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DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

MAGNETISM AND MOLEUCLAR INTERACTIONS AT SOLID SURFACES

Final Report
for Period
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ABSTRACT

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Photoemission extended x-ray absorption fine structure, or PEXAFS, has been developed as a new technique for determining the atomic structures of surfaces and adsorbates on surfaces. PEXAFS has several unique advantages over other EXAFS methods that should make it attractive for use by other surface scientists. We have applied it to studies of the oxidation of technologically important polycrystalline and single crystal materials, aluminum, iron, manganese and manganese compounds, nickel and silicon carbide and of the promotion of oxidation by minute amounts of potassium. In the case of aluminum, for example, PEXAFS made it possible to determine the structural changes associated with the evolution of various oxide phases depending on oxygen exposure and temperature. Even bulk and surface plasmon-loss peaks were used for the first time to obtain PEXAFS. The electron spin polarized version of this technique, called SPEXAFS, has important potential for providing key information about the spatial dependence of magnetic correlations in solids. The original goal of this program was to develop and apply SPEXAFS. Preliminary results were obtained on the antiferromagnets manganese fluoride and manganese oxide but must be confirmed before the effort can be considered successful.

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The grant period of this final report is June 1, 1984 to August 31, 1989. The research program actually started, however, with a prior DOE grant initiated June 1, 1981, that made it possible to build the necessary UHV facilities and start the experimental program.

The goal of the original program was to study magnetic correlations in solids by means of a technique invented by Dr. Rothberg called SPEXAFS, spin polarized photoemission x-ray absorption fine structure. He described this technique and the related one of spin polarized photoelectron diffraction in "A New Technique for Studying Magnetic Order and the Spin Dependence of Electron Scattering by Means of Photoemission", J. Mag. Magn. Mat. 15-18, 323 (1980).

Practically everything about SPEXAFS was new, and it had to be shown first that, indeed, EXAFS could be measured by counting directly the photoelectrons emitted from the absorber atoms. This was achieved for polycrystalline materials during the first year of the subject grant period. The non-spin-polarized version of photoemission EXAFS is called PEXAFS.

The creation of the PEXAFS technique is the most significant result of the program so far. Its many advantages compared with other EXAFS techniques will be discussed briefly below; some of these advantages are unique. Its principal disadvantage is that vacuum is required, but this is necessary for most surface studies anyway. As the potential of PEXAFS becomes better understood by the surface science community it should be used widely.

The advantages of PEXAFS include the following:

- (1) Outer core levels as well as inner core levels may be used. Other methods suffer from overlapping fine structures from closely spaced absorption edges. Since photopeaks do not cross each other as the photon energy is varied, PEXAFS does not have this limitation. Auger electrons, since they have fixed kinetic energies, can cross photopeaks and may or may not be a problem. Auger electrons from outer core levels will often have energies smaller than the kinetic energies of photoelectrons in the EXAFS region, that is, above about 50 eV, and will not appear in the data.
- (2) All elements except H and He have low energy core levels and since photopeaks never cross, materials with more combinations of elements may be studied.
- (3) VUV light may be used so the range of photon energies usable for EXAFS is greatly extended. In principle almost any beamline with a monochromator scanning a few hundred eV can be used.
- (4) More than one element in a material may be studied with the same monochromator and more than one peak of an element.
- (5) The technique has high surface sensitivity due to the short

electron mean free path. In our work electron kinetic energies have been such that mean free paths were near their minima of 5-10A. Other nominally surface sensitive methods often detect signals from depths of 100A or more.

(6) Various features of the photoelectron spectrum may be used to obtain EXAFS and thereby extract additional structural information. Thus we reported the first measurement of EXAFS using surface and bulk plasmon-loss photopeaks in the system aluminum plus oxygen. It was possible to determine that we observed extrinsic plasmon production, that is, after the production of the photoelectron and not simultaneously as would be the case for intrinsic production. Since the plasmon-loss photoelectrons are produced roughly twice as deep in the material as the elastic photoelectrons it was possible to probe the bulk as well as the surface regions.

(7) The technique has chemical sensitivity, so the atomic structure may be studied around a given element in different chemical environments in a single sample. Chemical interactions often shift core binding energies by resolvable amounts, and both the shifted and unshifted photopeaks may be used to obtain PEXAFS.

The chemical sensitivity of PEXAFS is probably its most valuable aspect. We have used it to study the oxidation of aluminum as a function of oxygen exposure and temperature, of iron, and obtained preliminary results for nickel and silicon carbide. Most recently, after the termination of the grant, we have studied the tremendous increase in oxidation produced by even fractional monolayers of potassium. Because of the unique capabilities of PEXAFS it was possible to obtain EXAFS structural information for each of the different atomic species present at the surface. For example, in the case of Al+K+O the Al 2p, O 2p and K 3p photopeaks were used. Information of this kind is essential to a proper theoretical understanding of oxidation, catalysis and surface molecular interactions in general.

In 1988 we demonstrated clearly that PEXAFS may be applied successfully to single crystal surfaces also by determining the Cl-Ni interatomic distance of Cl on Ni(111) using both PEXAFS obtained with use of the Cl 1s photopeak and surface EXAFS obtained using the Cl Auger electrons. The angle averaging provided by our cylindrical mirror electron energy analyzer was sufficient to eliminate photoelectron diffraction effects.

The ability to study single crystal surfaces is clearly important, and we have since investigated the oxidation of Al(111), Fe(100), and SiC(100) and determined that the reconstruction of the Ni(110) surface produced by potassium is a missing row structure.

To support this program within our laboratory at Stevens we also conduct structural studies using electron energy loss fine

structure (EELFS) measurements. This technique is not nearly as useful as PEXAFS, but at least it can be carried out at home without the need for synchrotron radiation. One of the outcomes of this work has been a better understanding of the limitations of the EELFS method, which at times has lead to contradictory results in the literature.

The original goal of this program to carry out spin polarized SPEXAFS studies has not been achieved satisfactorily. Spexafs measurements have been made on the antiferromagnets MnF₂ at 300 K and MnO at 93 K, which is below the Neel temperature of 115 K, and at 300 and 725 K. The MnO data show similarity to the expected behavior: the electron spin up and spin down EXAFS at 300 K are very similar in shape but differ in phase, and at 93 K they differ in shape also. The 3p and 3s EXAFS at 93 and 300 K yield the MnO structure, but at 725 K there seems to have occurred a structural change. The MnF₂ and MnO results agree at 300 K and are interpreted as due to a difference in absorber atom phase shift for electrons of spin up compared with spin down arising from the exchange interaction in the absorber. The results should be duplicated before they can be considered convincing evidence of spin polarized EXAFS.

SPEXAFS has been difficult to observe for a number of reasons. For several years the reliability of the VUV ring at NSLS was too poor to permit the necessary statistical accuracy, and even when all the equipment functions normally well it still takes longer to do SPEXAFS than PEXAFS. The research program also has always had to take into account the need for graduate students to complete their doctoral research in reasonable amounts of time. For this reason PEXAFS was developed as a parallel program which, fortunately, is significant in itself. During the period of DOE support three students have earned their PhD degrees and gotten good jobs in surface materials science, and two more students who began their training in this period will complete their dissertations within a few weeks. The average rate of production of PhD's in this program is, thus, better than one per two years.

The SPEXAFS measurements were made on evaporated thin films. Now that it is known that single crystals may be used the materials preparation and characterization might be improved in future work. The appearance of intense sources of circularly polarized light at some synchrotron radiation facilities opens up many more experimental possibilities for studying magnetism and for applying the principles of SPEXAFS.

Journal Publications

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G.M. Rothberg et al., "Photoemission EXAFS Study of (R3XR3) Chlorine on Nickel (111)", Bull. Am. Phys. Soc. 34, 988 (1989)

Papers in Preparation for Refereed Journals

S.T. Kim et al., "Surface Structure of Clean Aluminum and Aluminum Oxide Studied by Photoemission EXAFS".

S.T. Kim et al., "Chemically Sensitive and Plasmon Loss Extended X-Ray Absorption Fine Structure Applied to Clean Al and Al-O Films".

S.T. Kim et al., "Electron Energy Loss Fine Structure of Ni, O/Ni and CO/Ni".

M.S. Oh et al., "Photoemission EXAFS Study of Potassium on Ni(110)".

G.M. Rothberg et al., "Photoemission EXAFS Study of (R3XR3) Chlorine on Nickel (111)".

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