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Title and Subtitle: X-RAY and Γ-RAY SPECTROSCOPY of SOLIDS UNDER PRESSURE

Principal Investigator: Robert L. Ingalls, Professor
Department of Physics, FM-15
University of Washington
Seattle, Washington 98195

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I. Introduction

This report briefly describes our studies of various materials at high pressures, in the last year, 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 are 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. During this report period we have been able to obtain synchrotron beam time from the Stanford Synchrotron Radiation Laboratory at a rate of approximately two weeks per year. Moreover conditions there have recently been excellent.

Gamma-ray absorption spectroscopy, the Mössbauer Effect, which is somewhat complimentary 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 surroundings, and to changes, such as those due to phase transitions.

II. XAFS Studies of Polyhedral Solids.

A class of materials which has attracted considerable attention is "polyhedral solids," that is, compounds which may be thought of as collections of molecular polyhedra linked together to form a crystal lattice. Interest in such materials is due to a common characteristic: structural phase changes in which the polyhedral units remain rigid while they buckle and twist in relation to their neighbors. Below we report further work on a member of this class, namely rhenium trioxide. Of more general interest are such materials in which additional atoms lie in the vacancies between polyhedra. The geophysically-important perovskites fall into this class. Such compounds not only undergo structural transitions similar to those of their simpler cousins but exhibit other interesting phenomena, such as ferroelectricity and superconductivity. Rubidium tungsten bronze, discussed below, falls into this category.

As discussed in previous reports, we have been examining the XAFS of the compressibility collapse transition in rhenium trioxide (ReO$_3$). In this case the ReO$_6$ octahedra undergo static collective rotational displacements starting at about 0.53 GPa. The main thrust of this work is to use a full multiple-scattering analysis to extract the relevant bond angle change through this transition. The FEFF program of our colleague, J. Rehr, et. al. allows for very good fits to the data, though the extracted rotation angles tend to be slightly higher than those determined by neutron diffraction measurements. We also find that the Re-O-Re atomic bridge in which the oxygen atom vibrates perpendicularly about a position collinear with the rhenium atoms yields an XAFS contribution indistinguishable from that of a static displacement of the oxygen. In order to obtain more precise determination of the necessary bond angles it has been deemed necessary to carefully analyze the results for the third coordination shell. With this goal in mind we have recently obtained state of the art measurements on this compound, taking full advantage of the excellent
beam conditions now available at SSRL. Analysis of this data is still in progress.

We have also measured the XAFS spectrum of the rubidium K- and tungsten L_{III}-
edges in rubidium tungsten bronze (Rb_{31}WO_{3}) as a function of pressure. The low pressure
phase of this material has a simple hexagonal structure, composed of layers of corner-linked
WO_{6} octahedra, arranged in hexagonal rings, six to a ring. Each octahedron is common
to two rings with each ring containing one Rb atom. The c-axis repeat length is the width
of a single layer. However, diffraction studies have failed to yield the coordinates of the
rubidium atoms within the hexagonal voids.

From our rubidium edge spectra we interpret the marked difference in the data at
atmospheric pressure and at pressures above 20 GPa as indicative of a structural phase
transition, which we find to be reversible. The main component in the radial distribu-
tion derived from the spectra corresponds to the oxygen near neighbors. At atmospheric
pressure the associated bond length is derived to be roughly 0.5 Å smaller than if the
rubidium were at the center of the hexagonal prisms. However above the transition it is
reduced another 0.4 Å. This indicates that not only are the rubidium atoms not at the
centers of the prisms, but that the transition is undoubtedly of the compressibility collapse
type, similar to rhenium trioxide above. In support of this interpretation, the spectra from
the tungsten edge spectra show that the WO_{6} octahedra do not compress appreciably but
rather must undergo some kind of rotation instead. This work is continuing.

III. Mössbauer Study of Sodium Nitroprusside.

Sodium nitroprusside, SNP, (Na_{2}[Fe(CN)_{5}NO]-2H_{2}O) is of special interest for several
reasons. It can be optically switched with blue coherent light into an extremely long-lived
metastable state at low temperature, and then switched back either with red coherent
light or by increasing the temperature. Of interest to Mössbauer spectroscopists is the fact
that it has a relatively large quadrupole splitting which exhibits very little temperature
dependence. Its isomer shift is one of the most negative of all iron compounds, and its line
width one of the narrowest. For these reasons is has been useful as a Mössbauer Doppler-
velocity calibrant and standard. The metastable state has been shown to produce a higher quadrupole splitting and less negative isomer shift, while the literature of twenty years ago shows high pressure and temperature causes the sample to change to a high spin Fe(II) state.

We have reexamined the pressure dependence on the Mössbauer spectrum in SNP using state of the art diamond anvil cell techniques. We find high pressure slightly increases the quadrupole splitting at a rate of 0.01 mm/s/GPa up to 10 GPa, and gradually lowers it again afterward. Meanwhile, the isomer shift is lowered at a rate of 0.008 mm/s/GPa, which is somewhat greater than the previous literature results. In contrast, however, we do not observe the claimed single-line component in between the lines of the normal quadrupole doublet. When using blue He-Cd laser light, normally for ruby fluorescent pressure calibration, we find the laser spot turns the sample black above a pressure of 13 GPa. In fact the whole sample changes from transparent brownish to black above about 14 GPa. Above 20 GPa, a second spectral component with a smaller splitting and more positive isomer shift appears and grows in relative intensity. This spectral component resembles that for the nitrosyl complex after it has been reduced, a new result that differs from both the earlier optical and Mössbauer work. This new component persists after recuction of pressure, so that the transition is not reversible over the time scale of several weeks. However upon reduction of pressure we do find a high spin Fe(II) component resembling that in the literature found at elevated temperature. We intend to study this oxygen-reduction phenomena and the high-spin state in more detail. In addition one must determine if there is an accompanying high pressure structural transformation. Finally it would be of interest to observe how high pressure affects the interesting optical-switching phenomena found in this material at low temperature.

IV. XAFS Studies of Phase Transition Mechanisms.

We have continued to study the effect of high pressure on metallic iron as revealed by our XAFS measurements, having measurements from 1 bar, through the bcc to hcp
transition at about 13 GPa to over 21 GPa. Using the FEFF program, involving multiple scattering paths, we have successfully been able to fit the experimental data, obtaining both molar volume vs pressure, and nearest neighbor, mean-square atom-pair bond length deviation, \( \sigma^2 \), vs. molar volume. At present we are able to fit in this way either bcc or hcp single phase results, as distinguished from the mixed phase region in the vicinity of the transition. For the bcc phase, this involved 25 paths with 8 variables, and 42 paths with 10 variables for the hcp phase. The variables include a general amplitude factor, lattice constant(s) as well as Debye-Waller factors, or rather, \( \sigma^2 \). In fact since each path has an associated \( \sigma^2 \), and there are so many paths, we cannot fit every \( \sigma^2 \) factor as a free parameter. Instead we fit only those \( \sigma^2 \) factors associated with single scattering paths, and use the Debye model to estimate \( \sigma^2 \) factors associated with the other multiple-scattering paths. The argument behind this fitting scheme is that the single paths are the most important ones as far as their contribution to the EXAFS, while the double and higher-order paths are relatively less important. Therefore the effect of modeling instead of fitting the other \( \sigma^2 \) factors will be minimal. As for the bcc-hcp mixed phase, there are so many paths that the number of variables we can fit will be limited. Therefore using models to estimate Debye-Waller factors will be inevitable. Such work is continuing.

V. Multiple Scattering Analysis of XANES.

Progress has also been made on an old problem, namely understanding of the marked changes in the XANES part of the spectra at a pressure-induced phase transition. Some of the most marked changes occur in the NaCl-CsCl type transitions occurring in the alkali halides. Although the physics that underlies the change in the XANES is clear, namely that the near-neighbor atomic, cage sampled by the excited photo-electron, changes from an octahedron to a cube, quantitative agreement with theory was lacking. As discussed in previous reports it has only been with the improvements in multiple-scattering analysis that one has been able to tackle this problem. One such approach was reported last time, a collaborative effort with Livins and Rehr which emphasized the importance of
careful background removal. For comparison we are also collaborating with the group of A. Soldatov which is applying a density of states, variable cluster approach. During this past year some of the results of this latter effort have been submitted for publication.

VI. Experimental Advances.

Besides the improvement in synchrotron beam conditions discussed earlier, and analysis, we also are making advances in our XAFS methodology. A new pressure cell designed for low temperatures and pressurized by helium gas, is being constructed a year earlier than anticipated. It is to be tested Summer of 1994. At the same time anvils with smaller tips, together with tinier samples will be used with the more intense and stable x-ray beam. This will presumably extend the high pressure limit of our technique.

VII. Publications.


VIII. Papers in Preparation.

"XAFS Study of the Mixed Valence Compounds SmS and SmSe at High Pressure,"
K. R. Bauchspiess, E. D. Crozier and R. Ingalls.

"Focused Multiple-Scattering EXAFS Analysis of Bond-Angle Changes in ReO$_3$,
B. Houser, R. Ingalls and J. J. Rehr

IX. Reports and Presentations.

"Pressure-Induced Transition in Rb$_{31}$WO$_3$ as Measured by XAFS," B. Houser and
R. Ingalls, 1993 Joint AIRAPT/APS Topical Conference on High Pressure Science
and Technology, Colorado Springs, Colorado, June 28-July 2, 1993

"Sodium Nitroprusside under High Pressure - Mössbauer Study," I. Choe and R. Ingalls,
International Conference on the Applications of the Mössbauer Effect, Vancouver,
B.C., August 8-13, 1993.

"Structural Parameters of ReO$_3$ under Pressure from XAFS," B. Houser, R. Ingalls
and J.J Rehr, 8th International Conference on X-Ray Absorption Fine Structure,

"Local Symmetry Influence on the Formation of X-Ray Absorption Near Edge Structure
in KBr and RbCl," I.E. Stekhin, A. V. Soldatov and R.Ingalls, ibid.
X. Personnel.

Robert Ingalls - Principal Investigator

John Whitmore - Graduate Student

In-Jerng Choe - Graduate Student

Fuming Wang - Graduate Student

Shelly Jones - Graduate Student

B. Houser - Collaborator (Eastern Washington University)

E.A. Stern and J.J. Rehr - Collaborators (University of Washington)

A. V. Soldatov - Collaborator (Rostov University)

E. D. Crozier - Collaborator (Simon Fraser University)