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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 continuation 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 scintered boron carbide anvils, since diamond anvils generally produce Bragg glitches which spoil the high quality EXAFS 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.

The past year has been unusually productive for several reasons. The increased flux available at the Stanford Synchrotron Radiation Laboratory (SSRL) has permitted our going to smaller beams, on the order of 300 $\mu$m in diameter, for precision probing of the sample region. At the same we have received unprecedented amounts of beam time at SSRL, three separate runs, 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 latest work. Some has been recently been submitted to the Physical Review, or soon to be. On the other hand, some of the pending papers are

\*No $\gamma$-ray research was, in fact, performed this report period.
reports on systems that been under study for some time and only during this report period
have they been put in final form. Some of this work has been described in past progress
reports and, as such, will not be described again here.

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

Numerous studies\(^3\)–\(^5\) have been performed to investigate the pressure driven iron bcc-
hcp transition since its discovery by Bancroft et. al.\(^6\) This transition is known to be very
sluggish and hysteretic. It starts at 13.0 GPa and spans about 8.0 GPa at room tem-
perature. The atomic mechanism of this transition is still not well understood. For ex-
ample, conflicting \(c/a\) values of the hcp phase have been reported by Refs. 3 to 5 (see
Fig. 1). Differences in pressure transmitting medium and method of determining the lat-
tice constants from the diffraction peaks were suggested in Ref. 5 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 bcc and hcp phases during the forward and re-
verse transition, our further experimental XAFS investigation of this aspect of the transi-
tion was deemed necessary. Most of the previous studies on this transition used diffrac-
tion techniques, which probe the long range structure of the system. However, using
XAFS, we were able to probe the structure during the transition from a local standpoint.

![Image](image1.png)

**FIG. 1.** Various \(c/a\) results for hcp-Fe, including present results.

![Image](image2.png)

**FIG. 2.** 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{7} and FEFFIT\textsuperscript{8} 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. 2), similar to the findings of Ref. 5. Also, as shown in Fig. 2, 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. 3 and 5. However, a model first proposed by Burgers\textsuperscript{9}, 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. 9. 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. 9, is that after a shearing along the $[1\bar{1}1]$ direction and along the $(\bar{1}12)$ plane, alternate layers of $(110)_{\text{bcc}}||(002)_{\text{hcp}}$ 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 Measurements of Local Structural Changes in KNbO$_3$**

The ferroelectric material, potassium niobate, is of interest because there are conflicting reports\textsuperscript{10,11} 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,\textsuperscript{12} and in another case\textsuperscript{13} several displacive transitions in the range 2-15 GPa. Here we report careful measurements of the Nb k-edge XAFS in KNbO\textsubscript{3}, together with silver foil as pressure calibrant. The work was performed at SSRL. Fig. 3 shows typical data, and the enhanced signal caused by the high pressure. Recently we have extended this work to 77 K.

The XAFS data for both the sample and calibrant were analyzed using the UWXAFS\textsuperscript{14} and FEFF6\textsuperscript{15} 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. 4, 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. 10. These results strongly support an order-disorder mechanism for the ferroelectricity.

FIG. 3. Nb k-edge EXAFS of KNbO\textsubscript{3} at ambient pressure and 15.8 GPa.

FIG. 4. O and K atomic displacements and Nb [111] off-center displacements in KNbO\textsubscript{3}. 
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.

**The Effects of Pressure on the Local Structure of $K_{1-x}Na_xTaO_3$ and $KTa_{1-x}Nb_xO_3$.**

The work discussed in this section is closely related to that in the previous section. In particular, $K_{15}Na_{85}TaO_3$ has an antiferrodistortive distortion\textsuperscript{16,17}, while $KTa_{13}Nb_{87}O_3$ is ferroelectric.\textsuperscript{18} 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

![FIG. 5. Magnitude of the Fourier transform of KNb$_{87}$Ta$_{13}$O$_3$.](image1)

![FIG. 6. K$_{15}$Nb$_{87}$TaO$_3$: Reduced cell parameters (▲) and oxygen rotation angles (●).](image2)
of the XAFS for the second system are shown in Fig. 5 along with standard fits in the range 1.0 < r < 4.1 Å based on the methods in Refs. 8 and 15. For KTa$_{13}$Nb$_{87}$O$_3$ as shown in Fig. 6, 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, as shown in Fig. 7, similar to the pressure effect in ReO$_3$.$^{19}$

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 as shown in Fig. 8. The result here 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. 6.

**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 $\sim$ 35K at $x = 0.15$ and then decreasing in the overdoped regime.$^{20}$ 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.$^{20}$ 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\textsuperscript{21}. 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 X-ray Absorption Fine Structure (XAFS) experiments at the Cu K-edge of pure $La_2CuO_4$ at 300K and of $La_{1.85}Sr_{0.15}CuO_4$ at $T=77K$. The work was done at both SSRL and NSLS. For these samples and temperatures, the pressure-induced LTO-HTT phase transitions occur at $P=1.7GPa$ and $4.0GPa$, respectively\textsuperscript{22}. Pressure was calibrated by measuring \textit{in-situ} the XAFS of Nb powder. Fig. 9 shows the amplitude of the complex Fourier transform of the Cu K-edge XAFS for the $x = 0.15$ sample at $P=7.8\pm0.5$ GPa together with the fit (which includes multiple scattering contributions) using FEFF6\textsuperscript{15} as a

![Graph](Image)

**FIG. 9.** Fourier transform magnitude for Cu k-edge XAFS in $La_{1.85}Sr_{0.15}CuO_4$ at 77K, compared with theory.

### Table I. Linear compressibilities of different distances as measured by XAFS in $La_{1.85}Sr_{0.15}CuO_4$ at 77K.

<table>
<thead>
<tr>
<th>Distance</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-O(1)</td>
<td>-2.6(1.2)</td>
<td>-2.3(0.8)</td>
<td>-3.4(1.5)</td>
</tr>
<tr>
<td>Cu-Cu</td>
<td>-2.1(1.1)</td>
<td>-2.8(0.8)</td>
<td>-3.7(1.7)</td>
</tr>
<tr>
<td>Cu-O(2)</td>
<td>-2.4(1.1)</td>
<td>-2.8(0.8)</td>
<td>-3.7(1.7)</td>
</tr>
<tr>
<td>Cu-La</td>
<td>-1.4(0.8)</td>
<td>-1.9(0.8)</td>
<td>-1.9(0.8)</td>
</tr>
</tbody>
</table>

### Table II. Same type of information as in Table I for $La_2CuO_4$ at 300K.

<table>
<thead>
<tr>
<th>Distance</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-O(1)</td>
<td>-2.15(6)</td>
<td>-4.22(5)</td>
<td>-1.83(2)</td>
</tr>
<tr>
<td>Cu-Cu</td>
<td>-2.15(6)</td>
<td>-4.22(5)</td>
<td>-1.83(2)</td>
</tr>
<tr>
<td>Cu-O(2)</td>
<td>-2.15(6)</td>
<td>-4.22(5)</td>
<td>-1.83(2)</td>
</tr>
<tr>
<td>Cu-La</td>
<td>-2.15(6)</td>
<td>-4.22(5)</td>
<td>-1.83(2)</td>
</tr>
</tbody>
</table>
theoretical standard. Figs. 10 and 11 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.) Tables 1 and 2 summarize the compressibilities obtained for all bond lengths and are compared to values reported in the diffraction studies$^{22}$.

![FIG. 10. La$_{1.85}$Sr$_{0.15}$CuO$_4$: Normalized distances at 77 K.](image)

![FIG. 11. La$_2$CuO$_4$: Normalized distances at 300 K.](image)

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.

**Study of the High Pressure Structure of AgCl**

The silver halide system AgBr$_{1-x}$Cl$_x$ is of interest from the XAFS standpoint. The measured local structure appears to differ from the expected NaCl average structure, in that static buckling behavior and homogeneous mixed phases appear to occur over a large concentration range.$^{23,24}$ This picture of various bond angles in a disordered array
appears to be somewhat analogous to a frozen spin-glass system. In fact, molecular dynamics simulations\textsuperscript{24} have lead to the suggestion that the pure compounds, AgBr and AgCl will have increasing bond buckling with pressure and transform to new phases at pressures on the order of 10 GPa. Early diffraction measurements\textsuperscript{25,26} on these materials indicate there is a phase change at room temperature around 7 GPa but did not agree on the structure. More recent work on AgCl\textsuperscript{27} shows that transition is to the KOH structure, which occurs at somewhat lower pressures as the temperature is lowered, as shown in Fig. 12. It is then followed by a second transition to the TlI structure at about 11 GPa, a transition that appears to be independant of temperature. At high temperature the transition is apparently directly from the NaCL to CsCl structure.

![Phase diagram](image1)

**FIG. 12.** Phase diagram\textsuperscript{27} for AgCl.

![Fourier transform](image2)

**FIG. 13.** Fourier transform magnitude for AgCl at 1.6 GPa and 77 K and FEFF\textsuperscript{615} fit.

Very recently we have carried out XAFS measurements at SSRL on the Ag k-edge of AgCl at 77 K, using niobium as the pressure medium. Our results indeed show two transitions that roughly agree with Ref. 27. Fig. 13 shows a fit\textsuperscript{15} to the magnitude of the Fourier transform of the data for 1.6 GPa, corresponding to the radial distribution about the silver in the NaCl phase. Fig.14 shows the transforms for the postulated KOH structure that we find above 6 GPa. Although still under analysis, the first peak appears to be fit well with a model of seven nearest neighbor Cl atoms. In the actual KOH monoclinic structure there are indeed seven such neighbors all within a range of only 0.2 Å. The fact that the first nearest neighbor peak does not increase in strength with pressure (the expected increase
in $\sigma^2$) indicates some relative softening of these bonds. Above about 10 GPa yet another structure is evident as seen in Fig. 15. This presumably indicates the TII type phase which is closely related to the KOH structure. There is an obvious reduction in $\sigma^2$ in this phase. In general, such behavior is also seen when a material makes a transformation to a disordered or amorphous state. This is an intriguing finding because the work of Ref. 24 suggests that for the mixed $\text{AgBr}_{1-x}\text{Cl}_x$, not only will pressure cause buckling, but will also lead to a much more disordered transition, perhaps continuous, to a new kind of amorphous-like phase. Besides the local structural aspects, our continuing studies of this whole system are expected to have possible technological significance for infrared optical fiber production.\textsuperscript{28,29}

![FIG. 14. Fourier transform magnitude for AgCl at 6, 6.7 and 7.9 GPa at 77 K.](image1)

![FIG. 15. Fourier transform magnitude for AgCl at 9.8 and 10.4 GPa and 77 K.](image2)
Publications


"The Effect of Hydrostatic Pressure on the Local Structure of K1-xNa_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 (in press).


Reports and Presentations


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