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CORE LEVEL EXCITATION EFFECTS

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ABSTRACT

The recent availability of intense polarized radiation tunable over the range 20 - 150 eV enables several core levels to be excited. Several remarkable effects have recently been reported when core excitation thresholds have been reached. For example, an increase in yield of 50% was observed in GaSe at the Se 3d threshold ($\hbar\omega \approx 57$ eV). A considerable increase in photoemission intensity at 6 eV binding energy has been reported by Guillot et al. for Ni at the 3p threshold. We have made a very careful study using the CIS, CFS and EDC modes of photoemission spectroscopy of core threshold effects in Ni, Pt and GaSe. We find a modulation of the Ni Fermi edge emission as a function of photon energy which we attribute to a configuration interaction between $3p^5 3d^{10} 4s$ and $3p^6 3d^9 4s$ cf. Similar effects occur in Pt at the 4f threshold involving the configurations $4f^{13} 5d^{10} 6s$ and $4f^{14} 5d^9 6s$. Further, the line-shapes of the Pt and Ni upper valence band CIS's resemble those obtained by electron energy loss (ELS) and photoabsorption, all of which can be fitted theoretically to a Fano model. Emission from levels lying well below the Fermi level often has superimposed contributions due to incoherent effects which complicate the interpretation. In cases in which core levels are excited well above threshold, the CIS technique may be used to examine final states. Of particular interest is the possible consequent determination of adsorbate site geometry. We present data for 2p emission from a c(2x2) Na overlayer on Ni (001).

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I. INTRODUCTION

The availability of very intense synchrotron radiation, tunable over the range 20 - 150 eV and beyond,¹ permits the excitation of shallow-lying core states to be studied by means of photoemission spectroscopy. The phenomena of particular interest in the core level excitations can be described generally as final state effects. In this report we focus on two distinct kinds of effects, namely those occurring at the threshold for core level excitation and those occurring at higher energies. We present experimental results exemplifying these effects in a number of systems including Ni(001), Pt(001), and GaSe(0001), and the overlayer system Na on Ni(001).

The experiments were performed at the University of Wisconsin Synchrotron Radiation Center using the 240 MeV storage ring, Tantalus I. The radiation was dispersed using grazing incidence monochromators.^{2,3} The GaSe samples were cleaved in vacuum to reveal 8mm $\times$ 8mm basal surfaces. The Ni and Pt crystals were cleaned by standard sputtering/annealing techniques. The surface cleanliness and order was monitored by Auger spectroscopy and medium energy (3 keV) electron diffraction. The electrons were detected using a commercial cylindrical mirror analyzer which has been modified to restrict detection to either a $\pm 2^\circ$ or $\pm 6^\circ$ aperture.

II. CORE THRESHOLD EFFECTS

If radiation of sufficient energy to excite a core level is incident upon a sample there will be more than one final configuration

to which the system may be excited. For example, if Pt in its ground state configuration $4f^{14}5p^65d^96s$ is excited by photons of energy $h\nu > 72$ eV, two final configurations, $4f^{13}5p^65d^{10}6s$ or $4f^{14}5p^65d^86s$ ef, can be reached by direct photoexcitation. Due to a configuration interaction between these states, the final state must be taken to be an energy-dependent superposition of the two configurations. The consequence of the coherent superposition of these states is to produce interferences⁴ which have been observed in ELS and photoemission spectra.^{5,6} In Figure 1a, two indistinguishable decay channels whereby the coherent interference effects are produced are indicated by the solid and dashed lines. This type of decay has also been referred to as direct recombination.⁷

In contrast to this coherent decay is the ordinary Auger decay mechanism as depicted in Figure 1b. Although this is another decay channel for the discrete core excitation, the final state which contains two valence band holes is distinct from that for direct valence band excitation so, clearly, interferences do not arise: the Auger emission simply adds incoherently to the direct emission. In the present discussion the terms coherent and incoherent are limited to the relationship of the discrete core excitation and its decay products to the direct valence band emission.

Experimentally, the core threshold effects are characterized by modulations in the emitted energy-resolved photocurrent as the photon energy is swept past the core excitation threshold. The coherent and incoherent effects may frequently be distinguished by the line shape

of the modulation and by the range of kinetic energies at which the enhanced emission occurs.⁷

GaSe

A remarkable enhancement (~50%) in the total photoyield occurs in GaSe at the Se 3d core threshold⁸ and is shown in Figure 2. Williams et al.⁹ had previously observed the effects of core hole decay following excitation of the Ga 3d level to two narrow conduction bands below the vacuum level. Similar but stronger effects are evident at the Se 3d excitation threshold. The character of the observed enhancement was established by taking photoemitted energy distribution curves (EDC's) in the region of the enhancement. Figure 3 shows two such EDC's, plotted with respect to initial state energy. The photon energies of 54 eV and 57 eV correspond to just below the threshold and on the peak of the observed yield enhancement, respectively. The difference curve gives the energy distribution of emitted Auger electrons. That these are Auger electrons can be confirmed by taking difference curves between the 54 eV EDC and enhanced EDC's at other photon energies. Then the peak of the difference curve is seen always to have the same kinetic energy. The energy level diagram, Figure 4, indicates that the primary Se 3d core excitation is to a conduction band state ~3 eV above the VB maximum (VBM).^{9,10} The width of the distribution is about twice that of the VB, or 16 eV.

Platinum and Nickel

In these systems the observed decay was of the coherent type, as

shown in Figure 1a, where the initial core excitation is to a final state just above the Fermi level. The interferences were most readily observed by measuring the emission at a variable kinetic energy corresponding to a fixed initial (or binding) energy as the photon energy was swept across the core threshold. This is the CIS (constant initial-energy spectra) mode of photoemission spectroscopy. Figure 5 shows a CIS for Pt in the region of the 4f core threshold. This plots emission intensity vs. photon energy of a point in the 5d valence bands about 0.5 eV below the Fermi level.

It clearly shows the modulation characteristics of an interference phenomenon. It can be shown theoretically¹¹ that the photoemitted intensity modulations should resemble the absorption coefficient. On the same figure are plotted the behavior of the absorption coefficient and electron energy loss at the same core threshold.¹² The behavior is indeed the same in each case and confirms the interpretation of the latter work.

In Figure 6b (upper curve) we show a similar CIS for Ni which clearly shows an interference effect at the 3p threshold. The apparent doublet has a splitting of 1.8 eV and so is tentatively identified as being due to the spin-orbit splitting of the Ni 3p core. The platinum curve (Figure 6a) is reproduced for comparison. The lower curve in both sets is a CIS taken at an initial energy -7 eV and -6 eV for Pt and Ni, respectively. These energies correspond to the equivalent initial energies at which incoherent Auger emission occurs at onset. Guillot et al.¹³ previously reported emission intensities for Ni of

the 6 eV binding energy peak. The lineshapes of the latter CIS's are similar to each other and different from those taken near E_F . At these deeper initial energies strong incoherent Auger effects occur. Further since these remain at fixed kinetic energy while the analyser remains at fixed binding energy, such spectra contain contributions from both distributions.

III. PHOTOELECTRON DIFFRACTION FROM Na C(2x2) ON Ni(001)

When electrons are photoexcited to kinetic energies in the range up to ≈ 100 eV, they may be expected to show diffraction effects in the final state in analogy with LEED. The possibility of using core photoelectron diffraction as a surface structure probe has been considered in a number of works.¹⁴⁻¹⁷ In photoelectron diffraction one is interested in photoexcited electrons which are scattered by neighboring atoms and then emitted into a small solid angle. It is convenient to choose a core level as the initial state because of the constancy of the initial state energy and the location and identity of the emitting source are clearly defined.

A significant advantage over LEED is that long range order is not required so as to produce discrete diffracted beams to measure. It is assumed, however, that all the emitting centers occupy identical sites. Photoelectron diffraction is dominated by forward scattering and so differs from surface extended absorption fine structure (SEXAFS)^{18,19} in which a spherical average over all backscattered beams is taken to derive the nearest neighbor distance.

So far two experimental approaches have been applied to the study of

photoelectron diffraction. First, azimuthal variations in the amplitude of the core emission at fixed kinetic energy have been studied for Na and Te overlayers on Ni(001), for In Se and for oxygen overlayers on Cu(001).²⁰⁻²² Second, core emission intensities in a given direction have been measured as a function of photon energy for Se on Ni.²³ Both techniques have shown photoelectron diffraction effects but at this stage their relative merits have not been assessed.

In the present study of the Na-Ni system, the diffraction effects were observed in the emission from the Na 2p core. This system was chosen since it has been thoroughly investigated using LEED and the site geometry and the phase shifts necessary for calculations are well known.²⁴ A CIS was taken in which the initial energy was set at the core level binding energy. Since the Na 2p core level at -31 eV is superimposed on a relatively large background of secondaries, the background was removed by running parallel scans on each side of the peak and subtracting the average from the peak emission. Figure 7, the upper curve, shows such a CIS. The general trend, as expected from atomic cross section considerations, is of decreasing amplitude with increasing photon energy. Superimposed on this monotonic decrease, however, are low amplitude oscillations caused by final state interferences which may provide surface geometrical information. These data are compared with a calculation by Li and Tong²⁵ which assumes that the Na atom sits in a c(2×2) hollow site at a distance of 2.23 Å from the Ni surface layer (Figure 7, lower curve). Their two-step model involves photoexcitation followed by scattering using a time-

reversed LEED function, and predicts peak positions more accurately than peak intensities. Indeed a good correspondence is obtained for the peak positions as shown by the vertical dashed lines. Due to the magnitude of the inelastic peak at low kinetic energies, it was not possible to measure accurately the 2p emission in the energy range 10 eV above threshold. Also, Auger emission coincided with the peak at photon energies around 90 eV making it difficult to derive the peak. However, in regions where the background variation was less violent, even in the region of the Ni 3d excitation, the averaging technique worked well.

IV. DISCUSSION

Final state effects which accompany core excitation contain information about the electronic and atomic structure of the emitting surface. Because of its tunability and wide range of photon energy, synchrotron radiation allows these effects to be studied conveniently by photoemission methods. The possibility of detecting and locating empty conduction band states which lie below the vacuum level has already been noted in reference 9 and references cited therein.

The energy distribution of the decay products and the detailed lineshape of the CIS spectrum allow one to distinguish between the decay processes depicted in Figure 1. In the experiments reported here, the GaSe showed evidence for the ordinary Auger process but none for the coherent decay, while the Ni and Pt systems showed both. In this connection the presence or absence of the coherent decay mechanism should provide useful information about the relative symmetry of the final states

through the possible vanishing or non-vanishing of the configuration interaction matrix elements.

For surface science, perhaps the most important potential for core level photoemission spectroscopy is the determination of surface structure by means of photoelectron diffraction. This application is particularly important for systems where LEED is inapplicable because of insufficient long range order. That photoelectron diffraction does in fact work in such circumstances has been demonstrated experimentally.²⁶ The results we have presented for Na on Ni as well as the investigations of others show that the photocurrent modulations agree qualitatively with those calculated for systems of a known geometry. Which of the variations of this technique will work best and the extent to which an unknown system can be solved by such means will undoubtedly become clear in the progress of future experimental and theoretical investigations.

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FIGURE CAPTIONS

1. a) Schematic illustration of the coherent decay of a core hole.
The emitted electron kinetic energy is a function of the photon energy.
- b) Schematic illustration of the incoherent decay of a core hole, the product being an electron of fixed kinetic energy, independent of the incoming photon energy.
2. The photoelectron yield of GaSe in the region of the Se 3d core threshold.
3. A comparison between two EDC's for GaSe, one before and one on the resonance, showing the kinetic energy distribution of the enhancement.
4. Energy level diagram for GaSe.
5. a) CIS for a Pt(100) crystal at an initial energy 5 eV below ϵ_f .
- b) Photo absorption spectrum from Pt foil reproduced from reference 22.
- c) Electron energy loss spectrum obtained by reflection of 500 eV electrons from a Pt(001) surface (after Reference 22).
6. a) CIS plots for Pt at initial energies 0.5 and 7 eV below ϵ_f .
- b) CIS plots for Ni at initial energies 0.5 and 6 eV below ϵ_f .
7. a) Photoemitted intensity (above the secondary background) of the Na 2p core level for a c(2×2) Na overlayer on a Ni(001) surface in normal emission. The radiation was incident in the (010) plane, the electric vector of the incident radiation being 47.7° from the sample normal.
- b) Calculation after Reference 23 for the geometry described in a).

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7