X-RAY and γ-RAY SPECTROSCOPY
of SOLIDS UNDER PRESSURE

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Summary of Progress
X-Ray Spectroscopy of Solids under Pressure

Introduction

This report describes our recent synchrotron x-ray absorption fine structure (XAFS) measurements on a number of systems that undergo pressure induced changes in local structure at high pressure. The reader should also refer to the accompanying renewal proposal for a more in-depth discussion of the general scope of this program, and its relevance to condensed matter science. We merely state that the methods here are aimed at using XAFS\textsuperscript{1} to probe the various phenomena that are caused by high pressure, especially including various structural, and/or electronic, changes or transitions. Our general technique\textsuperscript{2} is based upon a pressure cell which utilizes scinttered boron carbide anvils, since diamond anvils generally produce Bragg glitches which spoil the high quality XAFS necessary for precision structural measurements. Sample pressure is determined at the beam-line by measuring and analyzing, via XAFS, the compression of some cubic material contained within the sample chamber. Recently we have extended this work to 77 K using helium gas for the applied force, rather than hydraulic oil.

This report period has been productive. The increased flux available at the Stanford Synchrotron Radiation Laboratory (SSRL) has permitted our going to smaller beams, on the order of 300 \( \mu \text{m} \) in diameter, for precision probing of the sample region. At the same time we have received ample amounts of beam time at SSRL, in part because of the high rating of our latest user proposal. We also were invited to share some of the beam time at the National Synchrotron Light Source (NSLS) assigned to the group of our collaborator, E. A. Stern.

Below we describe in some detail our recent work. Some of the pending papers are reports on systems that have been under study for some time and have been described in past progress reports and, as such, need not be described again here.
XAFS Measurements of Local Structural Changes in K\(\text{NbO}_3\)

The ferroelectric material, potassium niobate, is of interest because there are conflicting reports\(^4,5\) as to whether the transition is of the displacive or order-disorder type, going from the high temperature cubic phase to the low temperature rhombohedral phase. High pressure Raman studies suggest a transition to the paraelectric cubic structure at 9-10 GPa in one case,\(^6\) and in another case\(^7\) several displacive transitions in the range 2-15 GPa. Here we report careful measurements of the Nb K-edge XAFS in K\(\text{NbO}_3\), together with silver foil as pressure calibrant. The work was performed at SSRL. Fig. 1 shows typical data, and the enhanced signal caused by the high pressure.

The XAFS data for both the sample and calibrant were analyzed using the UWXAFS\(^8\) and FEFF6\(^9\) methods. The general results show no definitive evidence of sharp local structural transitions at either temperature. We do find that the niobium atoms are displaced in the [111] directions from the centers of the oxygen octahedra at all pressures. However, as shown in Fig. 2, the magnitude of these displacements decreases gradually with increasing pressure by almost a factor of two in comparison with the lattice parameter, which only decreases by 3% within the same pressure range. Thus our work suggests that local rhombohedral distortions exist throughout the ferroelectric-paraelectric region, consistent with the XAFS temperature study of Ref. 4. These results strongly support an order-disorder mechanism for the ferroelectricity.

Our measurements extend out to the fifth nearest neighbor of the central absorbing niobium atoms. One of the parameters measured is the mean-square deviation in the various relative distances, \(\sigma^2\). For the first three neighbors, corresponding to O(1), O(2) and Nb(3), the \(\sigma^2\) values decrease with increasing pressure, which is the normal stiffening behavior. However for O(4) and Nb(5), the \(\sigma^2\) values anomalously increase with increasing pressure, indicating increasing static or dynamic disorder, something certainly not seen in any diffraction experiment. As for the Nb-O(4) distance, we interpret its increasing \(\sigma^2\) as a disorder in oxygen octahedral positions with pressure. This disorder, either a buckling or a rotation,
indicates a lack of rigidity of the oxygen sublattice, probably leading to some form of amorphization. The increasing disorder in Nb-Nb(5), however, is explained as a shortening of the correlation length between Nb-Nb displacements. The latter could occur if the [111] type displacements in different domains had different orientations.

FIGURES

FIG. 1. Nb k-edge EXAFS of KNbO₃ at ambient pressure and 15.8 GPa.

The Effects of Pressure on the Local Structure of K₁₋ₓNaₓTaO₃ and KTa₁₋ₓNbₓO₃.¹⁰

The work discussed in this section is closely related to that in the previous section. In particular, K₀.₁₅Na₀.₈₅TaO₃ has an antiferrodistortive distortion¹¹,¹², while KTa₀.₁₃Nb₀.₈₇O₃ is ferroelectric.¹³ These were both studied at room temperature during an XAFS run at NSLS. The K-edges of Ta and Nb, respectively, were measured and copper was used as the pressure calibrant.

Examples of the absolute values of the radial-distribution/Fourier-transforms of the XAFS for the second system are shown in Fig. 3 along with standard fits in the range 1.0 < r < 4.1 Å based on the methods in Ref. 9. For KTa₀.₁₃Nb₀.₈₇O₃ as shown in Fig. 4, the well known off-center Nb [111] displacements were observed to decrease with pressure,
much as in the pure material KNbO$_3$ and reflects the tendency toward the paraelectricity. The NbO$_6$ octahedral rotation angles about the [111] axes in K$_{15}$Na$_{85}$TaO$_3$ were observed to increase similar to the pressure effect in ReO$_3$.  

![FIG. 3. Magnitude of the Fourier transform of KNb$_{87}$Ta$_{13}$O$_3$.](image)

![FIG. 4. K$_{15}$Nb$_{85}$TaO$_3$: Reduced cell parameters (△) and oxygen rotation angles (●).](image)

Here, as for KNbO$_3$ in the previous section, we find for KTa$_{13}$Nb$_{87}$O$_3$ that $\sigma^2$ associated with Nb-O(4) also anomalously increases with pressure. This result can be understood if one assumes that pressure indeed induces disordered oxygen octahedral rotations. In the first approximation these rotations do not affect the Nb-O(1) distances, but they do affect the Nb-O(4), thus contributing to the large $\sigma^2$. Therefore there is a distribution of angles about the values in Fig. 4.

**XAFS Study of the Iron bcc-hcp Transition**

Numerous studies$^{16-18}$ have been performed to investigate the pressure driven iron bcc-hcp martensitic transition since its discovery by Bancroft et. al.$^{19}$ This transition is known to be very sluggish and hysteretic. It starts at 13.0 GPa and spans about 8.0 GPa at room temperature. The atomic mechanism of this transition is still not well understood. For example, conflicting $c/a$ values of the hcp phase have been reported by Refs. 16 to 18 (see Fig. 5). Differences in pressure transmitting medium and method of determining the lattice constants from the diffraction peaks were suggested in Ref. 18 as a possible source of this conflict. Since monitoring the $c/a$ values are quite important in understanding the nucleation and growth behavior of the hcp and bcc phases during the for-
ward and reverse transition, our further experimental XAFS investigation of this aspect of
the transition was deemed necessary. Most of the previous studies on this transition used
diffraction techniques, which probe the long range structure of the system. However, us-
ing XAFS, we were able to probe the structure during the transition from a local standpoint.

![Graph 1](image1)

**FIG. 5.** Various c/a results for hcp-Fe, including present results.

![Graph 2](image2)

**FIG. 6.** Lattice constant for bcc-Fe during the bcc-hcp transition.

High pressure XAFS spectra of the Fe K-edge were obtained at SSRL and analyzed using FEFF\textsuperscript{9} programs. Copper was used as the pressure calibrant. For the resulting data analysis, the mixed-phase region was modeled as a simple mixture of bcc and hcp phases. General agreement with previous studies on the transition pressure and molar volume as a function of pressure was achieved in this study. The c/a ratio was found to be anomalously large at the beginning of the forward transition (see Fig. 5), similar to the findings of Ref. 18. Also, as shown in Fig. 6, anomalously large lattice constants of the bcc phase, when the amount of the bcc phase became below approximately 10\%, were found for the first time.

We have investigated several models to explain these observed structural anomalies, based on some form of inter-phase strain. The results appear to rule out the model invoked by Refs. 16 and 18. However, a model first proposed by Burgers\textsuperscript{20}, a two step process suggested to depict the zirconium bcc-hcp transition upon quenching from high temperature, was found to fit our data reasonably well. However we believe that inter-phase strain alone cannot fully explain these structural anomalies. Instead, two possible alternative intermediate phases are considered to help explain these anomalies. Both of these structures are actually suggested
in Ref. 20. In one case, a fcc structure is formed, which would have c/a close to what we find. This would then be followed by a shear movement to produce the hcp phase. The second possibility, also following Ref. 20, is that after a shearing along the [111] direction and along the (112) plane, alternate layers of (110)_{bcc}||(002)_{hcp} planes might not immediately shift to their final positions. Instead the atoms in such planes could stay in somewhat in-between, off-positions, pushing the planes in question apart, giving an anomalously large c value for the interphase regions.

**XAFS Study of the B1-B2 Phase Transition in RbCl**

Rubidium chloride undergoes a pressure induced phase transition from the B1 (NaCl-type) to the B2 structure (CsCl-type) at approximately 0.5 GPa. The published equations of state of both phases above and below the transition make the material useful as a pressure calibrant in its own right. X-ray diffraction measurements, which show an orientational relationship between the phases, indicate the transition is martensitic. However the question of an intermediate structure occurring in such transitions has been raised, and the diffraction lines become too broad at the transition to rule out such a possibility. The purpose of the present study performed at SSRL was to combine this information with precision XAFS measurements that extend right through the transition itself and settle the above question.

![Fourier transform of the Rb k-edge EXAFS in RbCl along with theory.](image)

**FIG. 7.** Fourier transform of the Rb k-edge EXAFS in RbCl along with theory. (a) Model based on the B1 structure at ambient pressure. (b) Model based on the B2 structure at 1.1 GPa.

As shown in Fig. 7, our measurements on either side of the transition, combined with
state-of-the-art theoretical analysis\textsuperscript{9} are in excellent agreement. Measurements at the transition itself, have been analyzed in two ways: 1) a mixture of the two phases, and 2) an intermediate KOH structure as suggested by Ref. 24. As indicated in Fig. 8, the mixed phase model perfectly fits the data, and the intermediate phase model does not. We note that this phase transition requires an excess pressure of about 0.2 GPa. Once the transition starts the system relaxes to a pressure of 0.5 GPa, which remains approximately constant until the transition is complete, in accordance with martensitic-like transitions. Our results also indicate that within the separate phases at the transition there is no more structural disorder than in the single phase regions, themselves.

**High Pressure Structure of the AgCl\textsubscript{2}Br\textsubscript{1-x} System**

As with RbCl and most other alkali halides, AgCl has the B1 structure at ambient pressure and B2 structure at pressures above ca 20 GPa. Kusaba, \textit{et.al.}\textsuperscript{24}, using x-ray diffraction, have found the following intermediate phases at room temperature: KOH-type (HPI) from 9 to 13.5 GPa, TII-type (HPII) from 13.5 to 17.5 GPa. Furthermore they have determined lattice parameters at pressure for the various phases, and have obtained the relationship between the most primitive KOH-type structure and the structure for each of the other phases. However this work did not determine the coordinates of the atoms within...
the unit cell for the HPI and HPII phases.

We have performed XAFS experiments of the Ag K-edge in AgCl at 150 K, using niobium as the pressure calibrant. These experiments have enabled us, by means of FEFF\textsuperscript{9} multiple scattering analysis, to determine such coordinates. The KOH structure can be thought of as a distorted bct cell occurring in the B1 phase (Fig.9). The monoclinic distortion is such that identical layers are no longer directly over each other. That is, the angle between the c axis and a-b plane is greater than 90°. Our results for the HPI phase are shown in Fig. 10.

![FIG. 9. The B1 structure with the KOH-type cell outlined.](image)

![FIG. 10. Unit cell for the AgCl HPI structure (KOH-type) as determined by XAFS.](image)

A picture of our results for the HPII phase would be similar, except with the angle increased to the point that a centered orthorhombic structure is the result. (A further increase in angle then produces the B2 structure.) In Fig. 11 we show a comparison with

![FIG. 11. The AgCl distortion angle, XAFS - open symbols, XRD - closed.](image)

![FIG. 12. The AgCl Lattice constants, XAFS - open symbols, XRD - closed.](image)
our angles and those of Ref. 24, and in Fig. 12, the lattice parameters. The agreement is quite good, with the exception at 150 K we observe the B1-HPI and HPI-HPII phase transitions to occur at lower pressures than in Ref. 24, which was based on room temperature results. While the change is not unexpected, it remains to verify whether the XAFS and XRD methods yield similar phase diagrams for this case. As we have seen earlier, such is by no means always the case.

At ambient pressure AgCl\textsubscript{1.5}Br\textsubscript{0.5} also has the B1 structure. If we consider a site that is occupied by a Br or Cl the probability of finding one or the other is 50 percent. That is, the ion site is randomly occupied by a Br or Cl. A buckling phenomenon has been proposed for this system\textsuperscript{27} which can be described as a displacement of the Cl and Br atoms from the line of Ag atoms. This mechanism may lead to amorphization at high pressure. This relatively simple crystal structure is ideal for studying such a process. XAFS is well suited to look for the buckling phenomenon, since it directly probes the distance between atoms, while diffraction techniques are less sensitive to disorder that averages to zero over many unit lengths.

Our results for this mixed system are shown in Figs. 13 and 14. At ambient pressure we see only one distance for the 1st nearest neighbors of Cl and Br atoms located at the center of each face of the unit cell at a distance of 2.8 Å, and only one Ag 2nd nearest neighbor
distance located at the center of each edge of the unit cell at a distance of 4 Å. With the application of a small amount of pressure (.5 GPa) we see a dramatic change in behavior. The Ag-Br distance slightly decreases, but increases for Ag-Cl along with the latter’s $\sigma^2$. We also find a splitting of about 0.15 Å in the Ag-Ag distances. This shows some support for the buckling phenomenon.

At 13 GPa, our highest pressure, we again find that all shells but the first are unobservable and even the first shell is diminished and very broad (Fig. 14). Our fit results also show that $\sigma^2$ has almost doubled for the Ag-Br distances and more than doubled for the Ag-Cl distances. At the same time the bond lengths for both of these shells has significantly decreased. This behavior indicates a large degree of disorder at high pressure as well as possible amorphization.

**Pressure-induced Changes in the Local Structure of Pure and Optimally Doped La$_{2-x}$Sr$_x$CuO$_4$**

Sr doping induces high $T_c$ superconductivity in La$_{2-x}$Sr$_x$CuO$_4$ for $0.07 \leq x \leq 0.25$ with $T_c$ increasing to a maximum of $\sim 35$K at $x = 0.15$ and then decreasing in the overdoped regime$^{25}$. Beside adding charge carriers (holes) to the Cu-O planes, Sr substitution leads to structural changes that can be described, at a constant temperature, as a second order phase transition from orthorhombic (LTO) to tetragonal (HTT) symmetry$^{25}$. Thus the contribution of these competing effects to the dependence of $T_c$ on $x$ is hard to evaluate.

Pressure measurements allow studying the effect of structural changes on $T_c$ for a fixed carrier concentration. In this system, $T_c$ is well known to increase linearly with pressure until the pressure-induced LTO-HTT phase transition takes place$^{26}$. In the HTT phase $T_c$ is nearly independent of pressure. It is then of importance to determine what are the structural changes taking place with pressure in both phases and whether any correlation between them and $T_c(P)$ can be established.

We performed XAFS experiments at the Cu K-edge of pure La$_2$CuO$_4$ at 300 K and of La$_{1.85}$Sr$_{0.15}$CuO$_4$ at T=77 K. The work was done at both SSRL and NSLS. For these samples
and temperatures, the pressure-induced LTO-HTT phase transitions occur at $P \approx 1.7$ GPa and 4.0 GPa, respectively\textsuperscript{28}. Pressure was calibrated by measuring in-situ the XAFS of Nb powder.

Figs. 15 and 16 show the pressure dependence of the measured bond lengths for both $x = 0.15$ and $x = 0$ samples, respectively. (In these figures the results for Cu-O(2) and Cu-La are displaced vertically for clarity. The dotted line indicates the location of the LTO-HTT boundary.)

It is clear that no significant differences exist in the compressibility of these bonds across the LTO-HTT phase transition, indicating that the peculiar $T_c(P)$ relation is more likely determined by correlated changes in the electronic structure of this compound. It is worthwhile noting, however, the larger than expected compressibility obtained for the apical Cu-O(2) bond length which is significantly larger than the $c$ axis compressibility found by diffraction. Even though the pressure induced changes in the Cu-O(2) distance could enhance the hole content of the Cu-O layers by enhancing charge transfer through enhanced hybridization of Cu 3$d_{3z^2-r^2}$ and O 2$p_z$ orbitals, it is by itself not enough to account for the apparent saturation of $T_c(P)$ in the HTT phase.

**Chain Buckling in YBa$_2$Cu$_3$O$_{7-\delta}$**

During this report period an analysis of an experiment begun several years earlier was completed, namely a study of the superconductor, YBa$_2$Cu$_3$O$_{6.95}$. This XAFS experiment
of the Cu K-edge was performed at 80 K, and the pressure calibrant was germanium.

The results indicate a buckling in the Cu(1)-O(4)-Cu(2) chains through the O(4) atoms. Using multiple scattering analysis, it is found that the buckling angle from colinearity, $\beta$, increases rapidly at low pressures then saturates at $\sim 6.5$ GPa. The magnitude of the saturation angle $\beta_{sat}$ is dependent upon details of the XAFS analysis. If the Cu(1)-O(4)-Cu(2) path is assumed to be linear at 1 bar, then $\beta_{sat}$ is found to be 12°. However, if the presence of static or dynamical displacements of the O(4) atom from the c-axis, as reported in ion channeling and neutron diffraction experiments at 1 bar, are included in the XAFS analysis by assuming that the path is already buckled by 3° at 1 bar, then $\beta_{sat} \sim 8.5°$. Because the multiple scattering effect decreases as $\beta$ increases it was not possible to follow this behavior above 6.5 GPa where the XAFS contributions from the Cu(1)-O(4)-Cu(2) path become too weak.

The anisotropy of the pressure dependence of $T_c$ has been reported from the discontinuities in the high resolution thermal expansion data. According to these studies the pressure derivative of $T_c$ is large and opposite in sign along the $a$- and $b$- axes but small along the $c$-axis, leading to an overall low pressure dependence of $T_c$ for YBa$_2$Cu$_3$O$_{7-\delta}$.29 The buckled structure can have important aspects explaining these anisotropies. Burns,30 proposing a coupling of superconductivity to the shear deformation along (110), showed $T_c$ increases with shear stress up to a point and then decreases.

The buckled structure can also have a contribution to $T_c$ according to the resonating valence bond model of Anderson31 in which the logarithmic volume derivative of $T_c$ is related explicitly to carrier concentration and to the transfer integrals parallel ($t_{||}$) and perpendicular ($t_{\perp}$) to the CuO$_2$ planes. With the distortion of the O(4), $t_{\perp}$ is expected to decrease. However the effect of this decrease on the pressure derivative of $T_c$ is expected to be small since, according to the model, the dominant contribution to the change in $T_c$ comes from the carrier concentration term.
Publications


“The Effect of Hydrostatic Pressure on the Local Structure of K_{1-x}Na_xTaO_3 and KTa_{1-x}Nb_xO_3,” F. Wang, B. Ravel, Y. Yacoby and E.A. Stern and R. Ingalls, J. de Phys. IV 7, C2-1225 (1997).


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