20^\circ$ and an electron exit angle $\theta_e = 90^\circ$ (normal emission). This data has *not* been corrected for detector response, nor for self-absorption effects. (c) Initial MARPE results for the O $1s$ -Mn $2p$ resonance as shown in previous work, again *not* corrected for detector response, and exhibiting a greater than 40% maximum enhancement in the O $1s$ intensity at the maximum of the Mn $2p_{3/2}$ absorption. The smooth dashed line indicates the approximate result expected in the absence of the suggested MARPE effect. In the bottom of this panel is shown a normalized curve in which the smooth background has been set equal to unity and subtracted.

Fig. 4-3 The measured response function of our multichannel detection system (dashed curves), as plotted against the linear reference of an ideal detector (solid lines). The ordinate is measured counts per energy pixel, and the abscissa is proportional to the "true countrate" expected, which is in turn proportional to the emission current of the x-ray tube and thus also the incident x-ray flux. The inset shows the same kind of plot over a much broader countrate range. The solid lines for the ideal detector are chosen to asymptotically agree with the slope of the measured curve at the lowest countrates, although the final corrected results in all of the following figures do not depend on this choice of reference.

Fig. 4-4 O 1s spectra from MnO(001) off resonance (photon energy $h\nu = 637.6$ eV) and on resonance ($h\nu = 640.2$ eV) are shown before (dashed curves) and after (solid curves) applying the correction for detector non-linearity. The inset shows the experimental geometry, with x-ray incidence for this case at $\theta_{hv} = 20^\circ$ and electron exit along the surface normal at $\theta_e = 90^\circ$. The radiation is linear p-polarized, with the electric field vector $\vec{e}$ lying in the plane of the figure.

Fig. 4-5 (a) O 1s intensities derived from fitting analytical peak shapes plus inelastic backgrounds to uncorrected (dashed curve) and corrected (solid curve) spectra such as those in Fig. 4-4 as a function of photon energy over the Mn 2p_{3/2} and 2p_{1/2} absorption range and for $\theta_{hv} = 30^\circ$, $\theta_e = 90^\circ$. Also shown in the bottom of the panel are the uncorrected (dashed curve) and corrected (solid curve) results for the Mn 2p absorption coefficient, as measured via the inelastic background underneath the O 1s peak. The vertical straight dashed lines locate the approximate positions of the maxima in the Mn 2p_{3/2} and 2p_{1/2} absorption peaks. (continued next page)

(Fig. 4-5 cont.) (b) As (a), but for $\theta_{hv} = 20^\circ, \theta_e = 90^\circ$ and extending over only the Mn $2p_{3/2}$ edge. Note that the absorption profile (as well as the MARPE profile) here shows the largest change of (a) through (d) after correction. This is due to the different portions of the detector response profile used in the scan as a function of both average count rate and dynamic range required to measure the O 1s peak over the absorption profile [15]. (continued next page)

(Fig. 4-5 cont.) (c) As (a), but for $\theta_{hv} = 10^\circ$, $\theta_e = 90^\circ$. The countrates here were actually higher than in (b), but spanned a smaller portion of the detector dynamic range, and hence the corrections are smaller in magnitude. (continued next page)

(Fig. 4-5 cont.) (d) As (a), but for $\theta_{hv} = 5^\circ$, $\theta_e = 90^\circ$. Note that the size of the modulations (percent effect) in the MARPE profile continues to increase as θ_{hv} decreases.

Fig. 4-6 Scanned energy photoelectron diffraction data for O 1s emission from MnO(001) as measured over a broader energy region centered on the Mn 2p absorption edges. Results are shown before and after the detector correction. Both the measured and corrected profiles have been normalized to the broad maximum in the overall profile at ~635 eV for comparison, and the positions of the Mn 2p_{3/2} and Mn 2p_{1/2} are indicated again as dashed vertical lines. Note that the MARPE signal is strongly effected by the detector correction, due to the inelastic background increase under the O 1s peak when tuning over the Mn 2p edge, while the overall change in the diffraction profile is primarily due to the changing intensity of the peak itself on a relatively level background away from the edge. The strong negative slope in the entire region of the Mn 2p edges explains the significant overall slope the O 1s intensity with photon energy as seen in the MARPE profiles over a narrower energy interval. Preliminary theoretical photoelectron diffraction calculations using multiple scattering formalism are in qualitative agreement with this measured profile, but are not shown here.

Fig. 4-7 Expected electron yield as a function of incidence photon angle for the Mn 2p absorption edges. The overall profile is based on the measured electron yield for $\theta_{hv} = 30^\circ$, with the variation in angle for all other angles calculated from simple theoretical considerations [29]. The changes occur due to the attenuation of the incoming light (also referred to as self-absorption) which can have a characteristic absorption length perpendicular to the surface that is comparable to the electron inelastic mean free path as a strong absorption edge is crossed.

Fig. 4-8 Azimuthal (ϕ) scans of the O 1s photoemission intensity from an MnO(001) crystal at a takeoff angle of $\theta=45^\circ$ and with the photon energy set (a) at the maximum of the Mn $2p_{3/2}$ absorption peak ($h\nu=640.2$) and (b) just before the peak ($h\nu=637.2$). (continued next page)

(Fig. 4-8 cont.) (c) The O 1s peak has been deconvolved via peak fitting into a primary (bulk) component and a surface component believed to be associated with the formation of hydroxyl compounds, with these two components being shown here above a Shirley type background. (d) The hydroxyl signals from (a) and (b) for the photon energies on and off resonance are directly compared. The distinct differences seen here may be associated with a MARPE effect on photoelectron angular distributions.

Fig. 4-9 Experimental results for Cr 2p emission from a $\text{Cr}_{0.49}\text{Fe}_{0.51}$ alloy as the photon energy is scanned across the Fe 2p absorption thresholds, before and after the detector correction (refer to text). (a) The sum of the Cr $2p_{3/2}$ and Cr $2p_{1/2}$ intensities as a function of photon energy. For the uncorrected results shown as the black curves, note the strong enhancement in the Cr 2p peak areas that closely follows (b) the Fe 2p absorption edge before correction. After correction (shown for two reasonable correction parameters representing the fraction of the detector pixels that were actually seeing electron-induced light pulses on the phosphor [15]), the modulations nearly disappear leaving behind in (a) only a small dip in intensity of a few % just before the peak in the Fe $2p_{3/2}$ absorption peak shown in (b). The inset in (a) shows a blowup of the latter region. Finally, (c) shows the Cr $2p_{3/2}$ full width at half maximum intensity (FWHM) before and after correction. Note that they the peak widths become much more constant (and broader) across the absorption edge after correction. (continued next page)

(Fig. 4-9 cont.) (d) Energy dependence of the Cr 2p intensity for a pure Cr film, which is also shown before and after correction. The oscillatory modulations in both the Cr 2p_{3/2} and Cr 2p_{1/2} peaks are due to photoelectron diffraction, with positions in photon energy that are shifted by very nearly the difference in binding energy of these two levels. Summing the two intensities tends to cancel out these effects due to their out-of-phase character. (e) Comparison of corrected Cr 2p_{1/2}, Cr 2p_{3/2}, and summed intensities from an Fe_{0.51}Cr_{0.49} alloy and a pure Cr film. Note that the obvious diffraction modulations in the Cr 2p_{3/2} and Cr 2p_{1/2} intensities for the alloy are very closely reproduced in the pure Cr film due to their similar epitaxial crystalline structure. There is also a suggestion of a residual MARPE effect as a dip around 712 eV, in the Cr 2p_{3/2} data for the alloy, although the statistical accuracy of both the data and the residual errors in the detector correction do not permit a definite conclusion on this point.

Fig. 4-10 Illustration of the x-ray optical calculations required to extract δ from β in the complex index of refraction, $n = 1 - \delta + i\beta$. (a) The experimentally measured absorption profile of $\beta = \mu\lambda_x/4\pi$ includes both resonant and non-resonant components of β . (b) Tabulated values for the non-resonant (one-electron) portion of β [27] can be used to obtain (c) the resonant portion of β . (continued next page)

(Fig. 4-10 cont.) (d) The Kramers-Kronig transform of the resonant portion of β yields the resonant portion of δ . (e) Further tabulations of the non-resonant δ [27] allow a final determination via summation of (f) the total δ profile due to both resonant and non-resonant processes.

Fig. 4-11 (a) O 1s intensity from MnO(001) as a function of photon energy and for $\theta_{hv} = 10^\circ$, $\theta_e = 90^\circ$: experimental data (connected points) are compared to theoretical curves calculated using Eq. 4-8 (thin solid line, second order microscopic many-body theory = single radiation scattering), Eq. 4-11 (thick solid line, infinite-order microscopic theory = multiple radiation scattering), and x-ray optical dielectric theory based on Eq. 4-15 and the experimental constants shown in (c) (dashed curve).

(Fig. 4-11 cont.) (b) O 1s intensity from MnO(001) as a function of photon energy and for $\theta_{hv} = 5^\circ$, $\theta_e = 90^\circ$: experimental data (connected points) are compared to x-ray optical dielectric theory based on Eq. 4-15 and the experimental constants shown in (c) (dashed curve). As also seen in (a), note that all features in the experimental data appear to be reproduced in by the theory, with the exception of the overall sloping background due to photoelectron diffraction as seen in Fig. 4-6.

(Fig. 4-11 cont.) (c) The final x-ray optical constants δ and β of MnO over the Mn $2p$ absorption region, as derived from microscopic many-body theory (dashed curves) and from experiment with corrected data for the absorption coefficient μ and Kramers-Kronig analysis as described in Fig. 4-10.

(Fig. 4-11 cont.) (d) Calculations of the O 1s intensity as a function of photon energy based on the experimental optical constants in (c) and Eq. 4-15 from x-ray optical theory. Curves are shown for various x-ray incidence angles. The inset shows the normalized magnitude of the negative-to-positive excursion in % as a function of x-ray incidence angle, as calculated using x-ray optical theory (solid points) and as measured for four incidence angles in this study (large open circles).

5 Correction for Detector-Induced Effects in MARPE and General Photoemission Measurements

5.1 Introduction and Nature of the Problem

As noted in prior sections, a new photoemission effect which we have termed multi-atom resonant photoemission (MARPE) has recently been demonstrated. This effect involves a distinct resonance between the photoemission from a core energy level in a given atom, A, in a solid-state sample and an energetically deeper core level in neighboring atoms, B, of a different atomic number [1-3]. After an initial series of measurements on different systems by our group [1-3] and two other groups using the same electron spectrometer and detector system [4,5], very recent investigations have demonstrated irregularities in the size and shape of the measured resonance due to the acquisition parameters used in the experiment, specifically involving the countrate at the electron detector [4]. Attempts to reproduce these results at other synchrotron radiation facilities and with other detector systems also appear to have yielded different results [6]. In this chapter, we thus explore these irregularities, specifically involving non-linearity in counting as a function of countrate density, in detail and demonstrate a quantitatively accurate correction procedure to allow for them in both the present and future work. Our analysis owes much to prior work by Seah and co-workers, who have studied non-linearities in detector systems for x-ray photoelectron spectroscopy (XPS), and described procedures for measuring them and correcting spectra for them [7-9].

The MARPE experiments require monitoring the photoemission intensity from the level on A, while tuning the excitation energy over then more deeply bound level on B. Modulations in the intensity from A indicate a resonance process between these two

energy levels in neighboring atoms. As the photon energy is tuned through the deeper level edge, substantial increases in the inelastic background of the monitored peak A are observed; this is due primarily to inelastically scattered Auger electrons from B that are initially at a higher kinetic energy and then scatter back into the spectral region of A being studied. This background level has been found to provide a convenient simultaneous measurement of the B absorption profile, but it also has the negative effect of driving any detector through varying portions of its dynamic range.

Inconsistencies in the measured magnitude of the O 1s-Mn 2p MARPE enhancement, as well as in the Mn 2p absorption profile, in the MnO system have lead us to investigate the cause of the problem. Similar problems have also been encountered in a parallel MARPE study of N 1s-Ni 2p from N₂ adsorbed on Ni(001) by Garnier et al. [4], who first informed us of this problem. As shown in Fig. 5-1, the O 1s-Mn 2p_{3/2} MARPE enhancement appears to gradually decrease in magnitude with decreased countrates at the detector, as obtained by decreasing the resolving slit of the analyzer. Scan 1 gives the highest rates (largest slit, lowest energy resolution), and Scan 7 the lowest rates (smaller slit, and higher energy resolution), with these scans further described later and in Table 5-1. At extremely low count rates, there is a convergence to a "true" maximum peak intensity enhancement of about 10-12%, as compared to a value of about 35% at the maximum measured count rate. The simultaneously measured Mn 2p_{3/2} absorption coefficients also show significant discrepancies as a function of detector countrate as seen in Fig. 5-2. Finally, the peak widths as shown in Fig. 5-3 do not show similar behavior from one scan to another and in fact do not even have qualitatively reasonable values from one scan to another. For example, the lowest resolution data as far as the analyzer

is concerned (Scan 1) actually has the narrowest peak widths, as we will discuss in detail later.

The changes in MARPE enhancement with countrates have been determined to be clearly associated with non-ideal behavior of the detector system used in these experiments (the standard detector supplied with the Scienta ES200 electron spectrometer). Here we present an investigation of the detailed behavior of the detector in order to determine how to properly correct measured spectra. We have then applied the correction procedure to the datasets shown in Figs. 5-1, 5-2, and 5-3 to determine the actual magnitude and profile of the MARPE effect in the O 1s–Mn 2*p* resonance in MnO and to demonstrate the ability to accurately correct for the less-than-optimal performance of the detector. The correction process as well as the results of the correction will be discussed.

5.2 The Detector System

The actual detector used throughout this work is the standard system delivered with the model ES200 electron energy spectrometer manufactured by Gammadata Scienta [10,11]. The initial stage of the detector system consists of a pair of 40mm diameter circular microchannel plates (MCP) stacked in a standard chevron configuration and held at 1.7 kV during these measurements. This provides cascade multiplication of electrons passed by the electron energy analyzer. Electron pulses emitted from the backside of the channel plates are accelerated by 3.5 kV onto a green P20 type phosphorescent screen with a reported afterglow of about 10 μ sec [12]. In this manner, the charge pulses are converted to visible light pulses. A standard CCD camera, mounted

outside the UHV chamber and focused on the screen through a glass viewport is finally responsible for recording the light pulses and therefore performing the actual event detection. This detector is inherently two-dimensional. The nature of the hemispherical energy analyzer to which the detector is attached [10] results in one pixel axis of the camera representing the electron kinetic energy. The perpendicular axis, for our purposes, simply represents multiplexed detection at each energy, although it can contain information about the horizontal spatial position on the sample surface or the polar angle of emission of the electron from the sample when the analyzer is run in particular modes. We will refer to these axes as the *energy* and *spatial* axis, respectively.

The particular voltage and threshold settings used for our detector were those established by the vendor during the installation of a set of upgrade electronics in October 1996. This upgrade permitted operating in two modes: black-and-white (BW) (later termed "digital" in descriptions of the detector by the manufacturer) and grayscale (GS) (later termed "analogue"), with the latter providing in principle the ability to count ~ 7 times faster without serious saturation or up to about 700 kHz over all pixels if uniformly illuminated by electrons.

A limitation in the detector system electronics used in all of our experiments is that the spatial axis information is not retained. The detector operates in a mode for which both the energy and spatial axes can be gated to include only a specific rectangular portion of the detector in the final binned data. However, once these limits are selected, all counts for a given energy axis coordinate (i.e. a line of pixels along the spatial axis) are summed in hardware and only this binned sum is available for readout. This sum of spatial axis pixels for a fixed energy pixel coordinate will later be referred to as a detector

channel, whereas a *pixel* will refer to one pixel of the CCD camera. The camera views the 40 mm diameter circular phosphor screen, with the rectangle circumscribing this maximum active region of the detector including about 370 pixels along the energy axis and 240 pixels along the spatial axis. Within this circumscribing rectangle, a fraction, $\pi/4$, of the pixels within the rectangle will actually include the phosphor screen image, leading to a maximum of nearly 70,000 pixels available for counting in two dimensions when the camera is gated to accept the entire screen image.

This limitation means that, with the standard electronic system used, the full camera image *cannot* be stored for analysis, thus preventing the most accurate corrections of the effects to be considered here. That is, only in the limit of using a *single* spatial axis pixel per energy channel can the actual per pixel countrate be obtained. Obviously, this limit would abandon most of the available spectral signal and so is not a favored option. The manner in which we have dealt with this problem will be discussed further below.

It should also be noted that there is an alternate version of the Gammadata Scienta hardware that does allow full two-dimensional images to be retained in both energy and space and readout from the electronics interface. With this system, it should be possible to apply the correction procedure developed here with even greater precision than that demonstrated here.

5.2.1 Characterization of the Detector System

With preliminary evidence of possible deficiencies in the performance of the detector system [4,6], it of course becomes of great interest to characterize the detector performance accurately. This will allow us to determine the extent to which the detector

can influence or corrupt the spectra measured with it. In addition, it will provide a correction procedure for data acquired in the future and perhaps reveal more appropriate operating criteria that can minimize the amount of correction required in future measurements.

Ideally, the behavior of the detector as a function of countrate should be completely linear. In this case, we have a relationship,

$$m(r) = \alpha \cdot r \quad [5-1]$$

where $m(r)$ is the measured countrate as a function of true countrate r . The scaling factor, α , would be constant and unity in an ideal system, but it is for us only necessary to know it to within some constant factor. For example, the factor α might be determined by an analysis of the measured countrate $m(r)$ and a comparison of the actual statistical noise provided that the system can be expected to display the Poisson statistics of a true counting system with standard deviation of $(m(r))^{1/2}$, but we will not pursue this avenue here.

The actual behavior of the detector is found to deviate from the ideal and must be described by,

$$m(r) = \varepsilon(r) \cdot r, \quad [5-2]$$

where $\varepsilon(r)$ is the *efficiency* function, describing the deviation from an ideal behavior as a function of true count rate. Recall that we generally don't know the point (if any) at which the measured and true countrates coincide, so there is an arbitrary factor, β , that can be multiplied into the efficiency as long as the true countrates are scaled by $1/\beta$ as in,

$$m(r) = [\varepsilon(r) \cdot \beta] \cdot \left[\frac{r}{\beta} \right] \Rightarrow m(r') = \varepsilon(r')r', \quad [5-3]$$

with an obvious meaning of r' .

In order to correct errors in measured spectra we need to consider not the measured counts as a function of true, but the true counts as a function of measured, so we trivially invert the relationship,

$$r(m) = \delta(m) \cdot m, \quad [5-4]$$

and designate the function $\delta(m)$ as a *deficiency* function which is simply equal to $1/\varepsilon(m)$ in which the argument of ε has been changed from r to m . To correct measured countrate spectra into true countrate spectra, only Eq. 5-4 is needed along with a known form for first the efficiency function and then, via inversion, the deficiency function.

5.2.2 Operational Modes: B/W and Grayscale

As briefly introduced above, the electronics used for readout of the camera pixel information can be run in one of two modes. The first mode is a simple "black and white" (BW) pulse counting mode and was the original mode supplied with the system by the manufacturer. More recent versions of the documentation for this mode refer to it as "digital". In this case, each camera readout (occurring at a frequency of 30Hz) involves simply testing if each pixel has accumulated enough charge to indicate one or more counts above a settable discriminator level. The readout frequency imposes a maximum countrate of 30Hz per pixel before hitting a rigid saturation condition. For low enough countrates that the probability of multiple pixel hits within the sampling time is minimal, one would expect quite linear behavior in the response function, but a poorly set discriminator can be expected to introduce significant deviations from this [7].

To provide approximate numbers here, with 30Hz per pixel and about 70,000 pixels, the corresponding fully saturated rate would be about 2.1MHz. However, in practice, only a fraction of this may be expected to be usable if one wishes to be able to ignore multiple per-pixel hits and the resulting necessity for deadtime corrections. In addition, if “multiple counting” (due to crosstalk) factors are considered in this value, the true event countrate is reduced by another factor that must be independently determined. We caution against the casual use of global countrate figures in describing the properties of any such multichannel detector without also considering the much more important per collector (pixel) countrate as well.

The second mode of operation was known originally as “grayscale” (GS) (although the documentation for more recent versions of this analyzer refer to it as “analogue” mode) and was also provided and calibrated by the manufacturer as an upgrade to the BW mode. In this case, the readout involves a measurement of the collected charge in the pixel with an 8-bit analog to digital converter (ADC). For the GS mode, the equivalent of the BW mode discriminator is a digital mask that eliminates low-order ADC bits in an attempt to discard spurious noise counts. This type of operation is significantly different than the BW mode in that it is an integrated charge counting mode and not a pulse counter.

Because the GS mode can distinguish up to 255 non-zero levels per readout compared to only one in BW, the maximum countrate is in principle dramatically increased. This is the reason the GS enhancement was added to the system after the initial delivery with only BW mode. The ADC mask of course reduces the number of GS levels. For example, only 128 or 64 levels are available for a 1 or 2 bit mask

respectively. But even with this reduction, the countrates available with the GS should be significantly higher. However, the influence of the mask on the response is not yet clear and the linearity of the ADC itself is not known to us.

Each mode produces a unique response function that must be determined independently. In addition, with each change in discriminator or mask level, or voltage across the microchannel plates, the conditions under which the detector measures a count are altered and the response function will be modified. However, we have intentionally not varied any of these parameters in the present series of measurements, choosing to instead focus on the characterization of the detector as used in our experimental work to date.

5.2.3 Measurement of the Response Functions

In order to determine the measured countrate as a function of true count rate (at least within the trivial multiplicative constant β), one simply needs to adjust the true countrate, which will be proportional to the number of electrons incident on the front face of the microchannel plate, in a controlled manner and record the resulting measured countrate at the detector. We have performed this experiment using the Scienta ES200 spectrometer and detector system located on the Advanced Photoelectron Spectrometer/Diffractometer (APSD) [13] at the Advanced Light Source (ALS). The chamber includes an unmonochromatized dual-anode Al $K\alpha$ /Mg $K\alpha$ x-ray source (Perkin Elmer Model 04-548), which has a power supply permitting variable emission current at fixed highvoltage. In particular, for fixed voltage, the emission current can be adjusted in 1 W steps in power with the anode potential held constant at 12.5 kV for this work. The

experiment is performed by monitoring the photoemission intensities from a W(110) single crystal in an "as-is" uncleaned condition (i.e. containing a stable amount of contamination in the UHV environment of the experiment) as the Al K α x-ray power is varied. Within a given scan of the x-ray power at constant high-voltage, the analyzer settings (pass energy, kinetic/binding energy, and resolution slit) are also fixed in order to illuminate a constant portion of the detector. In addition, only a narrow portion of the detector along the spatial axis is generally used in order to ensure uniform illumination over the active area. The region of the detector over which counts were accumulated is also indicated via the % of each of the two axes allowed in, and this can be adjusted via software. Specifications for the various scans discussed here are given in Table 5-2. With the exception of Scan05, all measurements were performed on reasonably featureless regions of in the inelastic background of the W spectrum in order to keep the detector as evenly illuminated over the active portion of the detector as possible. Only the Scan05 data represents non-uniform illumination, with the W 4*d* spectrum centered in the detector. A typical screen image of the detector with a spectrum of Cr 2*p* (unrelated to this work and shown only for example) centered in the detector window is shown in Fig. 5-4, with the energy-binned spectrum plotted along the vertical energy scale.

Before proceeding to the results, we note that there is a question as to whether a linear variation in the x-ray filament current at constant high voltage between filament and anode really results in a linear increase in the flux of photons at the sample, and thus of the electrons incident on the microchannel plate. If this is not true, then the calibration of the detector response would obviously require additional corrections so as to be related directly to the x-ray flux. We have tested this linearity of filament current versus

photoemission strength by simply recording the total sample current as a function of x-ray current (and thus also power if voltage is constant). This relationship is found to be quite linear over at least the used range of 5-300 W , with all quadratic or higher order terms contributing less than 5% of the linear component within this range. Using either the sample current or the x-ray power as a measure of the true countrate introduces only minor differences in the final response function analysis. Below 5 W , the x-ray appears to go into a shutdown mode with vanishing flux. We also did not set the power above 300 W (25 mA).

The detector and analyzer were run in a *fixed* or *snapshot* mode using custom software written as part of this dissertation and well adapted to this sort of testing [14]. In this mode, the analyzer settings determine the linear kinetic energy distribution over the energy-axis of the detector and are held constant. The per channel counts (sums of spatial pixel counts) are simply stored directly as read from the detector. By using only a narrow portion of the spatial axis over which the countrate is nearly constant, the recorded counts may be trivially converted to a reliable per pixel count rate.

Normally, photoemission experiments are performed in a more complicated *dithered* or *swept* mode that involves sweeping the kinetic energy of the electrons passed by the analyzer so that all energies in the final spectrum are accumulated in sequence by each channel in the detector. This is primarily done to allow parallel detection channels to be used while eliminating the channel-to-channel differences in the detector gain in the final spectra. This mode was not used here because the inherent averaging over the detector would be detrimental to the analysis of the detector behavior. It was however

used exclusively for acquisition of the MARPE datasets discussed later and so the final correction procedure will be developed for both cases.

It should be mentioned that care should be taken if using the manufacturer-supplied software for these measurements because the detector counts are multiplied by a scaling factor that varies with the operational mode (e.g. pass energy) of the analyzer. The nature of the scaling factor is immaterial to this discussion, but must be compensated for in order to properly and self-consistently determine per pixel count rates.

Once the detector signal has been acquired, we determine the average countrate *per pixel* as a function of the true countrate (in turn proportional to x-ray filament current), revealing the detector response function for the current detector settings (BW or GS mode, discriminator/mask setting, and MCP and phosphor voltages). The results for the BW mode are shown in Figs. 5-5,6 while various aspects of the GS mode response are displayed in Figs. 5-7 through 5-10. It is clear that the detector responds with significant deviations from the ideal linear behavior of Eq. 5-1, even at very low countrates and in either BW or GS mode, as will be discussed in detail below.

5.2.4 Analysis of the Response Function

A number of measurements of the response function with the detector and analyzer set differently were performed. The various parameters for each scan are listed along with labels for each scan in Table 5-2.

Several interesting points are illuminated by the analysis of these detector response functions. First, as illustrated in Fig. 5-8(a), various portions of the response may be measured and combined quite accurately into a larger overall measurement. In

this case, the analyzer settings were changed to allow varying uniform electron intensities at the active portion of the detector for each scan of 0-300W in x-ray power. Each change in settings in this manner effectively changes the true-count-rate scaling as in Eq. 5-3 and so a simple constant scaling of the final true-counts for each scan is all that is required to combine the various scans into one self-consistent plot.

We have observed that a general trait of the detector is a lower level of illumination of the center of the phosphorescent screen than at the edges when using the laboratory x-ray source. The reason for this is not well understood but may be due to voltage drops over the MCP from the current-supplying ring contact at the outer edge. There may also be some contribution from reduced gain in the plates in the center simply due to the known performance degradation of channel plates with total wall current extracted over time. However, it is not expected that the center of the plates should have experienced significantly greater integrated intensities than the edges because the normal dithered mode operation of the analyzer continuously moves any high intensity peaks over the entire detector face.

We can use this distribution over the detector to extract some information about the detector system by measuring the response function simultaneously in several small portions of the detector along the spatial-axis. As shown in Fig. 5-8(b), we have plotted the extracted detector response from various 10% spatial portions of the detector. The total countrate range differed significantly from one spatial window to the next and so sampled a varying amount of the overall detector response. But when properly normalized to true count rates, the response functions are indistinguishable in the overlapping portions. This is evidence that there is no significant change in the response

function over the surface of the detector, permitting us to much simplify the procedure for correcting spectra.

However, Figs. 5-4 and 5-8(b) at the same time illustrates a potentially significant difficulty in the procedure for correcting data acquired with the detector. That is, typical operating parameters involve setting the spatial axis to a size that includes essentially the entire illuminated portion of the detector. During the data collection process, spatial axis counts are simply added together, and in swept mode experiments, there is a summing over all energy axis pixels as well. Therefore, the final result may be composed of counts taken with portions of the detector that are running at substantially different countrates and a fully accurate correction for detector non-linearities would therefore require a weighted sum of an array of response function corrections that can generally only be approximated. When spectra are measured using a focused excitation source, such as a synchrotron radiation beamline, the fact that the sample is only illuminated over a small portion of the (in our case horizontal) spatial axis over which the analyzer slit can accept electrons leads finally, after passage through the analyzer, to a non-uniform illumination over the detector plane. Thus such additional concerns about non-uniform, or at best simply fractional but nearly-uniform filling of the detector, are generally found to be significantly more pronounced than those seen with the broad illumination of a standard x-ray source.

5.2.5 Behavior at Low Count Rates: Quadratic Response

Both Fig. 5-5(b) for BS mode and Fig. 5-7(c) for GS mode indicate a type of non-linearity for low countrates that can at least approximately be described as a quadratic deviation from linearity. In fact, over the countrate range from 0 to 20 Hz/pixel, the

fractional quadratic overcounting as measured relative to a hypothetical linear detector whose response is a straight line with slope equal to the asymptotic slope of the measured response as the countrate goes to zero is very nearly the same for both BW and GS modes. We return to discuss this point more quantitatively below.

All MARPE datasets discussed here and in our previous photoelectron and Auger electron emission work were acquired in grayscale detection mode with a maximum countrate of about 1600 Hz per energy *channel*. Each channel consists of about 50-100 illuminated pixels along the spatial axis, corresponding to half to a quarter of the full spatial axis due to partial filling of the detector and so this leads to maximum countrates of 32-16 Hz per pixel. Minimum countrates typically fall below 0.5 Hz per pixel. It is then over this particular range that we are most interested in accurately determining the response and deficiency functions. As introduced briefly above, we have found that in this range the detector response has a strong quadratic behavior in both BW and GS modes and therefore a strong linear component in the deficiency function. Ideally, the efficiency and thus also the deficiency which is its inverse would both have constant values. Thus, the deviations found in our measurements indicate a significant and clear need for corrections to the measured counts.

In Fig. 5-5(a), the measured detector response for BW mode is shown. Note the abrupt leveling-off of the response at a measured countrate $m = 30\text{Hz}$ per pixel in (a). This corresponds to the expected total saturation condition when every pixel has seen *at least* one count per camera readout. Since the readout occurs at a 30Hz frequency, the maximum number of counts that can possibly be recorded is the observed 30Hz per pixel. A more accurate measurement going only up to about 27Hz per pixel is shown in

Fig. 5-5(b) where deviations from the ideal linear behavior are clear over the entire useable range (i.e. the range below the onset of significant saturation) of the BW mode. Finally, Fig. 5-6 shows the efficiency and deficiency functions corresponding to the data of Fig. 5-5(b). We have here, as shown in Fig. 5-5(b), arbitrarily set the efficiency equal to unity at measured and true count rates of 20 Hz per pixel, thus establishing the scale between $m(r)$ and r .

The GS mode response function up to a measured rate of about 100 Hz per pixel and the resulting efficiencies and deficiencies are shown in Fig. 5-9. We have again arbitrarily set the efficiency equal to unity for a countrate of 20 Hz per pixel; although other choices are possible for this (e.g. unity at zero count rate), the final results of any correction we make are not affected by this choice, which simply scales the efficiency by a constant factor β , as noted previously in discussing Eq. 5-3.. For a measured range up to only about 50Hz per pixel, the grayscale response function is shown in Fig 5-10 along with a least-squares fit of a quadratic order polynomial, illustrating that the response function is indeed highly quadratic below about 30Hz per pixel. The type and degree of non-ideal behavior observed with such a detector may be altered by choosing other discriminator/mask settings, as pointed out by Seah et al. [7], but we have not explored these variables. In addition, the fact that other detectors of this type in two other laboratories [4,5] have yielded very similar results prior to non-linearity correction suggests that the qualitative behavior of Fig. 5-10 is a rather general property of the system as presently configured.

5.2.6 Application of the Efficiency Function to Spectra Correction

With Eq. 5-4 and an analytical (polynomial here) function describing the deficiency function, the correction of measured countrate data is a trivial task. However, the spectra to be corrected must first be processed from a typical distribution of total measured counts to a distribution of countrates *per pixel*. This process is not difficult but the details of the detector setup and the acquisition mode during a spectrum collection must be properly considered. For the case of a simple fixed-mode or “snapshot” spectrum collection as described previously, each data point in the spectrum will have been collected by a line of spatial pixels at a particular energy-axis coordinate. The correction from total measured counts for a given energy channel in the spectrum, M , to a countrate per pixel, m , is given by,

$$m = \frac{M}{\tau \cdot N_s \cdot f_s}, \quad [5-5]$$

where τ is the total dwell or accumulation time of the spectrum, N_s is the total number of active pixels along the spatial axis, and f_s is the fraction of the detector that is filled along the spatial axis. Note that M is defined per resolved CCD energy pixel as sent from the detector hardware to the computer, the natural energy step for a fixed-mode/snapshot spectrum. Later computer processing may sum these pixels into a given energy bin that represents the finest energy step to be shown on a plot. Here, we have assumed that the filled portion of the spatial axis has essentially uniform countrate over the summed pixels. If this uniformity condition is not met, the efficiency and deficiency may vary significantly across the spatial axis of the detector, and Eq. 5-5 will give only some sort of average spanning a part of the dynamic range of the detector.

For a swept-mode spectrum, every active pixel of the detector will contribute to each final data channel in the spectrum for the same per-energy-step dwell time, τ' . So if N_E is the number of active pixels in the energy-axis, the appropriate relationship is given by,

$$m = \frac{M}{\tau' \cdot N_E \cdot N_S \cdot f_S}. \quad [5-6]$$

Note that Eq. 5-5 is essentially Eq. 5-6, but the dwell times are related by the function $\tau = \tau' \cdot N_E$, where τ now still represents *total* accumulation time per data channel in the final spectrum, and τ' is the dwell time per dither step. The factor N_E simply reflects the fact that every pixel along the energy axis will contribute to each data point in the spectrum for a time equal to the dwell time per dither step, the essential characteristic of the swept mode collection method.

For either detector mode, the actual values of N_S and, to a lesser degree N_E , are not necessarily simple to determine. While the electronic gating may be set to a given fraction of the total available detector window, this fraction is not necessarily representative of the number of pixels that are actually electronically active *and* illuminated. This problem has been seen to be most prominent when spectra are acquired using a highly focused light source of $\leq 1\text{mm}$ spot size, such as typically obtained from a third-generation synchrotron radiation beamline. In this case, the illuminated area is also often not centered in the detector, apparently due to slight misaligned of the analyzer and sample relative to the beamline. The correction factor f_S indicated above for the fractional illuminated portion of detector along the spatial direction can thus be difficult to estimate accurately, and can make corrections to the data more difficult.

In order to make quantitative corrections in the simplest way, a polynomial fit to the response function is performed. This same polynomial is used with Eq. 5-4 to trivially derive the deficiency function, with some arbitrary point having been chosen at which to set the measured and true counts equal. Finally, making use of Eq. 5-4 again, this deficiency function is multiplied times the measured countrates at each point over a spectrum so as to derive a final spectrum that is proportional to the true countrates. We find that for the particular detector settings and the grayscale mode used throughout our experiments, the deficiency is well represented by a fifth-order polynomial,

$$\delta(m) = 2.00731 - 0.14457 \cdot m + 0.01103 \cdot m^2 + 5.32241 \times 10^{-4} \cdot m^3 + 1.36619 \times 10^{-5} \cdot m^4 + 1.40492 \times 10^{-7} \cdot m^5, \quad [5-7]$$

for countrates below 30Hz per pixel. To achieve the same degree of agreement up to ~60 and ~90Hz per pixel, seventh-order and ninth-order polynomials, respectively, can be trivially fit to the same dataset that was used over a smaller range to yield Eq. 5-7.

In addition, the deficiency function for the BW mode has been determined to be very well represented up to about 27Hz per pixel by a fifth-order polynomial,

$$\delta(m) = 1.62564 - 0.11166 \cdot m + 0.00886 \cdot m^2 - 3.78084 \times 10^{-4} \cdot m^3 + 7.15348 \times 10^{-6} \cdot m^4 + 2.15352 \times 10^{-8} \cdot m^5, \quad [5-8]$$

which is close enough to the absolute 30Hz rate that this may already be beyond a normally desirable range of operation. Note also that the normalized ratios of the first three coefficients for the GS and BW polynomials are not very different, at 1.000:0.072:0.005 and 1.000:0.068:0.006, respectively, indicating that both modes would

exhibit very nearly the same degree of non-linearity and quadratic overcounting at low countrates.

As a final reiteration, the overall arbitrary multiplier, β , in these deficiency functions has been *chosen* to force the measured and “true” count rates to match at 20 Hz per pixel. Another obvious choice would be to force the deficiency to unity at vanishing count rates as shown in Fig. 4-3. However this choice is not unique, as it is clear that it is at these low countrates (below about 15 Hz) the detector is exhibiting the most non-ideal (quadratic) behavior. In fact, if the discriminator level is responsible for this quadratic form as discussed by Seah [7], the detector is actually undercounting (overdiscriminating) at these low rates and so a deficiency greater than unity is also quite logical. However, the choice is arbitrary and consistency between corrections is the only important issue in the analysis presented here.

It should also be noted that only after a spectrum has been corrected from measured to true countrate is a photon flux correction appropriate. Such a correction is typically performed to data acquired with a synchrotron light source in order to compensate for loss of photon-flux as the stored current in the ring slowly decreases.

5.3 Correction of MARPE Scans and Absorption Profiles

As briefly discussed earlier, several O 1s–Mn 2p MARPE experiments have been performed under conditions of varying countrates at the detector. The parameters characterizing each scan are given in Table 5-1. Of great concern is the observed discrepancy between several features seen in the individual scans. First, as illustrated in Fig. 5-1(b), a series of Mn 2p_{3/2} absorption profiles recorded at varying countrates and

detector modes shows inconsistencies up to 50% in relative peak heights when normalized to common background levels for photon energies below the absorption edge. Secondly, the O 1s–Mn 2p_{3/2} MARPE profiles themselves exhibit decreases in magnitude of a factor of more than 3.5 as the countrate is lowered. There is also a possible overall shape change in the resonance profile as the countrate decreases. These changes are clearly shown in Fig. 5-2.

Finally, as presented in Fig. 5-3, the O 1s peaks in some cases show clear (>5%) modulations in their widths over the Mn 2p_{3/2} edge while in other cases, the widths remain nearly constant within the experimental statistics. Because the peak widths affect the peak intensities (which are always derived as areas) and thus also any MARPE signal, which is simply a modulation in these intensities over the edge, understanding the source of this varying width in the context of the detector correction is important. In addition to the varying widths within a scan, the average peak width for each scan actually appears to be decreasing along with decreases in instrumental resolution as defined by the changes in analyzer acceptance slit. For example, MARPE Scan 1 with the widest slit size and hence lowest resolution of all scans studied here has an O 1s peak width (FWHM) that varies from approximately 0.95 eV to 1.01 eV between the on and off resonance conditions. By comparison, MARPE Scans 5 and 6, both at the narrowest used slit appear to have a nearly constant and larger FWHM of about 1.10 eV.

In general, the lowest countrate scans (MARPE Scans 3, 5, 6, and 7 in Table 5-2) all appear to exhibit stabilization in both the magnitude and shape of the MARPE enhancement. In addition, the O 1s peak widths all appear to remain constant across the

Mn $2p_{3/2}$ edge, although in no cases do the relative widths between scans follow expectations based strictly on electron analyzer considerations.

5.3.1 Experimental Procedure

All scans shown in Figs. 5-1, 2, 3 were acquired during the first photoemission experimental shifts at the newly commissioned beamline 4.0.2, which makes use of the first Elliptically Polarized Undulator (EPU) [15] to be installed at the Advanced Light Source (ALS). The APSD chamber used in the earlier detector characterization was recently relocated to this beamline and has been used to acquire all data discussed here. The use of this beamline represents a distinct difference from our prior MARPE work: although all previous experiments also made use of the APSD chamber, they were performed at the ALS bend-magnet beamline, 9.3.2, as discussed elsewhere [1-3]. The EPU provides much more flux at a given resolving power than the bend-magnet and consequently, in order to avoid driving the detector even further into non-linear and/or saturation regimes, the scans were performed at a photon energy resolving power that was much higher than that used in the beamline 9.3.2 datasets. This resolution remained fixed for all of the MARPE scans in Table 6-1 and discussed here. This higher beamline resolution accounts for the increased resolution seen in the Mn $2p_{3/2}$ absorption edge (Fig. 5-2) as compared to older, similar work [1-3]. The dramatic increases in photon flux at the EPU also allowed the analyzer to be operated at lower pass energies and slits than possible at 9.3.2, further increasing the overall resolution of the spectra O 1s spectra compared to prior work. Over the course of the MARPE scans, the only parameters that were changed were the analyzer entrance slit (thus changing resolution and count rate) and the detector mode (BW/GS). The storage ring current also slowly degraded in the

normally expected manner over the course of a fill, which changes the photon flux at the sample and hence the detector count rate.

It is unlikely that the change of beamline has played any role in the problems seen with the spectral variations with count rate. All past spectra were acquired with a maximum countrate within the scan (the countrate of the O 1s peak with hv at the Mn $2p_{3/2}$ absorption peak) set to a particular value that roughly corresponds to the data of MARPE Scan 1 in Table 5-1. Although this EPU dataset was acquired at higher instrumental resolution than the 9.3.2 data, the overall countrate at the detector was approximately the same and the maximum size of the enhancement in uncorrected data (~35% now compared to 42% in typical BL9.3.2 data) was also similar. All scans were performed with unchanged beamline resolution settings, with instrumental changes occurring only in the analyzer entrance slit setting, the ring current of the synchrotron, and the electronic counting mode of the detector discussed above.

As in our previous work, the MnO(001) single crystal was cleaned by Argon ion sputtering and held at an elevated, stable temperature of about 625K during all data acquisition in order to eliminate (or at least minimize) charging effects in the O 1s spectra. For the scans listed in Table 5-1, only the Mn $2p_{3/2}$ edge was measured, simply due to beam time limitations and the several hour acquisition times required for the MARPE scans at the lowest countrates.

When comparing to previous work [1,3] we reiterate that the earlier measurements were recorded at significantly lower resolution than the datasets shown here.

5.3.2 Results After Detector Correction

The countrates for all spectra shown in Fig. 5-1 and listed in Table 5-1 remained below 20 Hz per pixel and so are within the useable range of the correction functions given in Eqs. 5-7 and 5-8. The result of applying these functions to these datasets will now be considered.

We first consider the effect of the correction on the background level of each O 1s spectrum in each of the MARPE profiles. Recall that variations in this level as the photon energy crosses the Mn 2*p* absorption edge clearly follow the Mn 2*p* absorption edge itself, and have in fact been used to measure the absorption profile. Also, recall that the measured absorption edges show significant (>50%) variations as a function of detector countrate when normalized to the low-energy background before the edge (cf. Fig. 5-1). We can now see the effect of the correction for two cases in Fig. 5-11, where significant changes in the shape of the profile are particularly pronounced in (a), appearing as a “stretching” of the profile at the peaks. Note also that the absorption profile peak height is decreased in Scan 1 while slightly increased in Scan 7 taken at much lower overall countrates. This behavior is simply due to the 20 Hz/pixel normalization choice of the deficiency curve. Other choices could make both spectra appear to decrease in magnitude or both increase, due to the arbitrary constant factor β involved in this normalization (cf. Eq. 5-3). The important change is in the relative values throughout each profile.

The full set of corrected absorption profiles are overlaid in Fig. 5-12(b), with the original uncorrected profiles repeated again in 5-12(a) for comparison. It is clear that the profiles show remarkably improved agreement, to within better than 5% for the worst-

case deviations. It is not surprising that there are such large corrections here because we have already noted the large variations in the deficiency function at the countrates seen in the O 1s backgrounds used to extract the absorption profiles. For example, the highest countrate scan shown in Table 5-1 has a measured background countrate that varies from <0.1 to >1.7 Hz per pixel, well within the rapidly changing portion of the deficiency curve as shown in Fig. 5-9.

With application of the corrections point-by-point to entire O 1s spectra, significant changes in peak shapes and intensities also become evident, in addition to the background level changes already observed through the absorption profile corrections. Fig. 5-13 shows for two cases uncorrected and then corrected O 1s spectra at three photon energies: below ($h\nu=633.0\text{eV}$), on ($h\nu=637.6\text{eV}$), and above ($h\nu=645.0\text{eV}$) the Mn $2p_{3/2}$ resonance. MARPE Scan 1, the highest countrate scan, exhibits significant modification in the peak, as judged easily by peak height to background ratios. After correction, the peak widths, as judged by full width at half maximum (FWHM), not only increase due to the elimination of peak stretching, but also become much more uniform, at about 0.92–0.95 eV throughout the scan. By comparison, the low countrate data in Scan 7 experiences minimal change with only slight background level increases and minimal, almost negligible, width increases. This is easily explained by the fact the countrate range in this scan (see Table 5-1) remains so low that the detector deficiency value is nearly constant throughout the scan.

After correction, the peak widths are not only nearly uniform within a scan (a 2-3% increase over the resonance seems to be consistently present) but now have values

that are in at least qualitative agreement with the changes in instrument resolution between scans.

Finally, a correction to the MARPE peak heights (see Fig 5-14) using the same efficiency functions again results in a general reduction of the effect for the higher countrate scans and a convergence to the ~10-12 % maximum enhancement level observed in all of the extremely low countrate profiles (Scans 5-7 in Table 5-1). It appears that in either GS or BW mode, measurements that are made at sufficiently low countrates can be expected to produce results requiring negligible correction, however, these countrates involve data collection times that are too long for routing usage. The plots of the peak heights will be essentially identical to the MARPE profiles (peak areas) because the widths are now nearly constant.

The correction procedure applied above clearly demonstrates a successful and consistent method for dealing with non-ideal behavior in our detector response function, a conclusion that has been reached previously by Seah, et al [7-9], but for different spectrometer and detector systems. It is also expected that even the very successful corrections shown here could be improved with specific experimental procedures, most importantly, the maintenance of a uniform illumination over the active portion of the detector screen. The MARPE scans discussed here were performed with a large active area on the detector but with uneven illumination that appeared strongly shifted to one side of the spatial axis. Because of this, the actual number of pixels to use in calculating the per-pixel countrates was not entirely clear, and a fractional filling, f_s , had to be assumed here, as based on visual observation of the CCD image on a monitor (cf. Fig. 5-4). In addition, as the analyzer slit width is reduced, a somewhat smaller fraction

of the detector remains illuminated, meaning there is a slight change in the number of illuminated pixels from scan to scan, even if all other parameters are completely constant. For the corrections discussed here, a constant number of pixels representing about a third of the active area during the experiment ($f_s = 1/3$) was used for *all* scans. This value is very reasonable compared to what one would expect from the visibly illuminated portion of the detector during data acquisition.

5.4 Implications for Previous and Future Work

Obviously, the type of detector correction performed on the MARPE datasets and presented here will be required for the quantitative analysis of a broad range of data acquired with the detector. In fact, any spectrum acquired with the detector will be at least minimally affected by the detector response and so the correction procedure should perhaps be considered a standard part of the data analysis in the future. In this case, it would be prudent to periodically repeat the measurement of the detector response function to assure continued compensation for any changes in the multichannel plate, the phosphor, and/or the electronics over time. In addition, more careful monitoring of the intensity distribution over the detector should become a standard part of the record keeping for any experiment. This can be done easily in at least a qualitative manner by simply using a frame-grabber attached to the real-time monitor signal of the detector, as shown for one case in Fig 5-4.

In the immediate future, a full study of the response functions for various detector discriminator and mask settings should be performed. It is possible that some of the spurious behavior so far observed is related to poor setting of these levels, at least for the

pulse-counting BW mode. Seah et al. [7-9] have in fact pointed out that the discriminator setting in a detector very similar to ours can be used to improve linearity in certain countrate ranges, although this procedure is not expected to eliminate non-linearity over a broader countrate range, especially in GS operation due to the nature of this mode. With proper adjustment, it may then be possible to achieve significantly more uniform efficiency/deficiency functions for some countrate range and so minimize or even eliminate the need for the correction process in many cases. However, the possible influence of such non-linearities should always be kept in mind for any case where measuring relative intensities accurately is important. This would include, for example, doing quantitative analyses for surface contaminants or determining sample bulk stoichiometries, where the peak intensities involved can differ by one or two orders of magnitude, and thus could occupy a significant portion of the detector dynamic range..

The corrections we have been able to perform indicate that while the process is not entirely trivial, it can be completed quite accurately given minimal information about the acquisition conditions during the experiment. We have seen a decrease in the magnitude of the O 1s–Mn 2*p* MARPE effect in MnO by a factor of about four due entirely to spurious detector behavior. However, an effect nonetheless persists as an intensity enhancement at the 10-12% level in passing over the Mn 2*p*_{3/2} absorption peak after all corrections are made. Thus, although uncorrected results indicated that the MARPE profile very closely if not exactly followed the absorption profile of the resonator level, both the corrected high-countrate scans and the corrected low-countrate scans agree with one another to within statistical accuracy, and indicate a significant deviation of the MARPE profile from the absorption profile. However, the enhancement

is clearly still associated with the activation of the deeper energy level, with the 10-12% enhancements in Fig. 5-14(b) occurring at the same excitation energy as the primary Mn $2p_{3/2}$ absorption peak. There is also an indication of a dip in intensity just before the enhancement, and this has been verified in the more extensive corrected data and theoretical analysis presented previously in Ch. Four.

It is of course fully expected that other measurements beyond the O $1s$ -Mn $2p$ MARPE process discussed here will be affected by non-linear detector response. However, we have presented a general procedure for correcting spectra for this behavior. By including this procedure as a standard step in the data analysis, the non-ideal detector behavior can be compensated for and the detector can be used to acquire quantitatively accurate data.

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Scan Name	Detector Counting Mode	Analyzer Entrance Slit (0.1mm x 0.1mm, Shape Indicator)	Analyzer Resolving Power $\Delta E/E_0$	Min. Measured Countrate (Hz per pixel)	Max. Measured Countrate (Hz per pixel)
MARPE Scan 1	GS	0.8 x 30, curved, 6	250	0.231	29.36
MARPE Scan 2	GS	0.5 x 25, curved, 5	400	0.125	7.59
MARPE Scan 3	GS	0.3 x 20, curved, 4	666.6	0.076	3.44
MARPE Scan 4	GS	0.3 x 20, curved, 4	666.6	0.082	4.62
MARPE Scan 5	GS	0.2 x 20, curved, 3	1000	0.008	0.36
MARPE Scan 6	BW	0.2 x 20, curved, 3	1000	0.003	0.11
MARPE Scan 7	BW	0.3 x 20, curved, 4	666.6	0.018	1.02

Table 5-1 Pertinent countrates for MARPE scans acquired at various overall measured countrates. Each scan was obtained with identical beamline settings, and each also entirely within one of several consecutive synchrotron storage ring refills. The estimated beamline resolving power was 3000. Countrate variation was accomplished via analyzer slit settings and ring current changes over a fill. All scans were acquired at an analyzer pass energy E_p of 75.0 eV from an MnO single crystal sample and with an identical active detector window. The scan labels given above are used throughout the text and other figures to refer to particular scans.

Scan Name	Detector Counting Mode	Analyzer Entrance Slit (0.1mm x 0.1mm, shape, indicator)	Analyzer Pass Energy, E_p (eV)	Analyzer Kin. Energy (eV)	Active Detector Spatial Axis	Active Detector Energy Axis	Maximum countrate (Hz per pixel)
Scan02	GS	1.5 x 30, curved, 7	500.0	825.0	40 - 60%	30 - 70%	180
Scan03	GS	1.5 x 30, curved, 7	500.0	825.0	60 - 80%	30 - 70%	706
Scan05a	GS	0.3 x 20, curved, 4	1000.0	1225.0	60 - 80%	25 - 75%	935
Scan05b	GS	0.3 x 20, curved, 4	1000.0	1225.0	60 - 80%	25 - 75%	1170
Scan06	GS	0.3 x 20, curved, 4	500.0	690.0	40 - 60%	25 - 75%	5
Scan08	BW	1.5 x 30, curved, 7	1000.0	825.0	40 - 60%	25 - 75%	30
Scan09	BW	0.8 x 30, curved, 6	500.0	690.0	40 - 60%	25 - 75%	27
Scan10	GS	0.5 x 25, curved, 5	500.0	690.0	10 - 90%	25 - 75%	24
Scan11	GS	0.5 x 25, curved, 5	500.0	690.0	10 - 90%	25 - 35%	13
Scan12	GS	0.5 x 25, curved, 5	1000.0	690.0	10 - 90%	25 - 35%	48
Scan15a-f	GS	0.8 x 30, curved, 6	500.0	690.0	10% increments	40 - 60%	170

Table 5-2 Countrate ranges and instrument settings used to calibrate the detector response functions. Variation in measured per pixel countrate was accomplished by changes in analyzer settings and x-ray intensity.

Fig. 5-1 Absorption scans over the Mn 2p_{3/2} edge at various countrates, as measured using the inelastic secondary electron background underneath O 1s spectra. (a) Unscaled absorption profiles indicating the relative absolute intensities of the measured profiles. (b) Normalized absorption profiles in which a scaling factor has been applied to bring the low-energy background at ~ 634 eV to the same value for all curves. In case of an ideal linear detector response function, these normalized curves should be identical.

Fig. 5-2 O 1s-Mn 2p MARPE scans from MnO(001) at various count rates, as given in Table 5-1. The variation in the size of the MARPE enhancement appears to change with the detector count rate, clearly illustrating a problem with the detection process. The irregularity in Scan 6 above about 640 eV is beamline-associated, and not relevant to the present discussion.

Fig. 5-3 Variation of peak widths in the MARPE scans of Fig. 4-2 as a function of countrate constitutes further evidence of a problem in the detection system used. Besides the variation in widths within some scans and not others, the peak widths actually appear to increase as experimental resolution has been decreased (e.g Scans 06 and 07 are recorded at higher instrumental resolution and lower countrates than Scans 01 and 02).

Fig. 5-4 Screenshot of the detector CCD camera image illustrating the problem of non-uniform filling of the spatial axis. In this case primarily due to the analyzer slit setting limiting the edges of the spatial axis, although some overall increase in the count rate is also visible from left to right across the spatial axis. The horizontal axis is the “spatial”-axis, while the vertical corresponds to electron kinetic energy. The active portion of the detector is indicated by the white box (15–85% on each axis shown here, with 0–100% representing the frame that just circumscribes the circular, 40mm diameter, phosphor screen and microchannel plate assembly). The sum of the spatial axis counts is shown in the histogram along the left side of the image. Illumination with a finely focused synchrotron radiation beam can lead to a much narrower illumination along the spatial axis, and a reduced filling fraction f_s . This specific image (of Cr $2p_{3/2,1/2}$) is not directly related to the work described here and shown only for illustrative purposes.

Fig. 5-5 The response function of the detector operating in black-and-white (BW or digital) mode. (a) Note the rigid ceiling of 30 Hz per pixel as expected due to the 30 Hz sampling frequency of the detector camera, which is clearly seen in this panel. (b) A more accurate measurement of the more useable portion of the response function. The dashed line indicates an ideal behavior, as arbitrarily scaled to allow $m=r$ at 20 Hz per pixel.

Fig. 5-6 The (a) efficiency and (b) deficiency = $1/(\text{efficiency})$ functions for the detector operating in BW mode. Note that the cutoff for the deficiency is at 30 Hz, beyond which the detector is fully saturated and cannot be uniquely corrected. The true count rate axis has been arbitrarily scaled to force $m=r$ at 20 Hz.

Fig. 5-7 The detector response function in grayscale (GW or analogue) for decreasing measured count rates. The small frames in (a) indicate the approximate ranges shown in (b) and (c), respectively. Note the strongly quadratic behavior at even very low measured countrates ($m < 35$ Hz)

Fig. 5-8 (a) Several grayscale-mode measurements of the response function, illustrating the ability to combine consecutive measurements over various measured countrates in order to most accurately determine the overall response function. The corresponding countrate ranges are given in Table 5-2 (b) Additional response functions simultaneously measured over various 10% portions of the spatial axis. Inhomogeneous intensities over the detector screen resulted in each portion having different simultaneous count rates, and therefore mapping different portions of the response function. This illustrates the importance of uniform countrates along the spatial axis in the active portion of the detector if accurate response corrections are to be made. On the other hand, the fact that all curves superpose also means that the detector behaves the same over all of its area, even though phosphor screen intensities are visibly brighter around the edges.

Fig. 5-9 (a) The measured grayscale mode detector response function up to about $m=100$ Hz per pixel. The quadratic behavior at low countrates (<30 Hz per pixel) is clearly visible. 20 Hz per pixel has again been chosen as the point at which measured equals true. (b) The efficiency function corresponding very accurately to a fifth-order polynomial fit. (c) The corresponding deficiency function $= 1/(\text{efficiency})$ clearly illustrating significantly non-ideal behavior below about 30 Hz per pixel.

Fig. 5-10 The response function of the detector operating in grayscale mode for the region needed to correct the MARPE spectra in Fig. 4-2 and in previous data obtained in this thesis. Note again the strongly quadratic behavior at very low countrates (<30 Hz per pixel), as emphasized by the shaded region which represents a second order polynomial least-squares fit to the data. Comparing this curve to Table 5-1 shows that all MARPE scans discussed in the text were acquired with countrates within the range shown here and so would be expected to exhibit some signs of this non-ideal detector response.

Fig. 5-11 Absorption profiles before and after correction for two cases, (a) MARPE Scan 1 with highest count rates and (b) MARPE Scan 7 with $\sim 1/30$ of that countrate. Note the opposite sense of the correction for these two cases, taken at different overall count rates, largely due to our having chosen 20 Hz per pixel as the normalization point between measured and true counts.

Fig. 5-12 Mn $2p_{3/2}$ absorption profiles acquired at various countrates as given in Table5-1. (a) The original measured profiles as presented also in Fig. 5-1(b), normalized to the low-energy background levels. (b) The same profiles after correction for the independently determined detector response function and again also normalization to background levels.

Fig. 5-13 Correction of several individual O 1s spectra in MARPE scans compared to uncorrected spectra. Three energies are chosen: 633.0 eV below the Mn $2p_{3/2}$ absorption peak, 637.6 eV right on this peak, and 645 eV above this peak. This illustrates the much reduced variation in peak widths after correction, as well as the differences between relative peak intensities due to the combined effects of the large background changes and the changes in detector response with countrate. Observe that Scan 1 peaks appear to have narrower widths than Scan 7, but upon correction the Scan 1 peaks are broadened significantly to values greater than in Scan 7. The corrected widths are in agreement with expected differences due to differences in instrument resolution between Scan 1 and Scan 7.

Fig. 5-14 O 1s–Mn 2 $p_{3/2}$ MARPE profiles collected at various count rates as given in Table 5-1.. (a) The measured profiles without correction and (b) the same profiles after correction for the detector response function. Note that all profiles converge to a common shape and magnitude after correcting for the detector, even though the low countrates necessary in this study still leave high statistical noise on some of the curves. The data for Scan 7 are not reliable above about 640 eV.

6 Development of a Next Generation One-Dimensional Detector for Electron and Other Spectroscopies

6.1 Nature of the Problem: Non-Linearity, Saturation, and Spatial Resolution

The continued development of synchrotron light sources throughout the world has resulted in increasingly intense vacuum ultraviolet (VUV) and soft x-ray beams for use in photoemission and related Auger and fluorescence emission based experiments. The development of the detectors used in these experiments has unfortunately not kept pace with these advances and, consequently, experiments are often limited by the capabilities of the detector. In fact, for photoemission from levels with high photoelectric cross sections as measured in high-transmission analyzers, even traditional laboratory x-ray and ultraviolet sources are sufficient to saturate many common detectors.

Our goal has thus been to design, build and test a prototype high-performance, one-dimensional pulse-counting detector that represents a real advancement in detector technology and is well matched to modern light-source fluxes and high-transmission electron-energy analyzers as typically used in photoelectron spectroscopy experiments. The one-dimensional detector we have developed represents a significant improvement in providing high-speed (with overall countrates of ~ 1 GHz), linearity over a large dynamic-range, and high-spatial-resolution. Although designed to detect electrons, this device can also be applied to counting VUV or to soft x-ray photons as well as ions, and thus should ultimately find applications in other fields outside of synchrotron radiation photoemission. The project is a collaboration of members of several divisions at LBNL including the Engineering Division, the Fadley research group in the Material Sciences

Division of LBNL and the UC Davis Physics Department, the Advanced Detector R&D Program in the Physics Division, and the Advanced Light Source Division.

To begin to appreciate the performance requirements of such a detector, we can approximate the expected detector countrates available in a typical solid state, photoemission experiment at the Advanced Light Source (ALS) in Berkeley. The number of photoelectrons emitted from a peak, k , in a semi-infinite sample may be found to be [1],

$$N = I_0 \cdot \Omega_0(E_k) \cdot A_0(E_k) \cdot D_0(E_k) \cdot \rho_k \cdot \left(\frac{d\sigma_k}{d\Omega} \right) \cdot \Lambda_e(E_k) , \quad [6-1]$$

where I_0 is an assumed uniform incident photon flux, Ω_0 is the accepted solid angle of the analyzer, $A_0/\sin\theta$ is the illuminated sample area accepted by the analyzer, D_0 is the detection efficiency of the instrument, related primarily to transmission of the analyzer, ρ_k is the atomic density of the atom containing level k , and Λ_e is the inelastic electron attenuation length in the sample. This result can be derived from Eq. 4-15, if the factors $I_0 \Omega_0 (A_0/\sin\theta) D_0 \rho_k$ are added, and all x-ray optical effects (resonant or non-resonant) are neglected, in which case the denominator reduces to $1/(\Lambda_e \sin\theta)$.

A typical value of $I_0 A_0$ at a high-flux beamline at the ALS is 10^{13} photons/sec in a 0.1% bandpass or with an energy resolution of $\Delta(h\nu)/h\nu = 1/1000$ [2]. For an angular acceptance of $\pm 6^\circ$ and with an assumed unit detection efficiency, $\Omega_0 D_0$ will be about 10^{-2} steradians. For a typical solid, we can also estimate $\rho \approx 5 \times 10^{23}$ atoms/cm³, and $\Lambda_e \approx 1$ nm (10^{-7} cm). The value of $\frac{d\sigma_k}{d\Omega}$ can also be as expected to be as high as

1-10 Mbarns (10^{-17} cm^2) or more, particularly when the photon energy is tuned near an absorption threshold [3]. Overall, these values in Eq. [6-1] result in countrates of up to 10^9 Hz, or 1 GHz, for a typical photoelectron peak. Because photoelectron spectra can in addition be expected to have a significant additional inelastic background component arising from photoelectrons initially created at higher kinetic energies, it is quite conceivable to have overall countrates in a given spectrum above the 1 GHz level.

Based on available flux levels then, our goal is thus to be able to count at up to 1 GHz over a detector with an overall acceptance area on the order of several cm^2 that is typical of the focal plane in current high-performance energy-dispersive electrostatic analyzers. Additionally this must be done with sufficient spatial resolution (directly associated with collector channel width and pitch) to match the high energy resolutions of approximately 10^{-3} which these analyzers can achieve. The fastest currently available one-dimensional detectors, several of which are listed in Table 6-1, are limited to countrates of 10–15 MHz before beginning to saturate, with generally poorer spatial resolution exhibited for the fastest per-channel detectors. The performance of two-dimensional detectors (e.g. as needed for high-resolution band mapping studies in magnetic or strongly correlated materials) is even worse at <1 MHz. We are thus in a situation of being from 100-1000× below the countrates needed to take full advantage of the capabilities of the ALS or similar third-generation synchrotron radiation sources around the world. And even the highest-intensity laboratory x-ray and ultraviolet sources can exceed the capabilities of current detectors for the most intense photoelectron peaks.

Because of the particular research interests within the development group, the detector has been specifically designed for use in electron detection along the energy

dispersion axis of a hemispherical electrostatic analyzer (Gammadata Scienta ES200) [4,5]. It is in this context that the detector has been developed and tested, although it also should have a wider range of potential applications where one-dimensional particle detection is required. We will first consider the basic characteristics of this type of analyzer and the standard detectors currently in use with such analyzers. After this introduction, we will consider the basic design, characterization, and finally the first experimental work performed with our new detector. Finally, we will consider improvements that can be made to the current design and the future direction of the project.

6.2 Background: Hemispherical Analyzers and Existing Detector Systems

Before discussing the detector in detail, it is beneficial to first review the fundamentals regarding the intended application of the detector. To this end, we will first discuss the hemispherical electron energy analyzer such as commonly used in high-resolution photoemission experiments. It is also interesting to consider the general requirements of such detectors as well as the types of detectors that are currently available and in common use.

6.2.1 Hemispherical Electron Energy Analyzers

First, we consider the principle characteristics of the hemispherical analyzer. The purpose of such an analyzer is to accept electrons from some solid angle Ω_0 as emitted from a sample and pass the electrons of a particular kinetic energy by means of

hemispherical deflector plates to the focal plane where the detector is mounted. A simple schematic of a hemispherical analyzer and detector system is shown in Fig. 6-1.

The voltages of the hemispherical deflector plates of the analyzer define a particular pass energy (E_p), which represents the kinetic energy that an electron must have to pass from the entrance slit of the analyzer, through the hemispheres and to the center of the focal plane at the detector port. In order to change the analyzer kinetic energy, one can either continuously change the hemisphere voltages (maintaining a constant resolving power $E_p/\Delta E$) or, as is the case we are primarily interested in, float the hemispheres on a retardation voltage that will retard (or accelerate) the analyzed electrons to the particular E_p set for the hemisphere. In this case, the analyzer is in a constant ΔE mode, where the linear kinetic energy dispersion over the detection plane remains constant. It is important to recognize that the detector front end must be floated on the analyzer retardation voltage in order to maintain a constant potential gradient between the analyzer and detector over the course of the scan.

The simplest detection method with such a system uses a single-channel detector, generally a channel electron multiplier (CEM), also known by one commercial name as a Channeltron®, the details of which are discussed elsewhere [7,8]). In order to collect an electron energy spectrum with a single-channel detector, the analyzer voltage(s) must be used to sweep the analyzed energy over the detector channel. The acceptance slit at the entrance of the CEM is typically larger than desired (for preservation of the overall instrumental resolution) and so an additional slit is often used to achieve the desired overall resolving power. We discuss below the precise relationship between detector aperture and energy resolution for the hemispherical electrostatic systems.

Generally, great advantage can be taken of the fact that electrons passed through the analyzer will exhibit a highly linear kinetic energy dispersion of the transmitted electrons over the radial dimension of the focal plane of the analyzer [6]. Compared to a single channel detection method, parallel detection of multiple energies over the focal plane thus greatly increases experimental efficiency, albeit at the initial overhead expense of more complicated detector and data processing to properly combine the parallel collection channels. In using such a multichannel detection system, we can take advantage of the analyzer energy dispersion via two different data accumulation modes. The first simply involves redundant, parallel detection during the sweeping of the analyzer, with each channel of the detector being used at each point in the spectrum scanning to accumulate a slightly different energy channel of the final spectrum. This so called *swept* or *dithered* mode has the virtue that variations in the channel-to-channel sensitivities or in the transmission efficiency of the analyzer across the dispersion axis are essentially eliminated from the final spectrum. This occurs because every detector channel contributes equally to every point in the final spectrum. Normally, this type of multichannel spectrum is acquired with the analyzer running in constant ΔE mode so that the addition of successive detector frames as the analyzer is swept can be easily performed.

A second data accumulation method to take advantage of the multichannel detector is to use the analyzer dispersion window for simultaneous collection of an entire spectrum. If the kinetic energy width of the detection window is sufficiently large (several eV to collect a typical core level peak) and the detector has sufficiently many channels to resolve the spectral features in this window with a desired energy resolution

then an entire spectrum may be acquired in a single detector frame. This *fixed* or *snapshot* mode can significantly increase the speed with which a spectrum can be acquired because the analyzer is not adjusted at all during the collection of the spectrum. In this case, the detector and analyzer non-uniformities over the focal plane will not be automatically averaged out, but measured correction factors can be applied to the final spectrum.

In order to ensure that the detector channel spacing is well matched to a particular analyzer, we must recognize that the ultimate resolution of a hemispherical analyzer with a mean radius of the hemispheres, R_0 , is controlled by the radial width of the entrance slit of the analyzer, ΔR_{ent} , the radial resolution of the detector, ΔR_{det} , and the solid angle of acceptance at the entrance to the hemispherical deflection electrodes. The overall resolution is given by the relationship

$$\frac{\Delta E}{E_0} = \frac{\Delta R_{ent}}{2 R_0} + \frac{\Delta R_{det}}{2 R_0} + [\text{solid angle terms}]. \quad [6-2]$$

For the particular analyzer considered here, the solid angle is adjusted with ΔR_{ent} so that its contribution to resolution is approximately equal to that of the entrance slit. Also, the entrance slit is curved in such a way that the spatial axis of the detector perpendicular to the radial (energy) direction corresponds to constant energy lines.

We wish to have a detector resolution that is well matched to commercial high resolution spectrometers. As an example, consider the particular case of a Gamdata Scienta ES200 analyzer, which has a maximum resolving power of 10^3 and $R_0 = 200$ mm. In this case, a detection channel width, ΔR , of $400 \mu\text{m} = 0.4$ mm would be required to just match analyzer resolution. In our prototype design, we have gone well beyond this

to an ideal 50 μm spatial resolution that should yield a negligible contribution to the energy resolution of the analyzer.

6.2.2 Microchannel Plates: Cascade Event Multiplication

A common component of all detector systems to be discussed here (except the already mentioned CEM) is the microchannel plate (MCP). Many detailed discussions of the properties and fabrication methods of MCPs exist in the literature [8,9,10], and thus only the most important features of consequence to the current project will be considered here.

A microchannel plate consists of a collection of leaded glass tubes that have been fused together into a bundle of parallel tubes and cut into wafers. These tubes are oxygen reduced in a hydrogen environment in order to transform the inner surfaces of the tubes from an insulator to a semiconductor. This allows the secondary emission coefficient of the surface to be greater than unity and the MCP becomes a functional array of independent multiplier tubes that have inherent spatial resolution in two spatial dimensions.

MCPs exhibit sensitivity to a large number of particles at the entrance side of the tube: photons in the UV to x-ray range, ions, and, of particular interest to this project, electrons. The common characteristic of each type of particle detection is that upon a single particle entering a tube and striking the wall, some number >1 of secondary electrons is produced. By biasing the backside of the tube at sufficiently high positive voltage (1 kV per plate is a typical value, but this depends upon the plate thickness and channel dimensions), the secondary electrons will propagate down the tube, striking the

tube walls along the way and resulting in additional secondary emission from the tube wall. Through this cascade process, a single event at the tube entrance can result in a gain of many orders of magnitude. In particular, 10^4 - 10^8 or more electrons can exit the tube array for each incident event, depending upon the specific application and operating conditions of the MCPs. This emitted pulse is then sufficiently large to be detectable with various electronic systems, with the actual pulse detection method being the distinguishing characteristic between various available MCP-based detectors. Note that, while the MCP is sensitive to various incident particles (and can even be manufactured to be optimally sensitive to a given particle type and energy range), the output pulse is always a large number (10^4 - 10^8) of electrons arriving over a very small time interval (~ 1 nsec). Therefore, the backend pulse counting electronics can be identical regardless of the particle type arriving at the front end.

The channel bias angle refers to the angle of the channel tube axes relative to the surface normal. The bias angle is normally $>5^\circ$ to ensure that particles incident along the surface normal must strike the tube wall near the entrance and not simply pass through the tube without amplification. Channel pitch, P , refers to the distance between pore centers in the MCP. The *ratio* of the channel (pore) length to its diameter, $L:D$, is the fundamental determinate of the MCP amplification performance, and so for a given performance goal, the MCP channel diameter may be minimized arbitrarily within the limits of the fabrication techniques. MCPs are commercially available with pore sizes down to at least $5\text{ }\mu\text{m}$, with the entire array having surface areas on the order of many square centimeters.

Because particles entering a tube are confined to this tube, precise spatial resolution of the incident particles over the MCP tube array is inherently preserved to a degree depending upon the tube diameter and pitch. An additional benefit of increased pore density (reduction of both tube diameter and pitch) is a concurrent increase the dynamic range per surface area. This can easily be seen by realizing that each tube requires a regeneration period between successive event amplifications. By simply packing more tubes in a given area, the average time between successive events in the same tube is increased, given a fixed event flux.

Various applications of such MCP arrays are possible. The simplest of these is to use a single straight tube array, generally with some small bias angle. The cascade pulses emitted from the individual tubes have some height (gain) distribution. This pulse height distribution (PHD) typically has a decaying exponential shape in such an array, with the characteristic decay length dependent upon the tube geometry (L:D, bias angle, and particle incidence angle) and the applied bias voltage over the tube. This means that the pulses are predominantly low-level and any noise in the channel plate will be indistinguishable from true event pulses. This type of PHD can be useful in certain applications where an integrated pulse current is of interest, but generally is not acceptable for high per-pore event rates. This is because small changes in MCP gain as a function of extracted wall current result in non-negligible changes in the PHD and hence nonlinear changes in the integrated pulse charge with countrate.

In addition, the straight channel MCP will only provide a gain of 10^3 – 10^5 , limited by the onset of ion feedback. At low pressures (typically $<10^{-6}$ torr as in our experiments), electron bombardment of the channel walls can desorb and ionize gas

molecules from the channel walls. At higher pressures, ambient gasses will provide similar opportunity for ion production. Ions produced in this region experience an acceleration back towards the front of the tube due to the same potential used to accelerate the electrons down the tube. When the accelerated ion strikes the wall of the tube, additional secondary emission occurs and the continuation of this cycle will result in instabilities and even breakdown of the MCP voltage. Elimination of the ion feedback is necessary if the MCP is to be run at a gain of more than about 10^4 to 10^5 .

We are interested in using the MCP in a pulse (event) counting mode. For a single event, we want to be able to unambiguously recognize a single pulse generated in the tube. The weak pulses dominating a single straight MCP array are indistinguishable from the system noise. It is well known that the elimination of ion feedback and the consequential dramatic increases in gain provide a solution to this problem. Methods for dealing with ion feedback are principally related to specialized MCP array geometries. In one case, the tube array may be manufactured with curved tubes. Another simpler solution is to stack two or three non-zero bias angle straight MCPs into *chevron* or *Z* configurations, respectively. In either case, the geometry prevents the ions from propagating back up the channel an appreciable distance, and hence limits both the kinetic energy with which the ion collides with the tube wall and the time between the ion induced after-pulses and the initial (primary) pulse emitted from the tube. A two-plate chevron array was chosen for this project, and a schematic of the electronic elements involved is shown in Fig. 6-2(a).

With the significant increases in the overall gain ($>10^8$ is possible with such geometries), a fortuitous and significant modification of the PHD occurs. The negative

exponential found in simple straight tube MCPs is converted to a Gaussian-like shape with a FWHM as narrow as 60-80% of the mean pulse height or better as is illustrated by Figs. 6-2(b), (c). This phenomenon can be understood by considering the high space charge density achievable in the tube once the ion-feedback has been diminished. This charge density reduces the kinetic energy of electrons as they propagate down the tube and this in turn results in decreasing efficiency of secondary production from the channel walls. At some point, the secondary emission coefficient stabilizes near unity and the MCP is space charge saturated. At saturation, an increase in MCP bias voltage no longer appreciably affects the MCP gain until the voltage is again sufficient to reintroduce ion feedback problems.

The effect of the saturation is that incident particles will produce a much more uniform distribution of event-related peak heights (the narrower the peak, the more uniform is the distribution). This is especially useful for pulse-counting systems, where as long as the PHD does not shift to appreciably lower average pulse heights at high pulse-rates, a discriminator level set between the PHD peak and the low-intensity noise pulses (see Fig. 6-2(b)) will not result in loss of recorded events.

6.2.3 Existing Multichannel Detectors

There are currently a number of detector options available for one-dimensional multichannel electron detection, and fewer for two-dimensional multichannel detection. In order to appreciate the objectives of the detector development to be discussed here, we will briefly discuss the attributes of several of these detectors. An overview of the most important performance values for an assortment of contemporary detectors is presented in

Table 6-1. Note that these detectors often make use of MCPs for the initial pulse amplification stage.

Resistive Strip Detector (Charge Division)

The resistive strip anode detector is a common, well-established, pulse counting technique, which is based on a resistive anode collecting the MCP generated charge pulses. By measuring the amount of charge collected with two electrodes at opposite corners of a roughly square-shaped anode for each pulse, the position of the incident pulse along that axis of the anode can be accurately calculated [11,12]. By further measuring the amount of charge with two similar electrodes in a direction perpendicular to the first, the position of the incident pulse can be determined in two dimensions. The primary difficulty with this design is that there is only one collector available for the entire detector. When a pulse is registered anywhere on the anode, the entire detector is dead to additional events until the pulse processing has been completed. An older, commercially available (Quantar Technologies) version of this type of detector will distinguish 256 channels over a 40mm width and a with total count rate of up to about 100kHz, or effectively 390Hz per channel. The maximum overall countrate for a more modern version of this system reaches 1-2 MHz, limited, as would be expected, by the pulse processing electronics [13].

The problem with using a single anode manifests itself in two significant ways. As already mentioned, the per-pulse processing time introduces a deadtime in the detector that must be properly determined and corrected for in final spectra in order to get accurate true count rates. While this correction can be accurately performed if the detector is sufficiently well characterized [14], it presents an additional step in data

processing and an additional source of potential experimental error. While any detector system requires attention to deadtime effects, the common anode makes the problem especially severe in this design.

The second, related, problem arises from coincident events (events occurring simultaneously as compared to the pulse detection time). In this case, the charge division sensors will not deduce the correct pulse positions, but instead will take the charge-weighted average of the multiple pulse positions. Such errors do not contribute in a simple manner to the counting statistics, but actually affect the overall resolution of the system.

As noted above, one significant feature of the resistive anode detector is that the pairs of pulse detection circuitry can be installed at perpendicular edge pairs of the resistive anode and so very easily achieve two-dimensional pulse detection. This can be useful in specialized operational modes of a hemispherical analyzer that preserve spatial or angular emission (from the sample) information along this direction, or in other applications such as LEED, or x-ray and electron microscopies.

CCD (Pixel) Detector

After the electron pulse is created by an MCP, it can be further accelerated onto a phosphorescent plate, converting the charge pulse to a visible light pulse. This has the advantage that the light pulse can be passed through the vacuum wall via a suitable optical-quality viewport, following which the actual counting electronics can then consist of a commercial charge-coupled device (CCD) camera [15] and standard binning electronics that can be located outside the vacuum chamber, with the camera focused on the phosphor screen through the viewport. Unfortunately, CCD camera technology is

limited in count rates when run in a true pulse counting mode. The only mechanism to unambiguously perform pulse counting is to require the count rates to be low enough to ensure no more than a single pulse will reach each camera pixel per readout (30Hz for cameras using typical, standard TV signal electronics, as discussed in Ch. Five of this dissertation). In this case, properly set discriminator levels may allow pixels that have counted a single event to be well distinguished from pixels that have not, although one must still be careful of pulses that may not decay quickly enough on the phosphorescent screen.

An alternative mode of operation is to perform an analog readout of the charge accumulated in each pixel. For example, the use of an 8-bit analog-to-digital converter (ADC) results in 256 distinguished count levels and in principle an increase in maximum countrates compared to the pulse counting mode by the same factor. This should enable extremely high countrates (kHz per pixel) and so seems promising. However, the primary disadvantage of this mode is that the detector is no longer running in a pulse counting mode. Each readout of the pixel charge includes an unknown amount of integrated noise-level pulses or pulses remaining from prior electron bunches striking the phosphor that cannot be discriminated out. In addition, the analog mode results in extreme sensitivity to nonlinearities in the gain of both the MCP and the phosphor signal conversion as well as in the ADC.

The photoemission and Auger electron emission data collected as part of the dissertation used a detector of this type, provided by Gammatdata Scienta with its ES200 system and other similar models. Substantial non-linearity problems in the detector have become apparent, attributable in large part to the analog (integrated) counting mode that

was used to avoid the strong saturation effects at low count rates in the pulse counting mode. We have over the course of this research observed sizeable nonlinearities in the detector response function, even at low countrates. Due to the lack of a true discriminator in the analog mode, these non-linearities are not expected to be able to be eliminated except by careful correction of acquired data via a carefully calibrated response function [16,17,18]. A thorough discussion of such a correction procedure is given in Ch. Five of this dissertation.

As with the resistive anode, a significant advantage of the CCD detector is the two-dimensional data collection that is inherent to the camera. In addition, the availability of commercial cameras and frame grabbers can greatly simplify overall detector development and cut costs considerably.

Multi-Anode Collectors

This family of detectors is characterized by an array of functionally independent detection channels distributed along a single detection axis.

The simplest multi-anode detector consists of a collection of CEMs mounted side-by-side in the analyzer focal plane. Unfortunately, the typical size of the CEM entrance slit prevents more than a few of them from being fitted into the limited available space in an analyzer focal plane. The individual channels are also rather widely spaced so that snapshot spectra with any reasonable number of points in the spectrum cannot be performed with good energy resolution. Depending on the particular CEM chosen, the detector aperture ΔR_{det} may also be too large to yield a desired energy resolution or too small to yield a sufficient countrate for a given application.

On the other hand, if an MCP is used for the initial electron amplification, an array of conductive collector strips or anodes can be placed just behind it. The pulses hitting each strip can then be handled by independent pulse processing and counting electronics associated with each strip. The simplest multi-anode detector consists of a number of isolated, closely spaced collector strips that have transmission lines running out of the vacuum chamber via suitable electrical feedthroughs and then connected to external (in atmosphere) pulse handling electronics, just as would be done with an array of CEMs. Although convenient in the sense that the multiple channels of electronics can all be accessed easily for repair, the long conductor paths for the low-level analog pulse signals can produce difficulties in pulse detection and interchannel crosstalk due to capacitive coupling in the long transmission lines. The number of channels in this sort of system is essentially limited by the number of transmission lines that can be taken out of the experimental chamber and so space and practicality issues become a limiting factor. Many similar variations on this concept have been attempted and are documented in the literature [19,20,21,22]. For instance, this sort of system has recently been used in a project at ELETTRA [23]. As illustrated by the values in Table 6-1, this detector, although now working very well for actual experiments, has apparently not been able to achieve overall countrates that represent a significant improvement over many other detectors [24], including being a factor of only about 5 better than the fastest version of the much simpler resistive anode design already discussed. It also appears from published accounts that this project is now headed in a direction that will move the pulse processing electronics inside the vacuum chamber [25,26], a philosophy similar to the approach taken with our prototype.

Finally, we consider a specific detector originally built by Integrated Sensors Ltd, in the U.K., that is again based on an MCP backed by individual collector strips, but with each collector connected to a dedicated set of application specific integrated circuit (ASIC) pulse counting electronics. By using in-vacuum integrated circuits (ICs) fabricated on a single wafer for the pulse processing, the transmission line lengths can be reduced substantially and a high channel density can still be maintained. This detector is conceptually similar to the approach adopted in our project, although there is no connection between these projects and there are no common components. Several publications discuss the reported performance of this detector [27,28,29]. The apparent general success of the design provides additional validation for the fundamental design choices made for our current project.

6.3 The LBNL Next-Generation Detector

We have developed a new one-dimensional detection system that addresses the limitations of typical detectors as discussed above, most specifically the compromise that must be made between the per-channel countrates and the number of channels in the detector. The detector operates as a pulse-counting system, with multiple, independent anode pulse processing. Our design adopts the microchannel plate as the primary amplifier of each electron event to a countable pulse of electrons, as used in other detectors [12,15,16,20-24,28,30]. However, in-vacuum integrated circuitry (IC) has been adopted for pulse counting and signal integration, allowing for significant gains in miniaturization, and leading to a very high spatial density in the anode layout. The adoption of IC pulse processing follows the philosophy used in modern high-energy particle physics detectors [31a,31b] For example, silicon detectors with integrated

electronics were critical in the discovery of the top quark [31c] and the silicon vertex detector (SVX) chip used for that work in the Collider Detector at Fermilab (CDF) was part of the development effort that led to the chip used in this detector, which we will fully introduce later.

6.3.1 Design Goals and Requirements

In order to represent a significant advancement in dynamic range, in particular one that will essentially match the countrates possible in modern synchrotron-radiation based experiments, we have already seen that the detector must be usable up to about 1 GHz overall. It is also necessary to work in a pulse-courting mode to avoid extreme sensitivity to MCP gain fluctuations, and so make possible a very large dynamic range. This large dynamic range is needed to allow the detector to be used in spectroscopic experiments that range between lower countrates for smaller cross sections and the highest energy resolutions (e.g. in some band structure studies via angle-resolved photoemission) and higher countrates for larger cross sections and lower energy resolutions (e.g. in core-level spectroscopy and photoelectron diffraction or holography). The detector is only required to preserve one-dimensional information, however, the channel packing density must be sufficiently high to prevent undesirable energy resolution losses. This means the energy resolving power of the electron energy analyzer should be lower than the detector, so that the detector does not present a significant limit to resolution.

The active area of the detector is about 10×40 mm with the resolved direction along the longer axis. This footprint is well matched to the experimental system in which

it is to be installed for testing, a 200mm radius hemispherical electron energy analyzer (Scienta ES200). This analyzer has electrostatic hemispheres of radii 160 and 240mm and, as delivered, a multichannel detector of the phosphor screen and CCD type discussed earlier, which accepts electrons transmitted through the central 40mm of the focal plane between these hemispheres. Hence, the 40mm energy-resolving dimension of the detector is ideally matched to the analyzer. The channel pitch of 50 μm , which we will see translates into roughly the same dimension for ΔR_{det} , (Eq. 6-2) even after allowing for crosstalk between channels, is primarily determined by the choice of pulse-processing chip as described in a following section. This pitch results in an ultimate detector resolving power of 1.25×10^4 or a resolution of 1:8000, as found from the appropriate term in Eq. 6-2. This is well below the maximum resolution of 1:1000 for the analyzer and actually improves markedly upon the standard CCD camera detector which has larger channel pitch: about 380 channels over the 40mm active area, resulting in a 1:3800 ultimate resolution that is not even fully realized due to blooming or crosstalk problems between neighboring channels in the detector [5].

We have ensured that all components in the detector, including epoxy adhesives used to bond chips to the substrate and make certain electrical connections, are compatible with ultrahigh-vacuum (UHV) experimental usage. This includes the ability to operate at UHV pressures of 10^{-9} to 10^{-11} torr while producing minimal outgassing at these pressures, and to be able to withstand at least a low-level (120°C) bakeout process. These UHV requirements are due to the experimental environments necessary in typical photoemission surface science experiments. Additional vacuum requirements are also imposed by the use of MCPs, which typically require 10^{-6} torr or better in the pores and

collector region of the detector in order to avoid high voltage breakdown or corona discharges due to the high field gradients required for the secondary multiplication and to maintain tight charge clouds between the MCP and collector for good position resolution. Attention has also been given to avoiding the use of magnetic materials in the detector head and to providing active water cooling to the entire assembly to compensate for the ohmic heating of both the MCPs and the in-vacuum ICs.

The detector is electrically isolated on a multi-layer ceramic substrate from the chamber so that it may be floated relative to the analyzer. The required electrical connections to the various ICs and the MCPs are made through this multi-layer and metalized vias connecting the layers. All electrical connections (including data lines) out of the vacuum chamber are through a 25-pin, 6" Conflat flange, with each pin rated at 3.5 kV operation, and internal lead connections are made to the detector at the outer rim of the substrate as can be seen in Figs. 6-3, 5. To accommodate the heat load of the MCP and ICs, the substrate is actively cooled through an aluminum heat sink installed on the bottom side of the substrate with an integrated cooling water line that is brought in on the same 6" flange.

6.3.2 Microchannel Plates

Microchannel plates manufactured by Galileo Corp. (now Burle Industries, Inc.) have been used in this project. A pair of resistance matched, stacked plates arranged in a standard chevron configuration was chosen in order to achieve the peaked PHD required for our pulse counting application, as discussed earlier. The plates are constructed with 10 μ m pore diameter, 12.5- μ m pitch, and a 40:1 L:D.. The pore diameter and pitch here

should minimize any loss in energy resolution simply due to single MCP pores depositing charge pulses across multiple collector strips. It is interesting to note that in the 10×40mm active area of the detector, this MCP will contain about 2.96×10^6 microchannel, and at a 1 GHz uniform rate, each microchannel would thus only be counting at a rate of about 340 Hz, a value that is quite small compared to the nanosecond scale pulse widths.

The plates used are manufactured with low wall resistance, allowing for a larger extracted wall current in each pore before MCP induced saturation becomes appreciable. This “extended dynamic range” or “hot” (high output technology) plate draws a total current of $<50 \mu\text{A}$ at about 2 kV bias voltage, and so dissipates less than 0.1W under quiescent conditions with no pulses being counted. For reference, at a gain of 10^5 per pulse, counting 10^9 initial electrons per second will result in a total additional current of $10^5 \times 10^9 \times 1.60 \times 10^{-19} \approx 16 \mu\text{A}$, or only about 1/3 more than the normal wall current. Thus, the total heating in the MCP will still be about 0.1 W. The active water-cooling of the entire detector substrate helps to eliminate heat dissipation problems. In order to see how the decreased resistance increases the dynamic range of each MCP pore, simply consider each pore to consist of a resistor and capacitor network. A decrease in R decreases the characteristic time constant, RC, of the pore which corresponds to the regeneration (dead) time of the pore after a cascade event. Significant increases in MCP dynamic range can be achieved through the use of these hot plates as compared to standard high-resistance MCPs [8].

The pulse-handling electronics, discussed later, are optimally used for charge pulses on the order of about 8×10^4 to 6×10^5 electrons (1.25 to 10 fC, , with $1 \text{ fC} = 10^{-15} \text{ C}$

= 6240 electrons). However, the MCP bias voltages required to maintain a saturated PHD will result in higher gains than this, typically in the $>10^6$ range. There are now two competing goals in our application of the MCP. On one hand, we desire relatively low gains in order to match the electronic inputs and to minimize the amount of heat dissipation in the MCPs. On the other, we need to run the MCPs in saturated mode, with the resulting typical gains of 10^6 – 10^8 for standard channel plates. In fact, this potential mismatch explains our choice of a chevron configuration over the Z configuration that typically has a more favorably peaked PHD. The Z configurations result in gains greater than 10^7 during saturated operation, and so were a poorer match to the electronics than the chevron.

Measurement of the PHD for our particular plate-set was performed early in the project. As shown in Fig. 6-2(a), the process is simple and requires operation of the MCP at a fixed bias voltages V_{MCP} and collection of the pulses on an anode over a known time period. The PHD is then just a histogram of the observed pulse amplitudes (peak heights).

The MCPs are rated to a maximum per plate voltage of about 1 kV each, or 2 kV for the pair, typical of an L:D ratio of 40:1. Clearly over a range of MCP voltages from 1.6 to 2.0 kV the expected quasi-Gaussian peak is observed (Fig. 6-2(c)). Note that the PHD widens appreciably at higher voltages. When the average pulse charge is greater, the pulse processing circuitry is required to accommodate a wider range of charge. Use of lower MCP voltages will result in narrower PHD but will require more accurate setting of discriminator levels to accurately distinguish true signals from low-level noise. For any given MCP voltage the change in PHD due to change in the collector voltage, V_{coll} , is

small, as this voltage has nothing to do with gain, but rather with minimizing the spatial spreading of the electron pulse on leaving the MCPs. These PHDs are all measured with inputs of the background electrons present in the test chamber, as produced by an ion gauge and ion pump. The effect of using UV illumination (not shown in the figures) for the signal is to add to the PHD to a strong decaying exponential component, so we deduce from this that this particular set of MCPs is not well matched to UV detection in a pulse counting system.

6.3.3 Collector Array

Once a pulse of electrons is emitted from the back of the MCPs, it will propagate across a 50 μm gap onto a 10×40 mm portion of an optically flat glass (borosilicate) plate containing the collector anodes, as illustrated in Figs. 6-3 and 6-4. This collector array plate consists of conductive lines (anodes), which straddle the 10mm dimension. The conductive gold-on-chrome lines were deposited on the glass plate using lithographic techniques, with a pitch of 50 μm and an optimal conductor width of 25 μm . The total length of each collector is 16 mm including an extension beyond the 10 mm collection area that is directly under the MCP so as to yield a bonding pad suitable for connection to the ICs. The complete plate contains 768 lines, each an independent collector to be directly bonded to an independent set of pulse recognition and counting circuitry as discussed in the next section. The collector is attached to the ceramic substrate with low-vapor-pressure epoxy, with care taken to avoid captured gas pockets by bonding at only a small number of points.

The 50 μm gap between the MCP and collector plate is maintained by an open rectangle frame of UHV-compatible polyimide (Kapton) that surrounds the active collector region of the plate. This small gap was chosen to reduce the possibility of charge pulse spreading or blooming between the MCP and the collector plate, as schematically illustrated in Fig. 6-4. Previous work [22] has shown that optimal reduction in blooming in this situation is achieved by reducing the gap to approximately the same size as the MCP pores (10 μm), so it is possible that an even thinner gap could be advantageous, provided the MCP is sufficiently flat to maintain this gap. However, interferometer measurements made on the plates used here indicate that the MCP surface planes have a saddle shape with hill to valley differences on the order of 10-15 μm , which indicates that it is not possible to maintain such a narrow gap. In any case, we will show later that the amount of blooming with a 50 μm gap is acceptably small.

Other multi-anode detector projects have used similar anode configurations, some with additional “guardrail” conductors placed between each collector in an attempt to reduce the interchannel crosstalk [21]. Such guardrails are a mechanism to reduce the splitting of the charge in a pulse that lands in the interchannel spaces on the anode plate. This splitting can result in a pulse reaching the two bordering anode channels with enough peak amplitude to pass the discriminator level in each channel. It is also thought that by proper biasing of the guardrails relative to the collectors, the local modification of the electric field can act as a focusing mechanism onto the channels. Nevertheless, the use of this technique is reported [24] to actually result in an increase in the overall capacitance-induced crosstalk between channels and was not used in our design.

Because the channel crosstalk in other multi-anode detectors has been found to be completely dominated by the capacitance of the transmission lines between the anode collector strips and the outside-of-vacuum pulse amplifiers, we do not expect the capacitive coupling between our minimal length anode lines to significantly contribute to channel crosstalk. Experimental measurement of the interchannel crosstalk will be discussed later.

Other multi-anode detectors [21,24] have also included curved collector line geometries to accommodate the focusing properties of the hemispherical analyzer and so increase energy resolution. Because the curvature should be matched to the analyzer radius, such geometries become instrument specific. However, the incorporation of appropriately curved entrance slits in the analyzer (as done in the Scienta analyzer used in this work) eliminates the need for this sort of correction and would be inappropriate for our purposes.

6.3.4 Application Specific Integrated Circuits

The MCP pulses arriving at the collectors must be processed in parallel, independent electronic channels. This is accomplished with very-large-scale integrated (VLSI) chipsets in which each collector strip is connected to a dedicated, independent analog preamplifier for pulse handling, and then a digital accumulator (counter). The analog and digital stages are performed in separate application-specific integrated circuit (ASIC) chips, each of which contains 64 parallel channels. Both chips are mounted in immediate proximity (with a few mm) to the collector anode channels they service, allowing the entire system to remain quite compact. Analog pulse signal lines are kept entirely within the vacuum chamber and the number of vacuum chamber feedthroughs is

significantly reduced by the ability to pass the digital data for all channels of all chips over a shared serial data line.

The entire detector consists of twelve chip pairs, resulting in a $12 \times 64 = 768$ channel detector with a $50\text{ }\mu\text{m}$ channel pitch. The schematic layout of these chips and other relevant circuit elements is shown in Fig. 6-3. The photographs in Figs. 6-5, and 6-6 include the chipsets and collector anode plate and clearly illustrate the collector-to-pulse processor and pulse processor-to-counter bonds.

Analog Pulse Processing Chip – The SDC Chip

The front-end analog chip used in the detector was designed at LBNL as part of the high-energy-physics Solenoidal Detector Collaboration (SDC) and originally intended for use at the Superconducting Super Collider [32a,b]. The chip combines low-noise preamplification, threshold discrimination and pulse shaping. It is designed to be capable of a 66nsec double pulse resolution and was manufactured with 64 channels at a $50\mu\text{m}$ input and output pitch. The availability and suitability of this chip to the detector design goals resulted in its adoption and established the detector channel pitch and number of channels per front-end chip. The chip is designed to optimally work with pulses of 1.25 to 10 fC (8×10^4 to 6×10^5 electrons) and so the already mentioned mismatch between saturated MCP pulses and the SDC is a potential difficulty in the system. However, as discussed later, the gain of the channel plates used here may be as low as 5×10^4 under adequately saturated conditions and so the matching requirement can be satisfied by appropriate choice of channel plates and operating conditions.

The double-pulse resolution of this chip is optimally 66 nsec (for 4 fC or 2.5×10^5 electron pulses), corresponding to about 15 MHz per channel. Under random counting conditions, we can expect pulse-pileup and resulting deadtime effects to begin to effect performance if the countrate exceeds $\sim 1/10$ - $1/20$ of this value. However, we should reasonably expect that a count rate of >1.0 MHz should be attainable with this chip with minimal deadtime effects. Thus, the overall countrate estimated for the detector is >768 MHz, and well along toward our 1 GHz goal.

The SDC chip accepts and discriminates the analog pulses from 64 separate collector strips or channels. Each of the 64 inputs has a corresponding low-level analog current output which is pulsed at 35 μ A when the input pulse is accepted by the discriminator/comparator. All channels within a chip are controlled by a common selectable discriminator level, and all chips are currently connected to a common discriminator level. This prevents chip-to-chip sensitivity optimization, but simplifies the design slightly and reduces the number of vacuum feedthrough lines required to support the chips. (A future improved design to be discussed at the end of this chapter will involve more individual and programmable control of chip discriminator settings.)

Digital Accumulator Chip – The DBC Chip

The 64 current pulse outputs from the SDC are fed into 64 complementary input channels on a digital double-buffered pulse counter chip, and both chips are designed to have matching 50 μ m channel pitches. This double-buffered counter (DBC) chip was designed specifically for this project at LBNL. It was based on techniques using discrete digital integrated circuit dual-in-line packages used in previous LBNL Engineering projects [33,34]. It was necessary to design the DBC input stage to accommodate the

low-level current pulses from the SDC. This is acceptable in this application because of the proximity of the SDC outputs and DBC inputs on the detector substrate, as shown in various figures (Figs. 6-3, 6-6).

For readout, an arbitrary number of these DBC chips may be cascaded into a shift register for bitwise serial transfer in the familiar “bucket-brigade” fashion. The counters are designed to be capable of at least 30 MHz input and readout frequency. Each channel can count pulses in a 15+1 bit counter, where the additional bit is treated as an overflow flag for that particular channel. The 15-bit depth allows a maximum count of $2^{15} - 1 = 32767$ before overflow. Therefore, we can trivially calculate the required servicing time of the counter buffer given a uniform input pulse frequency per channel, f , to be $2^{15}/f$. For example, a count rate of 1.3 MHz results in a maximum integration time of just over 25 msec before buffer swapping and servicing is required.

The double buffers in the DBC allow the detector to continue accumulating with one buffer during readout and processing of a previous buffer full of data. As long as the second buffer can be read out and processed within the integration time (25msec in the most conservative example above), no significant transfer induced dead time is introduced to the system. Buffer transfer in the chip is designed to take only 100 nsec resulting in an inherent system readout deadtime of less than $1:10^5$.

As with the SDC, the DBC chips are connected to a common reference voltage and power lines. They also share control signals (buffer swap, register shift, clear) and the serial data line for the shift register. This design minimizes the complexity of the system and the number of required vacuum feedthrough lines. Note that the serial data

readout order is determined by the order of the DBC shift register chaining which is in turn determined simply by the chip locations in the layout.

6.3.5 Electronic Systems External to Vacuum

Power Supplies

The in-vacuum detector components require several additional electronic components to complete the system. First is the basic need for various power supplies. The chipsets require both power and threshold (SDC) or reference (DBC) voltages to operate. In addition, the microchannel plates require a high voltage supply capable of at least 2 kV between the front and back of the chevron stack.

The power supply must be capable of setting each of these voltages relative to an input reference voltage. This reference or float voltage allows the detector to remain at a fixed voltage relative to the analyzer focal plane potential, which can be expected to range between +1.0 and -2.0 kV during normal operation of the Scienta ES200 electron energy analyzer (as discussed in detail later). In order to provide an integrated set of supplies, we have designed and built a custom power supply chassis that incorporates over-current protection circuitry for the channel plates and power and threshold voltages for the chips and supporting components. A simple computer interface allows for adjustment of IC threshold and reference voltages, monitoring of MCP wall current and an over-current shutdown procedure to backup hardware protection.

Data Transfer Hardware

The DBC chips require periodic counter readout (as fast as ~20 msec, as indicated above) to prevent overflow and to simply transfer data out of the detector. The readout of

the detector is done by a shift register formed by interconnection of all twelve chips, so that all $16 \text{ bits} \times 768 \text{ channels}$ (approximately 12kbits) are read out serially from the vacuum chamber by ECL logic level signals on twisted pairs of wires to minimize inductive pulse spreading. The DBC outputs are TTL and so TTL/ECL converters are required on the in-vacuum substrate. Digital circuitry automatically shifts the data bits out 16 at a time, as driven by a 10 MHz clock line, and recombines them into a single digital integer corresponding to the value in one DBC counter. The readout process is controlled by external control signals provided by a digital signal processor (DSP) that is described in detail in the following section. The full data transfer system is schematically shown in Fig. 6-7.

The digital ECL data lines float at the same voltage as the entire detector as they are passed out of the vacuum chamber. In order to allow communication with the control hardware (DSP and PC), this digital signal is optically isolated (and converted back to TTL logic with additional ECL/TTL drivers) in a “transfer box” that is between the ECL detector outputs and the DSP based control circuitry. This box also contains the timing circuitry and simple digital processing circuitry used for the 16-bit reads of the shift register.

6.3.6 Digital Signal Processor and Control Software Development

The use of a DSP as the primary controller of the detector results in a very flexible, easily modifiable system. Significant changes in the operation of the detector to accommodate changes in the detector itself or in the desired acquisition modes can be made by modification of the DSP software rather than actual rewiring or redesign of

hardware providing the same functionality. Such a system was adopted due to its success in previous projects, including interfacing to DBC ancestors already mentioned [35].

The detector is fundamentally controlled by software running on an AT&T 32C Digital Signal Processor (DSP), with a 50 MHz pipelined processor. The DSP is installed in an ISA bus slot in a standard PC [36]. The DSP software controls the digital control lines, data readout from digital chip buffers into DSP memory, and the precise timing between buffer readouts. The DSP software is itself controlled by a higher-level driver running on the host PC. Finally, user-level control of the detector in a practical, automated manner is provided by a user interface on the PC that utilizes the high-level driver software.

Although the DSP allows less hardware to be constructed to run the detector, it requires software to replace the functionality of that hardware. Compiler and linker tools provided with the DSP allowed a combination of assembler macros and ANSI C to be compiled into the necessary executable code for the processor. Additional ANSI C libraries supplied for use in the host PC of the DSP could be used with sufficient modification within a Win32 or 32-bit console application to implement the high-level driver. For reference in future use and development of the detector, the current source files used for both the DSP and PC drivers are listed in Table 6-2.

The model for the software can be best understood if the capabilities of the DSP are first outlined. The DSP consists of a 50 MHz microprocessor, blocks of high speed RAM, and an input/output (I/O) bus; it is thus a simple computer without a display, input or storage devices, or an operating system. Additional DMA (direct memory access) and IRQ (interrupt request) capabilities for programmed automatic data transfer and signal

handling between the DSP and PC are available but not used. Through the DSP I/O bus, a PC (through its own ISA bus) can, byte-by-byte, load native machine language (i.e. compiled and linked) code into the DSP RAM. Once loaded, the DSP can be instructed to begin processing the entry point of this block of code. Through the PC ISA bus, the PC can read or write to arbitrary positions in the DSP RAM. Thus, through mutually agreed upon memory locations, the PC and DSP software can communicate, synchronize, and transfer data.

The DSP control software is based on an infinite loop that periodically reads a specific "control line" byte in the DSP RAM. When an action is required (e.g. to start counting), the PC modifies the control byte and perhaps additional parameters at other memory locations. The DSP program then enters a subroutine dependent upon the control signal that was found. The routine of interest for non-testing purposes performs a detector integration for N timing loops, swaps the detector (DBC) buffers and reads the shift-register data from the detector, into DSP memory, finally raising the appropriate flags to indicate to the host PC that the data is available.

The detailed detector readout method is clear if we examine the detector hardware. The detector channel counters are double buffered and when readout is required, the "active" or counting buffer is latched. A second buffer then begins accumulating the channel pulses while this initial buffer is available to the serial readout. The sequence is shifted out one 16-bit word at a time by the transfer electronics as already discussed. The entire data transfer model trivially adapts to changes in the total number of detector channels to be readout.

In order to actually connect the DSP to the detector control lines, the DSP has had additional digital circuitry added to the “prototyping area” left by the manufacturer for such purposes. The added hardware allows external signal lines to be attached to particular 16-bit memory locations in the DSP RAM (I/O ports 0 and 1). The readout process requires four signals: *buffer-swap* (DSP writes), *data-shift* (DSP writes), *data-available* (DSP reads), and *data-read-value* (DSP reads). Since a single line can be used for both a read and write signal, we are reduced to needing only two control lines. In this case, the *buffer-swap* and *data-available* lines share DSP Port 0 and the *data-shift* and *data-read-value* share DSP Port 1.

To perform the entire readout, the following procedure is followed.

- Write to *buffer-swap* (set high). This initiates a parallel loading of all DBC counter values to be loaded in parallel onto the shift register outputs. The first 16-bit transfer is also performed.
- Poll (read) the *data-available* line until a low (zero) value is read in the lower 8-bits (ignoring meaningless high order bits). This indicates that the transfer box has completed the transfer of a 16-bit word that is now ready to be read by the DSP.
- Read the *data-read-value* line as a 16-bit counter value and store in the DSP RAM at the appropriate (channel dependent) address.
- Write to *data-shift* to begin transferring the next 16 bits. Continue to the second step and loop until all counter values are in DSP memory.

The data readout routine is the most critical portion of the DSP code. The detector control lines need to be sequenced and read with optimum timing control and hence processor cycles. Assembler-level coding has been used to maintain maximum control over the procedure.

The DSP software lowers/raises a status bit, or flag, in RAM to indicate that the readout is complete/in progress. The host-PC software monitors this bit through polling and, when the flag indicates completion, the data can either be read over the ISA bus for further processing or additional processing of the data in the DSP can be requested. It was speculated that the active polling of the DSP memory location (status bit) during the DSP dwell and readout sequence introduces some timing error in the system. This is because the PC access of the DSP bus prevents the DSP processor from using the bus and hence accessing memory. However, the number of "stolen" DSP clock cycles is minimal and does not introduce measurable delays into the DSP timing. Tests of this were performed during the timing calibration of the DSP as shown in Fig. 6-8. Despite purposely varying the rate of PC polling of the DSP memory, no detectable deviation from this calibration could be detected. Although clearly not necessary, it is possible to eliminate the PC polling entirely by instead using the DSP to either raise a PC interrupt (IRQ) or acquire control of the PC bus and then use DMA to automatically transfer the data.

The entire DSP controlled readout process takes less than 2.4 msec for all 768 channels, as found by monitoring the transfer clocking line with an oscilloscope. This time is significantly shorter than the minimum required ~20msec during which the

second buffer may be left to count at an overall GHz rate before overflow, and so there is sufficient time for additional processing and transfer to the PC between each read cycle.

After readout into the DSP, the resulting order in memory is Chipset 1, 2, 3, ..., 11, 12 as numbered in Fig. 6-3(a). This simply indicates that the chip numbering is according to shift register chaining. However, the logical channel layout (the physical channel sequence) across the detector in the energy axis does not match this ordering. The layout shows that the first half of the chips are interleaved with the second half so that the true data order is obtained by viewing the readout data in the reordered manner: 12, 1, 11, 2, 10, 3, 9, 4, 8, 5, 7, 6. In addition, chips 7 through 12 are reversed relative to chips 1 through 6 so that a mapping of individual channels in these chips from 1, 2, 3, ..., 64 to 64, 63, 62, ..., 1 is also needed. The final mapping is shown in Fig. 6-9. This processing is well suited to the DSP and can be handled at this point according to a mapping array loaded into DSP memory from the PC, or within the PC itself. As part of the mapping, the overflow bits can also be checked for each channel; the overflow is active low, so when not overflowed, bit 15 (of 0-15) still needs to be masked.

6.3.7 Experimental Characterization Results

Development Chamber

The initial tests of the detector required near UHV ($<10^{-8}$ torr) conditions in order to energize the MCPs and to confirm the operability of the system in a reasonable emulation of the final experimental environment. A standard stainless steel UHV vacuum vessel with an ion pump and ion gauge was assembled for these tests. Initial pump-down from atmosphere was provided by a turbo-molecular pump system capable

of reaching about 10^{-8} torr. The chamber was typically only baked to about 100°C in order to prevent damage to various detector components during initial tests; of particular concern were various conductive epoxy traces added to the detector to repair assorted substrate defects. The chamber was normally at a pressure of about $2\text{-}6\times 10^{-9}$ torr during operation of the detector.

Development Software

With the DSP software in place, PC analysis software that includes user interface, data display, and data storage is needed for actual testing of the detector. A menu driven, 32-bit console (DOS) application has been written for such testing purposes. This software allows a number of operating modes that assist in the testing and characterization of the detector. With this software, the detector can be run in either a single-frame or looped, integrated-frame mode, with individual channel averaging (overflow compensated) available across multiple frames. The per-frame dwell time can be arbitrarily selected between 1 msec and thousands of minutes in 1 msec increments (limited by a 32bit integer rollover in the DSP timing code). Histogram display can be chosen to include any combination of chips. These selected chips can be displayed either in the readout order or in the remapped physical collector position order (cf. Fig. 6-9). Data can be stored to an ASCII file for documentation and later analysis.

Because the console application was written in 32-bit ANSI C, the hardware driver portions were easily recompiled for use in a Win32 program (or other 32 bit PC operating system that allows simple I/O port access). Only minor modifications to library function calls (i.e. specific port I/O functions) not uniquely determined by the ANSI C standard library specification were required. With this code, the detector was in fact

incorporated into a previously developed program that simultaneously controls the Scienta hemispherical analyzer for testing and data collection in the target experimental system, as discussed in detail previously [37].

Linearity and Maximum Countrate

As thoroughly discussed elsewhere [17,18,19], the linearity of a detector response function over its entire dynamic range is a very desirable characteristic that is not realized by many detector systems. In these systems, precise quantitative data cannot be acquired without a (potentially difficult) detector compensation routine being applied to the raw experimental results.

In order to measure the response function of this detector, we require a variable intensity source that we can calibrate well enough to determine the measured countrate of the detector as a function of the input count rate or electron flux, at least within an overall constant scaling factor. The radiation source may consist of any particle to which the MCPs are sensitive, but because we are primarily interested in counting electrons and the response of the channel plates may itself change with particle type (and energy) we have performed these measurements with a low-energy electron flood-gun of the type normally used in photoemission experiments to compensate for photoemission induced sample charging. The electron energies were thus several eV at maximum. The flood-gun consists simply of a resistively heated filament and a low-voltage accelerating grid within an enclosure. A small hole in the enclosure allows electrons to escape and reach the sample or in this case, the detector. The flood-gun used was manufactured by Hewlett Packard for use with their 5950 series of x-ray photoelectron spectrometers (model 18622A gun with 18623A controller).

The flood-gun was placed in front of the detector head at a distance of about 30 cm. The filament current control is not expected to result in a linear emission current, and this has been found to be true (see Fig. 6-10(a)). In order to actually determine the current reaching the detector, we have measured the change in MCP wall current as a function of the filament current. This has been found to be a reliable measure of the change in incident particle flux against which to calibrate the detector response.

We also note that special precautions had to be taken to prevent background signals in the test chamber. Both the ion-gauge and ion-pump in the system have been seen to produce a distinct background count rate and so measurement of the response function was performed with both of these turned off. The MCP front voltage was for these tests also set to the chamber ground in order to prevent attracting or repelling the low-energy electrons emitted by the flood-gun.

In order to perform these measurements, the average of all counts over all operating channels in one chipset (64 channels total with 8 inactive) has been used as the measured countrate in order to improve statistics. The resulting response function is shown in Fig. 6-10(b) where a quite linear behavior is shown over the entire dynamic range, with no deviation from linearity being detectable within the statistics of the measurements. The “roll-over” at high countrates occurs at about 1.3 MHz, or >0.9 GHz over an entire complement of 768 channels. This limit agrees well with the projected operational range of the SDC chip, as based on its pulse-pair recognition, and is entirely compatible with our design goal of a GHz overall countrate.

It should be noted here that the MCPs experience an increase of wall current of nearly 25% between the zero and 1 GHz countrates. In this case, the MCPs may in fact

be expected to experience a reduced gain as the countrate is increased, with this potentially introducing difficulties in the accurate setting of a discriminator level in the SDC. However, with an estimated average gain of about 6×10^4 during these tests, this effect will be minimized and so not interfere with the ability to accurately set the discriminator level for optimum operation and linearity. More accurate tests of the detector response, more fully exploring the behavior as a function of both MCP voltage and SDC discriminator setting, are to be performed in the near future in order to determine the most acceptable window of operating parameters for the detector.

Channel Crosstalk

Channel crosstalk refers to the reaction of neighboring channels to a pulse reading in a given channel. It is important that a reading in one channel does not result in significant coupling into neighboring channels for at least two reasons. The obvious problem involves loss of spatial resolution. If every MCP pulse results in a registered pulse in neighboring collector channels, then the spatial resolution of the system is reduced. Effectively, there is a convolution function applied across the detector. Perhaps more significantly, crosstalk effects will directly affect the maximum true event countrate of the detector, simply because each crosstalk induced pulse occupies the counting electronics for the same amount of time as a true pulse. In general, the discriminator setting in the pulse processing might be expected to eliminate such problems, because the pulse charge induced in neighboring channels will be of lesser magnitude than the initial pulse. However, we must consider that the detector is already required to make use of a distribution of true event pulse heights as a limitation in the MCP performance. In this case, the larger true pulse heights may be expected to result in induced pulses of a

magnitude still characteristic of the MCP PHD. In this case, a discriminator setting sufficient to eliminate all induced pulses will also eliminate many true pulses and make the entire system much more sensitive to MCP gain changes and the corresponding PHD shifts [15,20].

For this set of tests, a UV transparent viewport was installed in the line-of-sight of the detector face, with a UV lamp mounted against this viewport. In order to determine the extent of crosstalk in the detector, a portion of the detector directly above a single collector channel was illuminated with the UV light. This was accomplished by placing a mask with a pair of collimating 25 μm slits in front of the detector, as schematically illustrated in Fig. 6-11(a). Rotational alignment of the slits so as to be highly parallel with the collector strips was accurately carried out by using a laser diffraction pattern produced by the effective diffraction grating of the collector strips. The slits themselves were mounted on a linear transfer inside the vacuum chamber, about 0.215" above the front of the top MCP (c.f. Fig. 6-11(a)). By translating the slits across the detector, one could clearly observe a series of single channels turning on and off as the slit passed over each one. The resulting detector response profile with the slit centered over a certain reference channel denoted as "0" is shown in Fig. 6-11(b). Relative to a constant, and for this test negligible, background signal, we note that there is definite coupling only between the centrally illuminated channel "0" and its immediate neighbors "-1" and "+1". This result indicates that the nearest-neighbor crosstalk is at a maximum level of about 3.5 dB in this detector design and will not limit the spatial resolution in a significant manner. Indeed, by fitting a simple Gaussian peak to the crosstalk spectrum, we see that an appropriate measure of the genuine spatial resolution has a FWHM of

75 μm , rather than the geometrically ideal 50 μm of the system due to collector pitch. Comparing this value to other detector systems such as those in Table 5-1 we see that this detector, even when including crosstalk effects, exhibits significantly better spatial resolution than all other detectors listed. This is especially remarkable considering that the figures given for other detectors are based on ideal, geometrical resolutions without allowance for system specific crosstalk effects.

The remaining crosstalk characteristics seen in the detector can be attributed to various phenomena. The first is a fundamental limitation of the detector: capacitive coupling between neighboring channels. In other detector systems, particularly those with long collector to pulse-analysis electronics connections, this can be a significant problem [15]. The compact design of the present detector, in particular the short distance between the collector and preamplifier (SDC chip) via a 2-3 mm bond inherently minimizes this problem [29]. Crosstalk tests of the SDC chips themselves [32] indicate that the observed magnitude in this system is similar to that of a system having 7 pF cross-channel capacitance and 7 fC pulses, but neither of these values is precisely known for the current system so this is only a qualitative comparison.

An additional source of crosstalk can come from the MCPs. Although the pore size (10 μm) of the MCPs is five times smaller than the collector pitch, there exists opportunity for some loss of spatial resolution at two points in the MCP. The first source is due to misalignment of the chevron stack, which in general will be expected (due to simple geometrical arguments) to distribute the original pulse in the top MCP over about three neighboring pores in the bottom MCP of the chevron. That is, the 10 μm ideal resolution can be smeared out over about $\pm 15 \mu\text{m}$, perhaps accounting for some of the

interchannel coupling, but certainly not all of it. The second potential problem is due to spreading or blooming of the pulses emitted from the MCP pores before reaching the collector anodes. This could result in crosstalk due to distribution of the pulse charge into the insulating spacing between each collector. The detector design does include the ability to apply a potential, V_{coll} , over the gap between the MCP back and the collector array (cf. Fig. 6-4), thus allowing the MCP generated electron pulses to be accelerated towards the channel and presumably reducing the lateral spread or bloom of the charge pulse. Applying voltages between 0 and 20 V over the 50 μm gap has not resulted in significant changes to the crosstalk behavior of the detector, although there may be some slight improvement in the intermediate 8-10 V range. We believe from the MCP PHD measurements shown in Fig. 6-2(c) that the PHD should be at least slightly affected by this potential difference, but whether this is apparent in the crosstalk (due to increased coupling with pulse charge) is uncertain. Also note the extremely large voltage gradients obtainable in this configuration: For example, a collector voltage of 50 V would correspond to a 1 MV/m, comparable to voltage holding requirements in standard X-ray anode sources, and this makes clear our caution in always staying below $V_{\text{coll}}=20$ V over the 50 μm gap in our operation of the detector.

Finally, it should be remembered that, even though the collector direction has been aligned to the double-slit mask direction as carefully as possible, some slight misalignment may still exist, and this could be responsible for a final portion of the observed crosstalk. By geometrical arguments, the angular alignment that must be achieved in the orientation of a rotatable Conflat-style UHV flange to which the detector is mounted must be better than 0.3 degrees before the slit would necessarily illuminate

only a single channel and its surrounding interchannel gap. It seems likely then that a portion of the minimal amount of crosstalk observed may actually be artificial, and that we have actually arrived at an upper bound in the crosstalk magnitude. Conclusive crosstalk tests would require a test probe to be used to pulse a single channel at a time, however this is problematic due to the technical difficulty of installing a probe with good electrical contact to a single anode and ensuring that the probe itself does not contribute to the interchannel capacitive coupling.

It should be noted that this test may be better performed in the future with the electron-gun providing the test pulses. We have observed that the PHD of the MCPs is not saturated (peaked) when illuminated with UV light and the effect of this on the tests is not well studied. Our failure to observe electron generated pulses when using the collimator is attributed to the presence of magnetic fields (ion pump, laboratory stray, and Earth) in the chamber that curved the electron trajectories sufficiently to prevent any paths from the flood gun being able to pass through both collimator slits. In any case, we view the tests with the UV lamp as sufficiently conclusive of excellent performance as to channel crosstalk.

6.3.8 Experimental Spectra

We have successfully tested the first prototype detector in a genuine experimental situation. The testing itself was very successful in that it for the first time confirmed the compatibility of the detector with various “real-life” requirements that could not be tested in the development chamber. This included the installation of the detector in the detector port of the Scienta analyzer, the successful bakeout of the system, the achievement of normal UHV conditions in the experimental chamber, and the final incorporation of the

detector software driver into a much more complex software package that is already in use for controlling the analyzer and related instrumentation [37]. In addition, operation of the detector in the mechanically and electrically much noisier environment of the chamber on the ALS experimental floor represented a real test of the system integrity. These tests marked the first time genuine photoelectron spectra were acquired with the detector.

Experimental Chamber

With the detector performing well in the UHV development chamber, and able to count both UV photons and low energy electrons of a few eV, the next obvious step is to test it in an actual experimental system. The initial tests were performed in the Advanced Photoelectron Spectrometer/Diffractometer (APSD) system at the ALS [38] using a commercial unmonochromatized $\text{AlK}\alpha$ x-ray source (Perkin Elmer) for photoelectron excitation. The APSD is a UHV experimental chamber designed primarily for surface science photoemission experiments at the Advance Light Source in Berkeley [38]. Mounted in this chamber is a Gammatdata Scienta ES200 analyzer, which is the primary target application of the detector.

During the test period, synchrotron-generated light was not available and so only the x-ray source could be used. The $\text{AlK}\alpha$ x-ray source is not capable of providing countrates as high as even the bend-magnet-based ALS beamline 9.3.2 where the APSD was stationed, and so we could not test the entire dynamic range of the detector. However, it is more than sufficient to saturate the standard (Gammatdata/Scienta CCD) detector supplied with this analyzer, and can under appropriate conditions provide a

countrate that is a substantial fraction of the 1.3 MHz/channel countrate that the detector is capable of measuring as based on the test chamber results.

The detector was installed in the analyzer with the front of the MCP chevron approximately 1.3 cm from the retarding grid of the analyzer. This minimum distance was greater than the 0.18–0.23 cm in the normal detector supplied with this analyzer, but was limited by a mechanical interference of protective shrouds on the detector with various magnetic shielding within the analyzer. Time restrictions necessitated proceeding with these first tests without eliminating these interferences. The result is that the detector face was not as close to the focal plane of the analyzer as it should be for highest energy resolution, but several millimeters back. If the highest resolving power of the analyzer is to be realized, the detector must in the future be positioned as close as practicable to the focal plane. This is because the electrons of a given energy enter and leave the focal plane with a certain distribution of angles, and there is thus a spreading of the image of each energy as they propagate beyond the focal plane. However, for the purposes of initial testing, this positioning of the detector was nonetheless sufficient to allow clear spectra to be measured.

The pressure in the experimental chamber near the detector was stable at approximately 1×10^{-9} torr. The analyzer lens was at a similar pressure, while the main experimental chamber was at about 3×10^{-10} torr. During the bakeout of the system immediately after installing the detector, the chamber temperature near the detector was kept below 120°C and so, especially in view of the conductance limitations between the detector and the primary chamber pumping, this base pressure near the detector is about what would be expected and is completely adequate.

It should be remembered that the detector system is built to allow the entire detector substrate to float on voltage levels between at least +1 to -2 kV. This is due to the operation of the analyzer to which the detector is attached. The analyzer operates by retarding and accelerating photoelectrons emitted from a sample to a particular pass energy. To accomplish this, the hemispheres and detector are themselves floated on the retarding/accelerating voltage. The pass energy may be as high as 1000 eV in the Scienta ES200, using standard pass energy settings prepared by the vendor. In this case, to observe electrons near zero kinetic energy, the electrons must be accelerated by about 1000 V. On the other hand, the lowest standard pass energy is 2 eV, and to observe the weakly bound photoelectrons that are emitted with nearly the full energy of the excitation source, $h\nu$, the photoelectrons must be accelerated by about $h\nu$. The maximum photon energy in the APSD as used to data is given by the $AlK\alpha$ source at 1487 eV. Hence the expected retardation range that the detector will see is the about +1000 to -1500 V, with an additional deceleration of the electrons possibly given between the analyzer and the detector face that is typically less than 100 V (to be discussed later). It should be recognized that the standard stacked power supplies of the ES200 analyzer can actually provide a range of -2013 to +2113 V, and although these extrema do not represent normal operating ranges, any detector should be able to withstand such reference voltages. Also, notice that these reference voltages represent the face potential of the detector, i.e. the MCP front potential. The MCP chevron itself is held at up to 2 kV front to back, and so the substrate (collector anode, and chipsets) may be referenced at anywhere between -2013 to +4113 V, depending upon the setting of the analyzer and the MCP voltage. These are very high voltages compared to the low voltages and delicate elements in the

integrated circuits, and so maximum precautions are necessary to prevent any kind of high voltage transient from damaging the onboard ICs and other circuit elements.

The detector was referenced to the analyzer through connection to the voltage supply line designated “DU3” on the ES200 analyzer. This line is the sum of all retardation power supplies (designated “AU1”, “AU2” and “AU8”) and a bias voltage (“DU3”) between the analyzer and the detector face. Due to apparent problems with the acceleration power supply “AU8” this element was temporarily eliminated from the system during these tests, preventing normal scanning of kinetic energies less than the analyzer pass energy. The “DU3” supply normally provides a slight retardation of the electrons between the analyzer retard potential and the front of the MCP. The analyzer has a terminating grid over the exit port of the hemisphere that is tied to the analyzer retardation potential. This is meant to prevent resolution-damaging fields from entering the hemisphere. However, low-energy secondary electrons at energies less than the pass energy of the analyzer and produced presumably by the deflected primary electrons hitting the inner walls of the hemispheres as well as the terminator grid can produce a significant background at the MCP that will be counted along with the primary electrons. Because the secondary electrons will have a distribution of energies less than the primary electron energy (the analyzer pass energy, E_p), a retardation voltage (DU3) between the analyzer and detector can greatly eliminate this background [4]. For these studies, spectra were collected with the DU3 retardation at 0 V although the normal setting used with the standard detector is $0.75 \cdot E_p$ with a power supply imposed upper limit of 100V. It is not clear to what extent this retardation potential affects the energy resolution of the system especially with the grid to MCP distance in these tests held at a greater than

nominal value. In fact, applying a negative voltage between grid and MCP would be expected to increase the spreading of a focussed image at a given energy as it leaves the grid and passes to the MCP. Regardless, the continued practice of using retardation to eliminate the background signal seems reasonable and will presumably be used in future installations of the detector.

To operate the detector under true experimental conditions, it was necessary to integrate the detector software into a more complete package that allowed simultaneous control of the analyzer and the detector along with appropriate data handling schemes, particularly dithered mode acquisition. The details of the software package are discussed elsewhere in this dissertation [37]. The DSP and host PC drivers previously written for the testing and development of the detector were incorporated into this software with essentially no modification.

First Experimental Results

Initial test spectra were acquired with a clean W(110) crystal, oriented for normal emission detection. This sample was mounted under a Ta foil clip used to hold the W crystal to the sample manipulator, which was also partially seen by both the wide-angle x-ray source and the analyzer entrance aperture. The first spectrum acquired is shown in Fig. 6-12 and includes the W 4f peak along with a Ta 4f peak resulting from the clip. This was measured with an analyzer pass energy of 500 V and a curved slit plus angular aperture capable of providing a resolving power of 133. Thus the energy resolution of the analyzer alone was about 0.2 eV, which compares well with the approximately 0.9 eV FWHM of the AlK α source [1]. Another spectrum over a wider energy window is shown in Fig. 6-13(a). Both of these spectra were acquired with the retardation between

analyzer and MCP front set to 0 V and the MCP bias at 1.95 KV. All spectra were acquired in swept mode due to a substantial number of missing channels in the prototype (see next section).

The use of the x-ray anode for excitation prevented the testing of the detector over much of its dynamic range when measuring the core level photoemission from the sample. However, by measuring a very intense low kinetic energy (<50 eV) signal arising from inelastically scattered electrons, the measured countrate could be increased substantially to as much as 0.7 MHz/channel. As mentioned previously, the acceleration power supply of the analyzer was not operational and so we simply biased the sample at -600 V in order to observe this low energy signal. This extraction voltage explains the presence of <0 eV kinetic energy electrons in the spectral profile as seen in Fig. 6-14, where we essentially probed the work function of the sample. In any case, the vertical scale of Fig. 6-14 verifies a per channel countrate for electrons of 0.7 MHz per channel that would scale up to about 500 MHz over a fully operational 768 channels. This provides additional verification of our ability to achieve the desired 1 GHz in a future prototype that is presently being constructed as a continuation of this project

Digital data corruption that was much less noticeable in the development chamber testing was more clearly seen in these tests. The typical level of the noise observed is seen in Fig. 6-13(b), although it was observed to also be significantly better or worse during different scans with no systematic reason as yet determined. A further discussion of this particular problem is found in the following section.

These spectra represent a sample of the data acquired during the first full testing of the detector. An appropriate next step would be a detailed measurement of the

detector response function at various SDC thresholds and MCP voltages, as illustrated in other work [19], in order to more accurately repeat the response function work shown earlier, especially in the very low count rate (<1 kHz/channel) range that was difficult to probe with the flood-gun technique. These tests will also reveal the most appropriate discriminator setting to use in additional testing and finally experimental work. Future testing using a brighter insertion device beamline at the ALS should easily provide countrates over the full dynamic range while measuring core level emission.

However, before proceeding and certainly before using the detector for experimental work, the problems encountered in the digital data corruption need to be fully addressed. This problem is considered in the next section, along with other difficulties encountered with the current prototype, in order to provide a sound basis for the future development of this type of detector.

6.3.9 Problems Encountered

As with any such complex project, a number of problems have been encountered during the construction of the first prototype. These problems can be divided into two general categories: problems arising from basic design decisions and problems encountered due to fabrication or assembly errors or problems.

The first design problem involves unexpectedly high heat generation and dissipation in the vacuum exposed and substrate-mounted circuitry of the detector. The DBC chips were found to continually draw a current when not counting, and the resulting heat could be seen to increase the detector temperature steadily once the detector was powered. The vacuum environment of course eliminates the possibility of convective

dissipation into the atmosphere that seemed to be sufficient during bench tests of the powered chips. We thus initially found that the detector, when operating in vacuum, steadily increased in temperature and upon reaching about 32°C (as measured on the ceramic multilayer, some distance from the chips) the behavior of the chipsets was compromised, resulting in severe problems that appear to be strongly related to the DBC. The symptom of the problem is an apparent overrun condition in the readout data, occurring in blocks of channels and beginning first in the data at the end of the shift register. This problem could be reduced by running with decreased dwell time per DBC readout, with the maximum useable time systematically reducing as the temperature rose. This problem is peculiar because the overflow bit is active low, so that if we are dealing with DBC bit corruption as discussed below, it seems to be appearing in a high order bit other than the overflow (bit 15 of 0-15) and then switching the overflow bit simply due to normal counter rollover.

The first solution to this problem is simply to actively cool the detector substrate. A copper heat sink has thus been installed behind the substrate and a cooling water line was securely clamped to this heat sink. The measured temperature now remains below 30°C during prolonged operation. A second, software derived, protection involved leaving the detector in an “active resting” state where the DBC buffers are continuously swapped and readout. This reduces the average current drain in the DBCs and hence the heat load.

Secondly, the digital data readout has sporadic bit corruption. This problem is currently being investigated and may originate in one of two locations. The first possibility is that the parallel load of the active buffer in the DBC chip onto the shift

register results in a large “jolt” to the circuitry, with resulting noise generation that is sufficient to corrupt the bits during the load operation. This problem would indicate a significant inherent problem with the DBC design (with an intended replacement of it in a next-generation detector to be discussed below). A second, more easily remedied problem would be for the data to become corrupted during the shift register transfer into the DSP. The test for this would be to intentionally preload the shift register with known patterns and see if it is preserved during readout. This test involves some electronic modification to the data transfer electronics and possibly software, but should be possible to perform.

It should also be mentioned that the DBC chip does seem to have at least a related digital noise problem associated with the buffer swap. It was observed early on that by using only one of the double buffers, the system noise was significantly reduced. This seems to indicate that the process of the readout on one buffer actually contributes digital noise in the second, actively counting buffer. For this reason, all data presented were collected in single buffer mode, ignoring the presence of the second buffer. This introduced a deadtime in the system equal to the time it takes for readout, on the order of one millisecond for every 20 milliseconds of running at the maximum count rate, or 1:20 fractional deadtime. Lower countrates allow longer accumulation times between readout and so a reduction in required fractional deadtime. By comparison, the original concept, using the double buffers, requires a deadtime equal only to the buffer-swap time that is less than 100 nsec (fractional deadtime of $< 1:10^5$) and so this problem definitely needs to be addressed in the next prototype.

For the initial beamline tests, this digital problem proved to be significantly correctable through simple manual correction of high significant bits in the data that result in large spikes in the spectra. Unfortunately, the low order bits are much more difficult to identify as incorrect because, depending upon actual average count rate and standard deviation (ideally Poisson derived since we are dealing with counting statistics), some number of the lower order bits are likely to be in either the on or off state. It should be mentioned that only bit changes from low to high (0 to 1) are observed: Any spike in the final spectrum is always additive, but generally not a simple single bit corruption (i.e. the spike value does not differ from the expected value by 2^N). This digital noise makes accurate determination of the overall detector noise difficult at present.

Additional problems actually encountered earlier in the project involved fabrication of the substrate ceramic. These included manufacturing defects in several interconnects and interlayer vias. The holes in the substrate used for mechanical mounting and powering of the microchannel plates were drilled in such a way that the mounting screws easily shorted the chip substrate "ground" to the MCP high voltage, at up to a 2 kV potential difference. This type of short was responsible for the gradual elimination of portions of the detector (chipsets) during electrical breakdowns. The breakdowns damaged the TTL/ECL translators and in turn damaged the output stage of the last DBC chip in the shift register chain. Consequently, that DBC chip would have to be bypassed and one entire SDC-DBC set would be lost, resulting in a 64-channel "hole" in the detector. Once properly identified, this problem appears to have been eliminated by improved isolation of the MCP mounting screws.

6.4 Future Development Directions

Despite the success with the first prototype detector, the experience acquired over the course of assembly and testing has revealed several directions for making improvements that will substantially enhance the capabilities of the detector and make it more broadly useful to a range of experimental programs at the ALS and elsewhere. Future developments will include a second prototype based on the initial design and SDC-DBC chipsets, but with various problems identified in the first prototype fixed. This is now in the process of being assembled. Beyond this, our approach for a second-generation high-speed detector will consist of several elements, with a key improvement being the replacement of the ASIC chips used in the first model with improved versions that eliminate most or all of the problems found in the current chipset.

In particular, the preamplifier chip will be replaced by the much newer “CAFÉ-M” chip (a descendent of the SDC chip discussed more specifically in Ref. 32) that has also been designed and produced as a component of high energy physics detectors. This continues the practice in this project of adopting preexisting components that have been proven and tested wherever possible. This new chip has several advantages over the SDC chip, including

- doubling of the SDC dynamic range, allowing up to about 2.0 MHz per channel,
- doubling of the channels per chip to 128 channels, but with the same 50 micron readout pitch, reducing the mounting area and preserving our desired spatial resolution,

- improved channel-to-channel gain uniformity within a chip,
- interface circuitry to permit utilizing on-chip DACs in the mating modified BMC counting chip (see below) for setting thresholds per chip and the operating point of the input stages, yielding more uniform response over the entire detector and better noise optimization,
- a 20% lower noise level,
- many small improvements relative to the SDC to improve overall stability and reliability (e.g. redundant bonding pads for critical connections) and more test points.

In addition, the present second DBC chip in the set will be replaced with:

- a redesigned buffered multichannel counter (“BMC”) chip, based on several IC modules already present in the existing and well-tested “ABC” chip from high-energy physics. This will involve several differences from the existing DBC chip:
- a redesigned input stage to eliminate the need to frequently read data out to prevent excess current drain,
- a more robust protocol for control and data transfer, which has led with the current DBC protocol to occasional erroneous channels,
- a single serial link for loading commands (incl. setting DACs, calibration, etc.) and reading out data,

- a serial link utilizing a single opto-coupler for multiple functions and improved high-voltage isolation (fewer links, better isolation),
- faster data readout rate due to 40 MHz clocking,
- improved failure mitigation in that faulty chips can be bypassed in the readout cycle, and master function can be reassigned to another chip,
- on-chip DACs to permit programmable control of CAFÉ-M thresholds and other functions,
- a larger buffer counting capacity (bit depth) to reduce the frequency of readout necessary at high countrates.

Finally, based on experience with the first-generation SDC+DBC detector, various improvements will be made to the power supplies and electronic interconnections in order to increase resistance to various failure modes (especially from the high voltages present) and overall user-friendliness. The result should thus be a detector suitable for replication by other groups at the ALS and in other laboratories, as well as eventual commercialization by Quantar Technology (a continuing collaborator on this project) or other companies, with enormous benefits to various types of spectroscopy.

6.5 Concluding Remarks

A first prototype of a high-speed, large-bandwidth detector has been built using ASIC technology developed for the high-energy physics community and other components designed at LBNL and successfully tested both off-line and in a real experimental situation. A second prototype based on the same components used for the

first full prototype will be assembled and should be ready for installation into an experimental chamber soon after the completion of this dissertation. The success of this project as proof of principle suggests that the project be continued using more advanced chipsets and taking advantage of the experience accumulated in this project.

There is a clear need to develop high performance detectors for use at facilities such as the Advanced Light Source in order to take full advantage of their capabilities. Detectors of this type are already a critical need for many types of experiments, which presently waste much of the available radiation due to lack of sufficient counting capacity. As more third generation synchrotron sources and insertion devices continue to come online, the need for higher speed detectors will only become more important. The work carried out as part of this dissertation represents a significant step toward addressing this need.

Although the detector described here has been designed specifically for electron detection in a hemispherical analyzer, it is more generally useful. Sensitivity to photons and ions is inherent in the system due to the use of the microchannel plate. Thus, selection of a specific MCP set designed for the particle type and energy range of interest can further optimize the detector to a particular application. Once the remaining problems discussed here are solved, we thus anticipate usage to extend well beyond the synchrotron radiation and surface science community.

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Detector	Channel Width Δr (μm) [a]	Resolution: $\Delta E/E_p$ $\times 10^{-3}$ [b]	Number of Channels	Maximum Count rate Per Channel	Maximum Overall Count rate [c]
ONE-DIMENSIONAL					
ELETTRA Project (Italy) [d]	320	8.0	96	5 MHz	5 MHz [e]
Integrated Sensors, Inc. (UK)	160	4.0	116	100 kHz	12 MHz
LBNL Highspeed 1 st generation	50	1.3	768	~1.1 MHz	0.8 GHz
2 nd generation	50	1.3	768	>2 MHz	>1.6 GHz
PHI MultiChannel (USA)	2000	50.0	16	~ 1 MHz	~16 MHz
TWO-DIMENSIONAL					
Quantar Resistive Anode (USA) [f]	155 400	3.9 10.0	256 100	300 kHz 1 MHz	300 kHz 1 MHz
Scienta CCD, grayscale mode (Sweden) [g]	110	2.8	~367	< 2 kHz	< 750 kHz

- [a] Channel width not including channel crosstalk effects. The LNBL detector has a 75 μm effective width including this crosstalk (cf. Fig. 6-11), still smaller than the non-corrected figures for all other detectors.
- [b] Resolving power is computed from the effective channel width, applied to the case of a 200 mm hemispherical electron analyzer (Scienta ES200). In this case, with E_p = pass energy after retardation and r_0 = mean analyzer radius, $\Delta E/E_p = \Delta r/2r_0$. Note that the best possible resolving power for the Scienta ES200 is $\Delta E/E_p = 10^{-3}$.
- [c] This figure represents all channels running at near saturation. In practice, the detector would generally be used to collect signals that vary in intensity across the dispersion axis (i.e. spectral features). This results in some channels perhaps running near saturation, but others significantly below the saturation level. In such cases, this overall actual count rate will not be as high as stated.
- [d] Non-commercial development project at the ELETTRA synchrotron radiation facility in Trieste, with first description in L. Gori, *et al.*, Nuc. Instr. and Meth. A, 431 (1999) 338-346.
- [e] Overall-detector linear countrates actually achieved to date, including combined limitations due to electron multiplier, preamp+counting electronics, and external data handling system. Thus, the final column is not always equal to the product of the two next to it.
- [f] Figures for two different Quantar models are given. The per-channel and global count rates are always identical due to the nature of the detector.
- [g] Grayscale mode is an *integrated*-pulse detection scheme that exhibits significant response function nonlinearities. An alternate true pulse-counting mode ("black-and-white") results in dramatically reduced dynamic range (maximum count rates).

Table 6-1 Performance characteristics of the existing one-dimensional and two-dimensional multichannel detectors for electrons and soft x-rays. The LBNL Highspeed, 1st generation is the detector discussed here, with the 2nd generation currently under development. When considering the per channel countrates, the number of channels, and the resolving power, this detector represents a significant improvement over other available detectors.

Filename	Language	Purpose
DSP CODE		
DSP.C	ANSI C	Entry Point and Command Processing
DSP.H	ANSI C	Private DSP Definitions
DSP_DEFL.H	ANSI C	Shared DSP Command Definitions
READDATA.S	Assembler	Data Readout Routine
MAKEFILE	N/A	ASCII Make file for the AT&T Compiler for use with the <i>ndmake</i> utility
HOST PC CODE		
32LIBRAR.C DSP32.H	ANSI C	DSP Control and I/O Corresponding Definitions
DSP_DEFL.H	ANSI C	Shared DSP Command Definitions
DSP_IO_A.C DSP_IO.H	ANSI C	Detector Command Functions Corresponding Definitions

Table 6-2 Software Driver Source Files for the High-Speed Detector. This code provides the low-level functionality required to control the detector hardware. The DSP code is compiled into a single object file that is loaded onto the DSP and run in order to begin processing control commands. The PC host code provides a library of control functions to communicate with the DSP routine for control and data transfer purposes. This control software can be considered to functionally be part of the detector electronics. Additional software makes use of this control software to actually provide user interface, display, and disk storage facilities.

Fig. 6-1 Illustration of a multichannel detector installed on a hemispherical electron energy analyzer. The analyzer distributes electrons in a particular kinetic energy range $E_p \pm \delta E$ over the face of the detector in a very linear manner. Clearly parallel detection of many energies will be more efficient than detection in just a single energy channel, even when the analyzed energy is scanned over the spectral region of interest. In addition, parallel detection can allow “snapshot” spectra to be taken if $2\delta E$ contains the entire region of interest and the number of detection channels is sufficient to clearly resolve the spectrum.

Fig. 6-2 Pulse-height distributions (PHDs) for the chevron-stacked micro-channel plates used in this project. The distinct quasi-Gaussian peak in the distribution, separated from the large number of low-level pulses (noise), ensures that pulses due to actual events (“real counts”) can be unambiguously identified and separated from the background pulses. (a) A schematic of the system used to measure the PHDs. (b) A particular PHD illustrating the features of the distribution. The small peak apparent in all PHDs (channel ~ 130) is seen even in the $V_{MCP} = 0$ V case and is apparently due to a problem in the pulse-analyzer electronics. (c) A series of PHDs as a function of MCP and collector voltages. Each frame illustrates the effect of varying the collector voltage for a particular MCP voltage $V_{coll} = 0$ -20 V over the 50 μm gap between the MCP and collector)

Fig. 6-3 (a) Schematic layout of the high-speed detector, illustrating the various application-specific integrated circuits and other key elements. The components are all mounted on a circular ceramic substrate. Electrons are dispersed in energy across the long 40 mm collector axis. The 10 mm collector axis is aligned along the 25 μm wide constant-energy collector strips beneath the channel plate stack. (b) Cross sectional view of the channel plate and collector anodes.

Fig. 6-4 Schematic layout of the microchannel plate multiplier, the collector array, the amplification and counting chipsets and the external electronics: power supply and data transfer system. The custom built power supply serves dual purposes: the microchannel plate HV supply with over current protection; and the supply for SDC/DBC chip power and threshold voltages. The supply permits a reference voltage input, finally the analyzer retardation voltage, V_{ret} , upon which the entire system will operate. The data transfer module provides optical decoupling of the chip control lines from the PC and the clock signals used during data transfer. This module is coupled with a DSP specifically modified for this project that provides the ultimate interface to the PC for detector control and data storage.

Fig. 6-5 Photograph of the assembled detector system. The microchannel plates have not been mounted, leaving a clear view of the glass plate with the lithographically constructed collector (anode) array. The ASICs surround the glass plate and are better seen in the next figure. The entire multilayer ceramic substrate can be seen, including the electrical contacts at the outer rim that connect the detector components to the 3.5kV rated UHV feedthroughs.

Fig. 6-6 Photograph of the assembled detector system. The primary individual components are clearly seen: (a) collector (anode) array with MCP stack removed, (b) amplifying, pulse shaping/discriminating (SDC) chip, (c) digital buffered counter (DBC) chip. The gold wire bonds between the anodes and SDC inputs (as well as between the SDC and DBC) can be distinguished. The collector lines (d) without bonds are attached to chipsets on the opposite side of the collector plate.

Fig. 6-7 Schematic layout of the digital counter control and readout system for the double buffered counter (DBC) chips. The DBC chips are read out through a serial shift register, allowing only two UHV feedthroughs to be used for differential data transfer. An additional two lines are required to control buffer swapping, and shift register clocking. These lines are all referenced to the same potential as the MCP collector (2 kV greater than the analyzer focal plane potential) and so require optical coupling of the digital lines to the DSP and PC. The transfer hardware automates the transfer of a single counter value (16 bits) at a time, while the DSP controls the overall readout by signaling for and storing these 16 bit words. Additional real-time data processing as well as the integration (dwell) timing of the counters is performed in the DSP. The host PC initiates procedures in the DSP and transfers processed data from the DSP for further processing, display, and/or storage.

Fig. 6-8 DSP dwell time calibration. The high degree of linearity here simply indicates that the DSP software can reliably provide the timebase for channel integration or dwell in the system. Accurate accumulation times are critical and host-PC polling of the DSP memory does not introduce measurable deviations to the software implemented timing loop. The slope of the line indicates that a dwell time of 15 msec requires 10000 timing loops in the DSP software, matching the expected value due to the loop instructions and the processor clocking.

Fig. 6-9 The mapping between readout position and physical collector position. The shift-register readout is performed through neighboring chips on each side of the detector and this does not represent the order of connection to channels across the collector strip. The direction of mapping within the chip depends upon which side of the collector the chip is bonded from. The chip number refers to its position in the shift register chain.

Fig. 6-10 The detector response as a function of countrate. A low-energy, variable intensity, electron flood gun source allows the measured countrates to be recorded as a function of incident signal strength. (a) The MCP wall current vs. flood-gun current which increases due to electron extraction from pore walls during the cascade multiplication. This is used to calibrate (b) the detector response function. The linear response up to approximately 1.3 MHz per active channel matches the expected limit of the pulse-processing chip (SDC). However, the loss of linearity at about 10 (ordinate units are in MCP wall current change as in (a)) when compared to the behavior of (a) in this range indicates that MCP limitations *may* be responsible for the cutoff. This per channel countrate corresponds to an overall countrate of about 1 GHz for a fully active 768-channel detector.

Fig. 6-11 Channel cross-talk test for the system. (a) A double-slit/mask is placed directly in front of the system with a slit width of about one collector strip ($25\ \mu\text{m}$) and a separation between slits of $0.5''$. (b) Significant crosstalk counts in channel "0" appear in only the immediately neighboring channels "-1" and "+1" at about the 3.5 dB level, and the Gaussian FWHM is only about 1.5 times the channel pitch at $75\ \mu\text{m}$. Crosstalk may arise due to charge pulse blooming between the channel plate back-end to collector strip, or capacitive coupling between neighboring collectors or SDC channels.

Fig. 6-12 First genuine experimental spectrum taken with the detector in “dithered” collection mode. In this mode, missing/dead channels do not affect the final spectrum, other than a corresponding overall loss in final spectrum count. The detector was installed in a Gammadata Scienta ES200 electron energy analyzer and the excitation was provided by an unmonochromatized AlK α x-ray anode. No digital noise filtering has been performed on this spectrum, but the degree of statistical noise in the spectrum is likely due to low order bit errors in the electronics.

Fig. 6-13 Additional survey spectrum taken with the detector. This shows W and Ta 4*d* and 4*f* peaks from the W crystal and the Ta retaining clip. (a) High order bit errors produced in the DBC chip or data transfer have been systematically eliminated, while low order bit errors are likely to be responsible for the apparent enhanced statistical noise in the spectrum. (b) The same spectrum without digital noise correction.

Fig. 6-14 Low kinetic energy scan of the W crystal, biased at -600 V in order to permit measuring the full secondary electron spectrum.. In this region, elastically scattered electrons tend to pile up in the spectrum, resulting in very high countrates. This spectrum represents the highest countrate obtainable with the x-ray source used for initial the tests and there is no evidence of saturation. At these countrates, all bits are likely to be active, so the digital noise is significantly less obvious and appears as low-level noise in the final spectrum rather than large spikes.

7 Conclusions and Future Directions

In this dissertation we have explored a new phenomenon, that we have termed multi-atom resonant photoemission (MARPE), in which photoemission from a given core level in a multi element system is influenced by the presence of another more deeply bound energy level in another element. The experimental evidence for and theoretical treatment of MARPE were discussed in Ch. Four. For the specific case of O 1s emission from MnO in the vicinity of the Mn 2p resonances treated here, a microscopic theory of the resonant process has been developed, as first discussed elsewhere [1]. This microscopic theoretical model, which is based on an extension of standard single atom resonant photoemission, is found to predict the experimental results very well. The model should also be capable of describing such core-core interatomic resonance effects in the intensities and angular distributions in photoemission from free molecules [2], as well as with straightforward generalization also to other recently observed valence-core interatomic resonance effects [3]. This theory can also be simply extended so as to apply to x-ray emission.

We have also found that the MARPE effect may be considered in terms of classical x-ray optical theory using experimental optical constants and that this theory reproduces experiment quite accurately. In future work, it will be of interest to study systems in which this more simple macroscopic optical treatment is not appropriate, and so only the microscopic theory may be used. It is theoretically predicted that this will occur in systems with more spatially dispersed resonating atoms such as in nanometer-scale objects and/or in free molecules. Here, MARPE should provide an element-specific probe of near-neighbor properties and many-electron interactions. The experimental and

theoretical approaches outlined in Ch. Four should provide a sound framework for such work, both for photoelectron and fluorescent x-ray emission.

Our work on MARPE [4] has directly stimulated several other groups to perform related experiments. Wang, *et al.*, [2] have studied MARPE-like photoemission from free molecules. In their experiment, angular distributions of photoelectrons emitted from S $2s$ and $2p$ in SF_6 molecules have shown a strong (5-15%) non-dipole contribution in resonance with the F $1s$ edge. These effects on angular distributions, which have also been studied in the context of our own MARPE work in solids, are perhaps related to the angular dependence seen in the MnO(001) MARPE data presented in Ch. Four, but it will require further experimental and theoretical work to fully understand this relationship.

By now, others have also performed MARPE studies very much like our own, including Kikas [5], in which a series of transition metal chlorides have been systematically studied for MARPE enhancements in the Cl $2p$ photoemission in the vicinity of the metal $2p$ absorption edge. These studies follow closely our own original work both in experimental method and final results, where the MARPE enhancement appears to closely follow the resonating absorption edge profile. We have found such absorption profile behavior in our own datasets to be associated with instrumental effects in the data collection, as discussed in detail in both Chs. Four and Five. With this in mind, we caution future researchers to take great care to avoid or correct for these sorts of instrumental effects in their own studies. For this work, the instrumental problem was in the nonlinear response of the detector system, a complication made especially acute in these measurements, as the dynamic range required for the measurement of MARPE scans is much broader than in much standard photoemission work.

In order to perform this experimental work, instrument control and data acquisition software has been designed and implemented by the author. This software, introduced in Ch. Three, has been important in automating the experimental work discussed in this dissertation, as well as other types of experiments that can now be more routinely performed with the Advanced Photoelectron Spectrometer/Diffractometer (APSD) endstation at the Advanced Light Source (ALS). The software has helped to make calibration of the detector response characteristics in Ch. Five relatively simple and has also been important as a component of the detector development project discussed in Ch. Six.

This detector development project addresses the sorts of performance problems noted in the present detector used for our MARPE research, namely the need for high countrate, multichannel detectors with a linear response over a broad dynamic range up to the GHz level and with sufficient spatial resolution. The detector corrections discussed in Chs. Four and Five provide a clear example of the need for improved detector technology to complement the current state-of-the-art in synchrotron light sources, such as the ALS. With the high-speed, large-dynamic-range, high spatial resolution detector that we have developed and presented in Ch. Six, we have demonstrated that detector improvements are clearly possible to a level that is indeed well matched to such light sources. In particular, the first prototype has 768 channels with a linear response range up to ~ 0.9 GHz and a single-channel resolution of ~ 75 microns. With continued development beyond the prototype level, this detector can clearly contribute significantly to the experimental capabilities in the surface science and synchrotron radiation communities and beyond.

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