High Pressure X-Ray Absorption Studies of Phase Transitions

J.M. Tranquada* and R. Ingalls

Department of Physics, FM-15, University of Washington
Seattle, WA 98195, USA

E.D. Crozier

Department of Physics, Simon Fraser University
Burnaby, B.C. V5A 1S6, Canada

CONF-840764--8

DE86 000548

1. Introduction

The application of high pressure to a substance generally changes all of its properties to some degree. One of the most striking changes is a pressure-induced phase transition. Here we review how such phase changes reveal themselves in x-ray absorption spectra. The examples given are from our own work at SSRL, the experimental details having been previously reported [1]. The EXAFS-derived bond compression of a standard are used to determine the pressure.

2. Pressure Dependence of the EXAFS

We have previously reported the effects of pressure on the XANES of some materials undergoing phase transitions [2]. Although we shall again discuss such effects, it is our main purpose here to show the characteristic behavior of the EXAFS in such cases. We choose to write the EXAFS interference function $\chi(k)$ in terms of the cumulants $\sigma^{(n)}$ which characterize the various pair distribution functions [3,4]. For a given shell,

$$\chi(k) = \frac{N}{kR^2} F(k) e^{-2R/\lambda} e^A \sin B \quad (1)$$

where the arguments A and B are given by

$$A = -2\sigma^2 k^2 + \frac{2}{3} \sigma^{(4)} k^4 + \dots \quad \text{and} \quad (2)$$

$$B = 2kR + \phi(k) - \frac{4\sigma^2 k}{R} \left(1 + \frac{R}{\lambda}\right) - \frac{4}{3} \sigma^{(3)} k^3 + \dots \quad (3)$$

As pressure is applied, essentially all of the parameters in Eqs. (1-3) are expected to vary, with the structural parameters N, R, and σ^2 expected to exhibit the most significant changes. Using standard EXAFS analysis, the term

$$\ln \left| \frac{N_a R_b^2}{N_b R_a^2} \right| - \frac{2\Delta R}{\lambda} - 2\Delta\sigma^2 k^2 + \frac{2}{3} \Delta\sigma^{(4)} k^4 + \dots \quad (4)$$

is extracted from the logarithm of the ratio of the amplitude of spectrum vs spectrum b. Similarly, the term

$$2k[\Delta R - \frac{\Delta\sigma^2}{R} (1 + \frac{R}{\lambda})] - \frac{4}{3} \Delta\sigma^{(3)} k^3 + \dots \quad (5)$$

is obtained from the phase difference between two runs. The main point here is that there is a minor degree of coupling between fits to ΔR and $\Delta\sigma^2$, vs pressure. Also, because of anharmonicity, one generally must deal with a nonlinear fit in k^2 or k , respectively.

* Present address, Brookhaven National Laboratory, Upton, NY 11973.

mf

The above type of analysis has been made for the Br k-edge spectra in NaBr. Figure 1 shows the transforms of the data for three pressures, where one clearly sees the effects of compression and decreasing thermal disorder. After a back transformation of the nearest neighbor peak, the various parameters in Eqs. (4) and (5) may be determined. We have found it advantageous to first determine the room temperature atmospheric pressure cumulants through comparison with low temperature data, which is assumed to correspond to the harmonic case. The main result from the pressure experiments yields ΔR and $\Delta\sigma^2$ values which appear to be nearly linearly related. For NaBr we express this relation as $\left. \frac{\Delta\sigma^2/\sigma^2}{\Delta R/R} \right|_{p=0} \approx 12$. Interpreting these results in terms of an Einstein model would lead to a Grüneisen constant $\gamma_E = \frac{d \ln \omega_E}{d \ln V}$ of about 1.56 [4].

Fig. 1. Fourier transforms of $k^3\chi(k)$ for NaBr

At atmospheric pressure RbCl has the same B1 (rock-salt) structure as NaBr. However, at about 5.2 [kbar] it transforms to the B2 (cesium chloride) structure. We have followed the EXAFS of RbCl through this phase transition and performed an analysis similar to that for NaBr described above. The main results are shown in Fig. 2. At low pressures ($\frac{\Delta R}{R} = 0$)

the data yield $\left. \frac{\Delta\sigma^2/\sigma^2}{\Delta R/R} \right|_0 = 16.7$, which would correspond to an Grüneisen

parameter of $\gamma_E = 2.78$. This result appears to hold for both phases, that is, both the near neighbor distance and its σ^2 decrease with pressure except at the B1 to B2 transition where they increase slightly. The slight increase in bond length at the transition reflects the fact that the

Fig.2. Change in σ^2 vs R for nearest neighbor distance in RbCl. Open(closed) symbols represent the B1 (B2) phase

coordination goes from 6-fold to 8-fold while the volume itself decreases by approximately 14%. The accompanying increase in σ^2 signifies a softening of the appropriate force constants. (The data is also consistent with N increasing from 6 to 8.)

We have carried out such an analysis in yet a more complex case, namely CuBr, which undergoes two phase transitions with pressure: a sharp transition from CuBr III to CuBr V (zincblende to tetragonal) at about 50 [kbar] and a sluggish transition from CuBr V to CuBr VI (BI structure) between 60 and 80 [kbar]. The data for both K edges are consistent with a nearest neighbor coordination of $N=4$ for the tetragonal phase, the exact structure of which is not yet known, and $N=6$ for the BI phase. Again, analyzing the data in terms of $\Delta\sigma^2$ vs ΔR yields a relation similar to NaBr and RbCl (Fig. 3). At each transition there appears to be an increase in $\Delta\sigma^2$ and ΔR followed by a decrease as the pressure increases further. We remark here that ZnSe also transforms to a rock-salt phase at high pressure; a similar instability is reflected in the pressure dependence of σ^2 for the second shell. This is discussed further in another paper at this conference [5].

Fig.3. Change in σ^2 vs R for the nearest neighbor distance in CuBr III (O), CuBr V (■) and CuBr VI (▲)

3. Pressure Dependence of the XANES

Figures 4 and 5 show the changes in the XANES with the pressure-induced changes in crystal structure, for RbCl and CuBr. A definitive detailed explanation of such behavior is not yet available. We have also been studying the mixed-valent materials SmS and SmSe which undergo isostructural insulator-metal transitions with pressure. Figure 6 shows the XANES

Fig.4. Rb k-edge XANES in the B1 (solid line) and B2 (dashed line) phases of RbCl

Fig. 5. a) Cu, and b) Br k-edge XANES in the CuBr III (solid line), CuBr V (dashed line) and CuBr VI (dotted line) phases

Fig. 6. Sm L_3 -edge XANES of SmSe at several pressures

behavior of the Sm L_3 edge in SmSe, for example. Although, to our knowledge, these spectra have not been explained from first principles, they represent the change from the divalent $4f^6$ to trivalent $4f^5$ state, in which the photo-excitation threshold is roughly 7 eV higher, accompanied by a volume collapse.

We also find that if the fractional valence is determined from the relative areas under the two peaks, it does not follow ΔR in a linear manner. That is after correcting for the usual compressibility, the collapse in ΔR occurs at a lower pressure than the valence change.

Similarly, and as reported by FRANK et al. [6] for SmS, we find that σ^2 for the nearest neighbor shell appears to increase and then decrease, going through the transition despite the large decrease in ΔR . This would be in contrast to the usual Grüneisen relationship described above for the other systems. It remains to be determined whether such a result is related to thermal disorder or some type of static structural disorder, possibly resulting from some type of inhomogeneity.

4. Acknowledgments

We would like to express our thanks to other members of our research groups, H. Alberding, R. Bauchspiess, B. Houser, R. Owen, A. Seary, P. Viren, and J. Whitmore. This work was supported in part by the U.S. National Science Foundation, the Department of Energy, and by the National Sciences and Engineering Research Council of Canada.

1. R. Ingalls, E.D. Crozier, J.E. Whitmore, A.J. Seary, and J.M. Tranquada, *J. Appl. Phys.* 51, 3158 (1980)
2. R. Ingalls, J.M. Tranquada, J.E. Whitmore and E.D. Crozier in *EXAFS and Near Edge Structure*, A. Bianconi, L. Incoccia and S. Stipcich, eds. (Springer-Verlag, Berlin, 1983) p. 153
3. J.M. Tranquada and R. Ingalls, *Phys. Rev. B* 28, 3520 (1983)
4. J.M. Tranquada, Ph.D. Thesis, Univ. of Washington, 1983 (unpublished)
5. J.M. Tranquada and R. Ingalls, this conference.
6. K.H. Frank, G. Kaindl, J. Feldhaus, G. Wortman, W. Krone, G. Materlik, and H. Bach, in *Valence Instabilities*, P. Wachter and H. Boppart, eds. (North Holland, Amsterdam, 1982) p. 139

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.