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, in the last three years, 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 high quality synchrotron beam time from the Stanford Synchrotron Radiation Laboratory and the National Synchrotron Light Source, at a rate of approximately one week per year.

Gamma-ray absorption spectroscopy, the Mössbauer Effect, which is somewhat complimentary to XAFS, is also well-suited to high pressure science. It 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 sensitive to the valence state and local atomic surroundings, and to changes, such as phase transitions.
II. Pressure Induced Crystalline Transitions

The pressure-induced B1-B2 transition (NaCl to CsCl structure) has been extensively studied at room temperature (RT) in a number of the alkali metal halides, in particular RbCl for which the transformation occurs at approximately 0.5 GPa. Of particular interest is the large volume decrease of approximately 14%, and a possible relationship between the crystal axes in the two phases. Using a new cryostat, described in section VIII, we have conducted liquid nitrogen temperature (LNT) Rb K-edge XAFS measurements of this transition as well as a state-of-the-art analysis of both the LNT and the previous RT data using the FEFF curved-wave, multiple scattering program. We find from the XANES spectra at LNT that the B1-B2 phase transition is much more gradual compared to the sharper RT transition. In Fig. 1 are shown the associated XAFS oscillations versus wave number. The change in character due to the phase transition is more apparent in such a plot. Also shown for comparison is the RT result at atmospheric pressure. High pressure and, especially, low temperature enhances the amplitude of these oscillations by reducing the mean-square deviations in the bond-lengths. The radial distribution about the x-ray absorbing atom is readily obtained from the magnitude of the Fourier transform of the type of data of Fig. 1. and is shown for the LNT data in Fig. 2, where the gradual change in structure due to the phase transition is evident.

![Figure 1](image1.png)

![Figure 2](image2.png)

Fig. 1. EXAFS oscillations at the Rb K-edge in RbCl at several temperatures and pressures: (a) RT and 0.1 MPa; (b) - (d) LNT and 0.1 MPa, 0.3 and 0.7 GPa, respectively.

Fig. 2. EXAFS determined radial distribution functions about the Rb ions in RbCl at LNT and several pressures.
Good fits to the data were obtained assuming both B1 and B2 phases to be present in this region at the same pressure. The relative amounts of the two phases are shown in Fig. 3. for both RT and LNT. If instead, sizeable pressure gradients are used to explain the presence of both phases, one would expect to extract different pressures for each phase, with the B1 phase yielding the lower pressure. This is not observed. In fact, it is common for Martensitic phase transitions to exhibit mixed phase regions that decrease in pressure range as the temperature is raised. Very recently we have begun a similar study of the 1.7 GPa transition in KBr. Our initial analysis indicates there is a broader mixed phase region in this case even at room temperature. Of course these systems show a pronounced hysteresis as pressure is reduced.

The bcc-hcp transition in metallic iron is another such example of a Martensitic transition that shows a broad mixed phase region in the pressure region 13 to over 21 GPa at room temperature as well as hysteresis. Our previous report discussed our results for this region. For example our XAFS radial distribution showed a rich evolvement of the one structure to the next, much like Fig. 2 does for RbCl. In a careful FEFF multiple scattering analysis, we found the structure of pure phases to be in excellent agreement with the latest x-ray diffraction results. For the bcc phase, our fit to the data involved 25 paths with 8 variables and 42 paths with 10 variables for the hcp phase. The variables include lattice constants and mean-square-relative-displacements, $\sigma^2$ for several coordination shells. We show in Fig. 4 the fitted first shell results of the latter, versus relative volume, into the transition.
Another recent study was the pressure induced Wurtzite to B1 transition in ZnO which occurs at approximately 10.5 GPa. Fig. 5 shows the change in the Zn K-edge XAFS as one proceeds through the transition. We find the transition to be relatively sharp at RT. (The measurement at LT has yet to be performed.) We are also currently analyzing extensive data on metallic zinc. Although no transition with pressure occurs, nor was expected, this will be an important test case for the FEFF analysis package. The reason is that anharmonic contributions are very important, so that ignoring them would lead one to conclude that the material contracts upon heating!

![Graph of EXAFS of the Zn K-edge in ZnO through the 10.5 GPa Wurtzite to B1 structural phase transition: curves a to d are in order of increasing pressure, with a and b below the transition and c and d, above.]

**III. Pressure Induced Amorphization**

Most amorphous materials have been prepared by rapid cooling of the liquid phase. Recent work has also shown that the amorphous state can also be obtained by hydrostatic pressurization of certain crystals. Pressure induced amorphous states, like conventionally prepared amorphous materials, have broad halo like x-ray diffraction patterns. In some cases the crystalline state is recovered upon decompression. The molecular crystal, tin tetraiodide (SnI₄), is a particularly interesting example. Diffraction studies show it to transform to a metallic amorphous state between 9 and 18 GPa and transform again to a similar crystalline phase ca 40 GPa. The same transformations in reverse also take place. How the the translational structural information hides in apparently disordered configurations is a very interesting question. Study of the local structure of this new kind of disorder is essential in understanding the mechanism of pressure induced amorphization.
We have made an XAFS study of both the Sn and I K-edges in SnI$_4$ to pressures in excess of 22 GPa. In the low pressure phase the SnI$_4$ molecules have tetrahedral symmetry, forming a cubic lattice. Sn K-edge spectra at different pressures are shown in Fig. 6. We observe that the amplitude of the oscillations in the high k range (8Å$^{-1}$ - 16Å$^{-1}$) drops considerably above 9 GPa, and then gradually decreases until it totally disappears at 19 GPa, only returning to its original value after release of pressure. We interpret this as a distortion of the SnI$_4$ molecule due to pressurization, and then a restoration after pressure release. Because the iodine atoms in crystalline SnI$_4$ interact very weakly with their iodine neighbors, the amplitude of the associated spectra is very small. However, at high pressure, the iodine atoms form stronger bonds among themselves and the amplitude of the XAFS spectra increases (see Fig. 7).

Our results from a detailed analysis of the distances obtained from fitting the data of the Sn-I bond indicate the SnI$_4$ tetrahedra hardly compress in the crystalline phase but are somewhat expanded and disordered in the amorphous phase that coexists above about 9 GPa. At the same time an I-I bond decrease in size and strengthens. We have made computer simulations that agree with these results. What seems to happen is that pairs of tetrahedra along the [111] type axes undergo correlated rotations and translations and possibly form dimers in the amorphous state. Very recently we have made additional measurements to further examine what is happening.

![Fig. 6. Sn K-edge EXAFS in SnI$_4$ at several pressures.](image)

![Fig. 7. I K-edge EXAFS in SnI$_4$ at several pressures.](image)
IV. Pressure Induced Octahedral Rotations

Improvements in the quality of XAFS data and analysis, such as the FEFF package of our colleague, J. J. Rehr, have permitted measuring the behavior around the absorbing atom out to the fourth coordination shell. These measurements then enable the determination of bond angles. One reason is that when there are atoms in between that which is photoexcited and that which is contributing to the backscattering, causing the XAFS oscillations, there are multiple-scattering pathways which enhance the effect. Another reason is more precise determinations of the scattering path lengths themselves.

We are applying these ideas to several systems. For instance in the perovskite material, ReO₃, pressure causes a second-order transition, at 0.5 GPa, in which the ReO₆ octahedra undergo a rotation along [111] type axes preserving the cubic symmetry. We have taken Re L₃-edge spectra in this system. Figs. 8 and 9 indicate the quality of the results. Our analysis of such data indicates that above the transition the rotation angles gradually increase and are quite consistent with diffraction results. However below the transition there appears to be rotational disorder that, at this point, can either be static or dynamic. Recently we have taken more measurements on this system at both room temperature and liquid nitrogen temperature to elucidate this point. This study is continuing.

Fig. 8. XAFS of Re K-edge in ReO₃: Fourier-transformed $k^2\chi(k)$ spectra for three pressures. The window function for the transforms was a gaussian, symmetrically placed between 2 and 19 Å⁻¹.

Fig. 9. XAFS of Re K-edge in ReO₃: Fit of the real part of the Fourier-transformed $k^2\chi(k)$ for a sample pressure of 1.7 ± 0.3 GPa.
In a related study we have measured the XAFS of the Rb K-edge and W L$_3$-edge in Rb$_{31}$WO$_3$. The low pressure phase of this material, rubidium tungsten bronze, has a simple hexagonal structure, composed of layers of corner-linked WO$_6$ octahedra, arranged in hexagonal rings. Each is common to two rings with each ring containing one Rb atom. Our work shows evidence of a pressure-induced structural phase transition in the vicinity of 2 GPa, which may be similar to the "compressibility collapse" transition in ReO$_3$, discussed above. Our proposed high-pressure phase remains hexagonal, with the c-axis spanning two layers, rather that the one in the low pressure phase, with octahedra in successive layers tilting in opposite directions.

V. Multiple Scattering Analysis of XANES

The investigation of the electronic energy bands and local crystal structures of the ionic compounds is presently of great interest. In the last few years the XANES spectra have also shed light on the behavior in the neighborhood of phase transitions. Theoretical K-edge XANES have been calculated using a band structure full multiple scattering approach for the B1 phases of NaBr and AgBr as well for B1 and B2 phases of RbCl, RbBr and KBr. For these latter structures and in spite of the close lattice parameters for both phases, the role of local symmetry around the absorbing site in the formation of the conduction band and resultings XANES of compounds investigated was able to be determined. The optimal cluster size that permitted making a correct description of whole crystal in the B1 phase (the second shell of surrounding atoms for AgBr and more than 30 atoms for RbCl, KBr) was estimated. It was found that a single scattering approximation works well in AgBr and less satisfactory in RbCl, NaBr, KBr, where multiple-scattering take place. The partial densities of Br and Rb p states in the conduction band of RbBr were obtained over a large energy interval for both the ground and the excited states. It was also found that the core hole potential weakly affected the conduction band electrons, therefore, one can derive the projected p-density of state directly from experimental XANES data. This method shows how the electronic structure changes in selected phase transitions. Figs. 10 and 11 show
the comparison between theory and experiment for the Br K-edge in RbBr. It should be remarked that such an approach is satisfactory but will presumably ultimately improve when FEFF type analyses are extended further into the XANES region.

![Graphs showing XANES of Br K-edge in RbBr: experimental and theoretical](image)

Fig. 10. XANES of the Br K-edge in RbBr: experimental.  
Fig. 11. XANES of the Br K-edge in RbBr: theoretical.

VI. Pressure Induced Structural Changes - New Initiatives

Very recently we have initiated a series of investigations that brings together all of the issues raised in the previous sections. Since this new work constitutes the major part of the renewal proposal that accompanies this progress report, only a brief description is given here.

Measurement of the Ag K-edge spectra have been taken for AgCl. This material and AgBr have been reported to undergo a transition from the B1 phase, at around 7 GPa, to another structure that remains to be conclusively determined. Our measurements indeed show evidence of such a transition which has also been predicted theoretically by A. Voronel and co-workers. Of even greater interest, however, according to the calculations, is that alloys of the above pure materials may undergo a type of bond buckling transition to an amorphous phase under pressure. Moreover there is reason to expect similar behaviors in alloys of of the alkali metal halides discussed in Section II. Both alloy systems have been shown by Voronel and co-workers to have a buckled structure at atmospheric pressure that does not show up in diffraction studies.

We have also undertaken new measurements in other oxide based perovskites. One
such material is ferroelectric KNbO$_3$. Our preliminary measurements of the Nb K-edge spectra show a transition above 12 GPa, possibly accompanied by octahedral rotations and reduced off-center displacements of the Nb atoms, presumably this high pressure phase is paraelectric. This appears to be consistent with what we recently found in the related system, KTa$_{1-x}$Nb$_x$O$_3$. We also find increasing octahedral rotation in the related antiferrodistortive (AFD) system K$_{1-x}$Ta$_x$O$_3$. Since some of the high T$_c$ materials are also AFD, it is proposed that such a behavior is relevant to such superconductivity. Again, as found by Y. Yacoby and co-workers. oxide perovskites are also examples where XAFS indicates more static angular bond disorder that diffraction measurements.

VII. XAFS Experimental Advances

This report period marks the achievement of a number of improvements in our XAFS spectroscopy at high pressures. These are due in part to the improved high intensity and stability of the synchrotron radiation from SSRL. Because of the greater flux we have been able to work with smaller beams, ca 200 $\mu$m and therefore smaller samples. This in turn has permitted smaller high pressure anvil tips and the attainment of routinely higher pressures, ca 30 GPa, with boron carbide anvils. These advances have also permitted our going to higher energy x-ray absorption edges, such as our being able to study niobates and silver halides, and especially materials like SnI$_4$ with K-edges of 29 and 33 keV, respectively. Instead of using pressure calibrants of Cu, Br or Rb we are beginning to utilize Nb or Ag. We have also extended our work to lower temperatures with the development of a pressure cell that utilizes a diaphram pressurized by helium gas rather than the hydraulic oil used at room temperature. Of course advances in the analysis package, FEFF by our colleague, J. Rehr have aided the precision of our structure determinations. We are looking forward to further advances provided by the anticipated move to the Advanced Photon Source, as discussed in the accompanying renewal proposal.
VIII. Mössbauer Studies

We have studied the pressure dependence of Na₂Fe(CN)₅NO·2H₂O (sodium nitroprusside dihydrate), to 27 GPa at room temperature using a diamond anvil cell and transmission Mössbauer spectroscopy. We have found two pressure induced partial phase transitions initiated around 21 and 27 GPa. We have also observed a sudden color change at 13 GPa, which is triggered by the blue He-Cd laser used for pressure calibration. However this optical change does not accompany any significant changes in the Mössbauer spectra. The first new phase occurring at 21 GPa has considerably smaller quadrupole splitting and more positive isomer shift that the normal phase, closely resembling the oxidation reduced nitrosoyl complex in water. On the other hand, the second new phase occurring at 27 GPa shows a large quadrupole splitting and isomer shift characteristic of the Fe(II) high spin state. These new phases persist upon release of pressure over the time scale of 10 days. The explanation for these transitions is presumably the mechanism of charge transfer between the central iron atom and surrounding ligands.

In response to recent x-ray diffraction measurements on iron at high pressures we have also initiated a Mössbauer investigation of this system, which is of geophysical interest. Iron shows a triple point around 10 GPa and 800 K where the standard bcc phase meets the high temperature fcc and high pressure hcp phase. The reports by Saxena, et. al. and also Yoo, et. al. indicate that in the 1000-1400 K temperature region and 10-40 GPa vicinity of the fcc-hcp boundary, there may be new phases present. We have recently begun taking measurements on this system and have made this the main Mössbauer experiment to be conducted in our renewal proposal.

Fig. 12. Mössbauer transmission spectra of Fe⁷ in sodium nitroprusside during one pressure cycle (from bottom to top). The spectra marked with "**" were obtained during pressure release.
IX. Publications


X. Reports and Presentations


XI. PhD Theses

"EXAFS Experiments at High Pressure with Small Samples"
  John Whitmore
  University of Washington, September, 1994

"High Pressure Studies of Iron Hydroxide, Iron Silicate Spinel and Sodium Nitroprusside"
  In-Jerng Choe
  University of Washington, December, 1994

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