

16-Molecular Structure Determination by Methods other than Diffraction

16.01 – NMR/EXAFS/XANES

MS-16.01.01 New Insights into the Structure and Reactivity of Biological Molecules Using X-ray Absorption Spectroscopy

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Structure and function in biological (as well as other) materials is often determined by an "active site" which commonly involves transition metals in a single site or in clusters. Accurate electronic and geometric structural information of such a site can provide the means to understand in detail how the material carries out a reaction. X-ray absorption edge and extended fine structure (EXAFS) provides a very sensitive way to probe a selected "active site" and obtain accurate structural details under physiologically-relevant and non-crystalline conditions.

This talk will review the basic principles underlying the use of X-ray absorption edge and EXAFS to obtain such information and compare these results with those that can be obtained from crystallography. New approaches to the quantitative analysis of EXAFS data will be described. The use of these methods to investigate several biological and non-biological systems will also be given. Included will be recent results on the nitrogenase enzyme system which illustrate the ability of EXAFS to probe longer-range order. Other examples will include Cu and Fe-containing proteins and non-biological materials.

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MS-16.01.02 DIFFRACTION ANOMALOUS FINE STRUCTURE (DAFS): UNIFYING THE SENSITIVITIES OF DIFFRACTION AND XAFS INTO A SINGLE NEW CRYSTALLOGRAPHIC TECHNIQUE. by Larry B. Sorensen, Department of Physics, University of Washington, Seattle, Washington 98195-USA

The simple theory and potential applications of a new x-ray structural technique, Diffraction Anomalous Fine Structure (DAFS) which combines the short-range order sensitivity of x-ray diffraction with the short-range order sensitivity of x-ray absorption, will be presented. Because of its combined long-range and short range sensitivities, DAFS is potentially a powerful adjunct and extension of conventional diffraction and XAFS methods for polyatomic and spatially modulated structures. For these systems, DAFS provides: (1) Spatial, or components, selectivity whenever different spatial regions, or components, of the sample produce diffraction peaks at separate locations in reciprocal space. Then the local atomic structure of each region, or component, can be measured using one of its characteristic diffraction peaks. (2) Site selectivity from DAFS crystallographic intensity measurements for inequivalent Bragg reflections. Since the DAFS signal from each Bragg peak is a linear combination of the DAFS contributions from the individual sites, the sites can be separated by resolving the individual contributions. Experimental demonstrations of each sensitivity will be presented.

MS-16.01.03 ON THE COMPLEMENTARITY BETWEEN MAGNETIC CIRCULAR X-RAYS DICHOISM AND MAGNETIC RESONANT SCATTERING By G. Schütz, Experimentalphysik II, Universität Augsburg, Germany, S. Stähler*, Fak. für Physik, E12, Technische Universität München

The availability of intense synchrotron light with well defined polarization characteristics led in the last decade to the development of powerful new methods to study the magnetic aspects of the electronic structure of solids using x-rays.

Two of these methods, the measurement of magnetic circular x-ray dichroism (MCXD) at inner-shell absorption edges and the study of magnetic resonant scattering with linearly polarized x-rays, are based on the same physical phenomenon namely the difference in the absorptive part of the scattering amplitude for right and left circularly polarized photons in magnetic matter.

The origin of this effect is explained in simplified pictures to demonstrate that the experimental data contain new symmetry- and element-selective information on the local spin and orbital moment and on the magnetic structures.

The principles, potentials and limits of the experimental techniques of these methods are outlined and typical results are discussed in terms of the complementarity of magnetic circular x-ray dichroism and magnetic resonant scattering studies to address a manifold of ferro(i)- and antiferromagnetic materials e.g. single crystals, polycrystalline (powder)-samples, (diluted) alloys, surfaces and thin layers.

MS-16.01.04 Structure Determination of Materials Using Non-Crystallographic Techniques

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The appropriate method for the structural determination of real materials is dependant on the degree of long range order present within the sample. If such long range order is absent, conventional single crystal or powder diffraction techniques are no longer applicable and X-ray Absorption Fine Structure (XAFS) spectroscopies offer some of the most versatile methods of probing the fundamental local chemical structure. They have been used, for instance, in conjunction with Magic Angle Spinning NMR (MASNMR), to probe the environments of alkalis and exchanged ion-exchanged cations in oxide glasses. Such direct determinations of local atomic structure point to specific microstructures supporting the particular ion transport characteristics of these materials. In metal oxides like LiNbO₃, XAFS measurements pinpoint the environments of particular impurities like Fe³⁺ and Co²⁺, thereby helping to explain the non-linear optical properties of these materials. There is considerable scope for extending these techniques to follow the development of order from the disordered state. We describe the recent work in which glancing angle fluorescence XAFS has been employed to chart the local structures of ion-implanted dopants in amorphised silicon during subsequent epitaxial regrowth. Fluorescence XAFS has also been used to

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follow the changing environments of nucleating sites during the formation of glass ceramics. In this context, Small Angle X-ray Scattering (SAXS) can give additional information on the intermediate nm scale, revealing details on the microstructures underlying crystallite growth. It is clearly valuable wherever possible to monitor XAFS and/or WAXS/SAXS in conjunction with X-ray diffraction in order that the degree of long range order is ascertained at each stage. This paper will discuss the various non-crystallographic X-ray techniques for obtaining structural information from disordered materials, describing typical experimental configurations and describing the latest developments where these techniques are being combined to facilitate novel twin detector experiments in which the varying degrees of order in a material can be characterised *in-situ*.

MS-16.01.05 Monolayer dispersion model of oxides and salts on supports as well as its EXAFS evidences

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The dispersion phenomenon of salts and oxides on supports with large specific surface area has been investigated widely. Quite a number of models, such as, forming surface compound (SC), cluster (CR), microcrystalline (MC), multilayer dispersion (MUD), solid solution (SS), and so on have been proposed already. But unfortunately, up to date, many problems about structure can not be well explained yet.

Recently, on the basis of investigation upon great deal of these systems, we find a interesting and quite common phenomenon that salts and oxides can disperse spontaneously in monolayer on the surface of a support and it have been confirmed by XRD, XPS, ESR, AES, ISS, SIMS, TEM, LRS, IR, UV, and Mossbauer spectroscopy etc. The principle has been applied successfully in the preparation of some commercial absorbents and catalysts.

The monolayer dispersion model takes into consideration of the possible effect of dispersion condition, (such as, loadings, surface behavior of support and atmosphere) on the structure, but most other models assume that the ions dispersed have its definite and characteristic structure. If the dispersion structure is described by coordination polyhedra of interested ions and their connection or distribution ways. Thier differences might be summarized as follows:

dispersion models	definiteness of polyhedra	connect. of polyhedra	effect on loading	coordination of surface behaviors
MOD	not so marked	not so marked	marked	marked
MUD	marked	marked	not marked	not so marked
SC	marked	marked	not marked	not so marked
CR	marked	marked	not marked	not so marked
MC	marked	marked	not marked	not marked
SS	marked	rather marked	not marked	not marked

For most spectroscopies, it is very difficult to recognize structurally the dispersion state as a monolayer among above models. But for the EXAFS, it becomes much easier, since EXAFS can give out plenty of information about chemical bonds and geometry distribution of atoms around interested ions. Much EXAFS structure information in this paper about NiO/ γ -Al₂O₃, CuBr₂/ γ -Al₂O₃, CuCl₂/ γ -Al₂O₃, NiSO₄/ γ -Al₂O₃, and etc. shows that monolayer dispersion is a spontaneous and chemical process and the monolayer dispersion state has particular coordination features. The coordination state of monolayer dispersion is close correlative and changeable with the dispersion condition. It is very different from MC, CR, MC and other dispersion models, but well agrees with the monolayer dispersion model.

Reference

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MS-16.01.06 EXAFS STUDY ON THE LOCAL STRUCTURE IN POTASSIUM TANTALATE. By Y. Nishihata*, O. Kamishima, A. Sawada and H. Maeda, Faculty of Science, Okayama University, Japan, and H. Kasatani and H. Terauchi, School of Science, Kwansei Gakuin University, Japan.

Many cubic perovskite crystals undergo phase transitions, where they transform to slightly distorted structures from the ideal perovskite structure. In KTaO₃, no phase transition occurs since long-range ordering of dipole moment is suppressed by the quantum fluctuation at very low temperatures. It was reported that the dielectric constant increases to a saturated value with decreasing temperature below 100 K (Samara & Morosin, 1973). An atomic vibrational analysis by the neutron diffraction implies that the mode of KTaO₃ at RT is of the Slater type (Harada, Axe & Shirane, 1970). A second-harmonic generation has been reported, although KTaO₃ is a centrosymmetric crystal (Vogt & Uwe, 1984). The purpose of the present work is to study a change of local structure from the ideal perovskite structure using the EXAFS technique.

EXAFS (Extended X-ray Absorption Fine Structure) measurements near the Ta-L_{III} edge of KTaO₃ at RT, 160, 80 and 32 K were carried out using the synchrotron radiation of the Photon Factory at the National Laboratory of High Energy Physics (KEK, Tsukuba). Figure 1 shows the x-ray absorption spectrum at 32 K. A well-defined EXAFS signal is found up to the Ta-L_{II} edge. The EXAFS function $\chi(k)$ was extracted from the spectrum in the usual way (Maeda, 1987). Figure 2 shows the radial structure function around the Ta atom at 32 K calculated by Fourier transform of $k\chi(k)$ in the range of $3.5 \leq k \leq 17.5 \text{ \AA}^{-1}$. The correction of phase shift is not taken into account. These three peaks can be assigned to O, K and Ta atoms, respectively from the crystallographic values obtained by the diffraction data. The broad distribution of the O atom is notable in comparison with that of the Ta atom. This broad distribution at very low temperature results from a large Debye-Waller type factor or a displacement of Ta atom from the center of oxygen octahedron. We use the Fourier filtering technique and a non-linear least-squares fitting method to determine the structural parameters. Preliminary result shows that the EXAFS signal $\chi(k)$ cannot be reproduced well by a 1-shell model because of the beat of $\chi(k)$. If we take the model that the Ta atom displaces from the center of oxygen octahedron along <001> directions; the peak of the O atom may consist of three shells and the peak of the K atom two shells. We will evaluate the direction of the atomic displacement and the distance from the center of the oxygen octahedron by the least-square calculations under restricted conditions.