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Title and Subtitle: **X-RAY AND γ -RAY SPECTROSCOPY
OF SOLIDS UNDER PRESSURE**

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Summary of Progress

X-Ray and γ -ray Spectroscopy of Solids under Pressure

I. Introduction

This report briefly describes our studies of various materials at high pressures by means of x-ray and γ -ray absorption spectroscopy. High pressure provides a very effective means of studying materials. Virtually every property is altered from the color and crystal structure to the electrical and magnetic properties. The fundamental reason, of course, is that the quantum levels depend upon the atomic spacing so that both the electronic and vibrational structure is affected.

Synchrotron x-ray absorption spectroscopy, which probes materials on the microscopic level is quite well suited to high pressure studies. Moreover, since this field is still being developed, the ability to alter the microstructure of a material by means of high pressure aids in our understanding of the theory underlying the x-ray absorption spectra. Here we shall frequently refer to XAFS (x-ray absorption fine structure) which covers both XANES (x-ray absorption near edge structure) as well as EXAFS (extended x-ray absorption fine structure). As the studies here show, this technique is especially sensitive to valence states, electronic structure, atomic vibrations, bond lengths, coordination numbers and atomic rearrangement during phase transitions. It must be mentioned that during this three year report period we have only been able to obtain synchrotron beam time on three occasions. The first two of these runs, at SSRL, (Stanford Synchrotron Radiation Laboratory) were only marginally successful due to generally recognized problems with that facility. In the third run, at NSLS, (Brookhaven's National Synchrotron Light Source) conditions were better although the flux was less than SSRL and the beam line was not quite as well suited to high pressure methodology. Our x-ray "drought" shows signs of ending soon, however, with beam time awarded Spring 1990 at both facilities.

Gamma-ray absorption spectroscopy, the Mössbauer effect, which is somewhat com-

plementary to XAFS, is also well suited to high pressure science. It of course probes the effect of the solid state environment on a nuclear transition taking place in an atom or ion within that solid. This method then probes internal magnetic and electric fields, internal electron density at the nucleus as well as atomic vibrations. These quantities are generally sensitive to the valence state and local atomic environment, and changes such as those due to phase transitions. As described below we have initiated an important in-house Mössbauer study of hydrogen in iron.

II. XAFS Study of the Mixed Valence Compounds, SmS and SmSe

SmSe and SmS undergo pressure-induced mixed-valence transitions. In the mixed-valence region the Sm ions fluctuate between the 2+ and 3+ valence state on the time scale of the Debye frequency. They are usually considered to be homogeneously mixed valent where the Sm-chalcogenide ion pairs take a single average separation rather than a dynamically distorted distribution with two different stable positions corresponding to the two valence states of the rare-earth ion. We have used x-ray absorption spectroscopy to examine the transitions at pressures up to 75 kbar. The experiments were performed at the Sm L_{III} -, L_{II} - and Se K-edges at room temperature on both compounds. In order to reduce the thermal contribution to the dynamical motion of the ions, the measurements were also made on SmSe at 77 K. These latter measurements represented the first low temperature x-ray absorption spectroscopy measurements to be made as a function of pressure.

Changes in the Sm valence with pressure were determined from the structure of the Sm L-edges. Sm-chalcogenide pair distribution functions were obtained from the EXAFS spectra. In SmSe the EXAFS mean square relative displacement between the Se and Sm ion pairs is observed to have a maximum in the mixed valent region. This maximum is related to the possible existence of two closely spaced Sm-coordination shells. From least-squares fitting in k- and in R-space and from a beating analysis of the EXAFS phase we conclude that if the lattice does respond to the fluctuation in the valence, then the two

Sm-shells are separated by approximately $0.12\text{\AA}$. To obtain this result it was first necessary to know the backscattering amplitudes and phase shifts for integer-valent Sm. This was accomplished by first principles calculations based upon curved-wave theory.

III. X-ray Absorption of High T_c Superconductors

During this report period several experiments were carried out on the new superconductors. In one series we explored the pressure dependence of the EXAFS spectra of both $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, the "90K superconductor" as well as $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-y}$, the "40K superconductor." For the 90K material our analysis strongly suggests that the oxygen bridges between copper atoms bend with pressure. Strong beating among the Y, Ba and Cu shells makes the analysis complex, and the evidence of chain bending is mainly from reduction of the amplitude of the Cu-O-Cu multiple scattering amplitude. Further work is needed to confirm and extend these results, in fact we twice scheduled low temperature runs on both the 90K material and a non-high T_c material with reduced oxygen content. Beam time problems and delays have caused us to reschedule this important work into the spring of this year and on into the subsequent grant period. In the case of the 40K material, the data was easier to unravel. Again we infer that pressure causes the Cu-O-Cu bonds to bend from 180° to $164^\circ \pm 10^\circ$ at 90 kbar. This implies that with pressure the Cu-O octahedra rotate and the consequent change in the electronic structure should be included in any theoretical treatment. In addition an XANES study of the temperature and pressure dependence of spectral features on the high energy side of the edge jump showed that they were *not* due to Cu^{3+} in contrast to some published interpretations.

In a separate experiment, a grown crystal of the $\text{Cu}_3\text{Y}_2\text{BaO}_6$ was slowly cooled in oxygen to form a twinned single crystal of the 90K material. The crystal studied was several hundred microns on a side with the crystalline c axis oriented perpendicular to the large face. The crystal was studied in three known angular orientations to the incident flux and to the polarization vector of the synchrotron radiation. Superposition of the single crystal data for the various orientations in the proper amount reproduced the data for

the powdered material so that the single crystal data provides a look at just a subset of the possible neighbors of the absorbing copper atom. This work is being continued with oriented powders by E.A. Stern and co-workers.

In another series of experiments the 90K superconductor with 2 to 5% nickel substituted for the copper was studied. Data for both the Ni and Cu k-edges were collected. In the sample with 2% Ni, the sample was predominantly in the proper high T_c phase. The maximum solubility found in the nominal 5% phase was 4% with the excess precipitating out as NiO. The Ni atoms in the high T_c phase were found to have approximately five O neighbors at 1.95Å. The best fit gave approximately five Y next neighbors at 2.96Å. Although the Ni atoms have a first-neighbor environment of oxygen atoms somewhat similar to the Cu site, the more distant neighbor distances are quite different. It was concluded from both the XANES and EXAFS that most, if not all, of the Ni atoms do not substitute in either Cu site of the high T_c phase, but are in some defect site.

IV. Studies of ReO_3 , GeO_2 , and Related Materials: Emphasis on Rotation of Polyhedral Units and Focussed Multiple Scattering

We have successfully made bond angle determinations for the high pressure phase of ReO_3 using a state-of-the-art XAFS analysis package based on multiple-scattering theory. In this material the ReO_6 octahedra undergo a rotational transition above a pressure of about 5 kbar. We are also in the process of demonstrating the validity of a new multiple-scattering approximation that yields results as good as the exact treatment of the XAFS problem. Preliminary fits to the above data show promise. These analysis steps are also being applied to the similar NaWO_3 system, which undergoes a structural transition with increasing temperature related to the pressure induced transition in ReO_3 . Here our interest is on two effects present in this system to which XAFS is sensitive, changes in both Debye-Waller factors and bond angles.

A related study involved the pressure effect on 9% Nb in KTaO_3 . At ambient pressure the Nb atoms sit displaced from the center of the O_6 octahedra. It was deduced from

published electric field polarizability measurements that high pressure induces the Nb atoms to move on center. Our XAFS results seem to measure this transition directly, and although Ta k-edge data are difficult to analyze, because of the high energy, they appear to confirm the inferred transition. We have also performed a pressure study of α -quartz GeO_2 . Our observations were consistent with published neutron diffraction studies but go to significantly higher pressure. From such results we produced a pressure-versus-volume curve and parameterized it using the Murnaghan equation of state.

V. EXAFS Study of Metallic Copper

We have spent considerable effort measuring and analyzing the EXAFS of metallic copper as a function of pressure to over 160 kbar. We find that considerable care must be exercised both in the theoretical formulation of EXAFS and in the data analysis in order to make copper a useful pressure marker. Two approaches have been taken involving use of phase and amplitude analysis which turn out to give practically identical results. These are treating the first-shell k -space data using both the ratio method and method of parameter fitting with the help of published theoretically calculated phase shifts and amplitudes. We find that for our purposes only nearest-neighbor distances and second cumulants need be considered. With Cu as the calibrant pressures can be measured with better than 5 kbar accuracy. We have also examined two models of the pressure dependence of the second cumulant: 1) a correlated Debye model along with simple parametrizations of the isothermal equation of state and Grüneisen parameter, and 2) a model for the calculation of the nearest-neighbor distance distribution from an expansion to third order in the potential energy.

VI. XAFS Study of Amorphous Germanium

We have investigated the XAFS of amorphous Ge under pressures up to 89 kbar. Contrary to some reports from the literature we have not found a transition to the crystalline state at about 60 kbar. Analysis of the XAFS phases of this a-Ge and Cu, which was used

as a pressure marker, allows calculation of the bulk modulus at 1 bar, B_0 of the *bonds* (as opposed to the bulk modulus of the bulk material, which contains voids) and its pressure derivative, B'_0 . The former has been determined to be 30% greater than for crystalline Ge. Fair agreement was obtained with a published two- and three-body potential formalism.

VII. Phase Transition in Metallic Iron: Preliminary XAFS Results

Three years ago, using refined EXAFS techniques we succeeded in obtaining preliminary EXAFS measurements of the α to ϵ transition in metallic iron. Excellent measurements were obtained with our B_4C high pressure anvils and a soft epoxy medium. In this first attempt no marker was used as pressure calibrant so as not to increase the absorption at the low k-edge energy of about 7 keV. However it was clear from the spectra that we obtained pressures well beyond the transition, ca. 120 kbar. In fact using the data itself and published lattice parameters for the ϵ phase (hcp) we inferred a maximum pressure over 200 kbar, a record for this type XAFS cell. We have since been able to only attempt one further run during this report period. In that case a copper pressure calibrant was included to more precisely check if the pressures inferred from the iron outside the transition region were accurate. Good data below the transition was obtained before the experiment was terminated due to beamtime constraints. Continuing this experiment is one of the key series of studies we are proposing in the accompanying renewal proposal.

VIII. Hydrogen Absorption in Metallic Iron Studied via the Mössbauer Effect

Because of recent reports of a greatly enhanced solubility of hydrogen by iron at high pressures and temperatures, we have begun a series of Mössbauer experiments to examine the problem, *in-situ*. Utilizing our new Mössbauer spectrometer purchased with D. O. E. funds, spectra have been obtained at room temperature up to 130 kbar. We find that both the internal magnetic field and isomer shift are affected by the absorption of hydrogen which initially takes place somewhere above 30 kbar. Although iron hydride has been reported to have the double hexagonal crystal structural, the similarity of our results to

α -Fe suggest that that assignment should be reexamined. More details on this subject and its geophysical as well as solid state interest are given in the accompanying renewal proposal to continue this important investigation.

IX. Structural Transitions in Thallium Rhenium Oxide

The material ReTlO_4 undergoes subtle structural transitions at approximately 5, 19 and 97 kbar. This latter transition has been speculated to have a simultaneous valence change of the Tl ion from a charge of +1 to +3, with an accompanying change from +7 to +5 on the Re ion, by Jayaraman et. al. at AT&T Bell Laboratories. We have obtained this material from Jayaraman and carried out preliminary XAFS measurements to approximately 160 kbar, at the NSLS. The 97 kbar transition manifested itself as marked changes in the XANES of the L_{III} edges of both the Re and Tl ions. This work including future plans is described in more detail in the accompanying renewal proposal to continue this interesting problem.

X. Interatomic Potentials from High Pressure EXAFS

The EXAFS of three alkali halides (NaBr, KBr, RbCl) has been investigated as a function of pressure with emphasis on determining the second and third cumulants. Monte Carlo simulations using various interatomic potentials such as the generalized Huggins-Mayer formalism with optional 3-body potential term have been carried out. The calculated cumulants turn out to be quite model dependent. While our method of calculation is still CPU-time intensive and not yet suited for parameter-fitting, proper, we find that high pressure EXAFS data contain sensitive information on interatomic potentials and thus on elastic constants. We are planning on a simpler mathematical formulation of the problem in order to use our high pressure EXAFS data as a new probe for determining elastic constants.

XI. Publications

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- "Hydrogen in Iron at High Pressure: Mössbauer Studies," I. Choe, J.M. Brown, R. Ingalls, Y. Sato-Sorensen and R. Mills, *ibid*, 708.
- "Pressure Calibration in High Pressure EXAFS Experiments," J. Freund and R. Ingalls, Proceedings of the 12th AIRAPT International Conference, Paderborn, West Germany, (July 1989).

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- "XAFS Study of the Mixed Valence Compounds, SmS and SmSe at High Pressure," K. R. Bauchspiess, E. D. Crozier and R. Ingalls.
- "Focussed-Multiple-Scattering EXAFS Analysis of Bond-angle Changes in Perovskites," B. Houser, R. Ingalls and E. D. Crozier.
- "EXAFS of Alkali Halides under High Pressure and Interatomic Potentials," J. Freund, R. Ingalls, E. D. Crozier and J. M. Tranquada.
- "X-ray Absorption Study of the High Pressure Structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$," E. D. Crozier, N. Alberding, K. R. Bauchspiess, A. J. Seary, S. Gygax, R. Ingalls and B. Houser.

XIII. Reports and Presentations

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- "Hydrogen in Iron at High Pressure: *In-situ* Verification and Application to the Earth's Core," In-Jerng Choe, J. M. Brown and R. Ingalls, Am. Geophys. Union Conference, San Francisco, December 1989.
- "Structural Transition in $TlReO_4$ Studied via XAFS," R. Ingalls, B. Houser, E.D. Crozier and A. Jayaraman. American Physical Society Conference, Anaheim, California, March 1990.
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