Physica Scripta. Vol. T115, 264–266, 2005

Correlations in the Vibrations of Atoms in Complex Unit Cells

Frank Bridges[1] and D. Cao[2]

[1]Physics Dept., University of California, Santa Cruz, CA 95064, USA
[2]MS-K764, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Received June 26, 2003; accepted November 4, 2003

PACS number: 61.10.Ht

Abstract

Correlations in the atomic motions can significantly change the interpretation of thermal effects in structural data. Including correlations of the stretching of the Zr-O bond with transverse O vibrations in the W-O-Zr linkage, in ZrW_2O_8, can explain the apparent discrepancy between a small σ^2_{W-Zr} in EXAFS data and a large O thermal parameter U^2. This work also shows that in some cases a small value of σ^2 does not always mean that the vibration frequency is high.

The presence of correlated atomic motions in crystalline structures is well known in the EXAFS community. Perhaps the best known example is the very narrow width (small σ) for the nearest neighbor pair distribution function when long wavelength acoustic phonons dominate the atomic vibrations. On a scale of a few unit cells, all the atoms locally are moving in the same direction, the stretch of the nearest neighbor bond length is small, and $\sigma^2 \ll U_A^2 + U_B^2$, where U_A^2 and U_B^2 are the diffraction thermal parameters for the two atoms. In this case, the displacements of the nearest neighbors are said to be positively correlated. Conversely if short wavelength optical phonons dominated, the displacements of the nearest neighbors would be in opposite directions (negatively correlated), and the bond length would have a large vibration amplitude. The very large value of σ^2 observed in that case would produce a low amplitude peak in the Fourier transformed XAFS data. For simple systems, the acoustic phonons usually dominate for $T < 300$ K, and the local atomic displacements are positively correlated.

For systems with more complex, open unit cells, new degrees of freedom exist. In particular, there are many optical modes; if some of them have low frequencies, they can dominate the vibration spectra. For ZrW_2O_8 which we consider here, the cubic unit cell (space group $P2_13$) is quite complex. This material is formed of corner-joined WO_4 tetrahedra and ZrO_6 octahedra, and has a number of unusual features:- a negative thermal expansion from 15–1000 K [1, 2], a large contribution to the specific heat at low T which has been modeled by two Einstein modes at 38 and 67 K [3], and two low energy peaks in the phonon density of states obtained in neutron scattering experiments at similar energies [4]. The unusual negative thermal expansion in ZrW_2O_8 has been attributed to these low energy vibration modes; EXAFS experiments suggest that these modes involve the massive WO_4 and ZrO_6 units. [5] Thus for the lowest optical modes these polyhedra units appear to vibrate as "large atoms", although some stretch of a unit is required. These motions involve highly correlated displacements of the polyhedral clusters and are not direct extensions of modes observed in simple systems.

The EXAFS data for the ZrW_2O_8 system have been presented previously [5] – here we focus on the correlations that must be present to understand the apparently conflicting results from EXAFS and diffraction. In Fig. 1 we show part of the crystal structure (a cut-away of the cubic unit cell, viewed perpendicular to a ⟨111⟩ axis) to show the local environment about the WO_4 tetrahedra. One corner of each tetrahedron, aligned along a ⟨111⟩ axis, is not connected to any other unit and is therefore unconstrained. The tetrahedra can move into empty space along this ⟨111⟩ axis with little cost in energy. The other three corners, in a plane perpendicular to the ⟨111⟩ axis, are linked to ZrO_6 octahedra. The EXAFS data show that the amplitude of the W-O peak (W L_{III} edge data) changes only a few percent up to 300 K; consequently, the W-O bonds are very rigid. For ZrO_6 however, there is a small broadening of the Zr-O pair distribution function – the Zr-O bond is not completely rigid up to 300 K in contrast to the assumptions in the rigid unit model (RUM) [6]; small distortions of this bond allow vibrations of the polyhedral units.

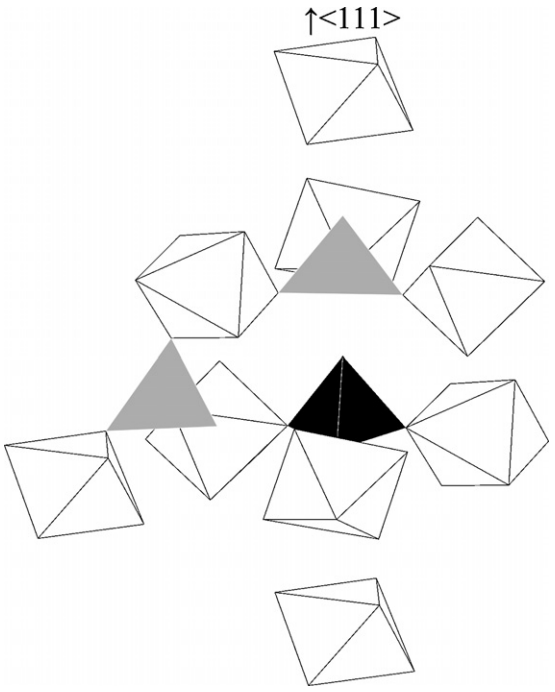

Fig. 1. A cut-away section of the cubic unit cell to show the local structure about the W(1)O_4 (gray) and W(2)O_4 (black) tetrahedra. Each tetrahedron is corner-connected to three ZrO_6 octahedra; the forth vertex, oriented along a ⟨111⟩ axis (vertical), is unconstrained. A third W(1)O_4 (gray) tetrahedron aligned along another ⟨111⟩ axis is also shown.

More surprising is the weak T-dependence of the W-Zr (or Zr-W) peak which includes multiple scattering path contributions. There is essentially no temperature change up to ~125 K and only a small change up to 300 K that is comparable to the net change for the Zr-O peak. The T-dependences of σ^2 for the Zr-O and the W-Zr (or Zr-W) peaks are very similar.

Diffraction measurements show a large U^2 parameter for the different O atoms and smaller but significant U^2 parameters for the heavy metals, U_W^2 and U_{Zr}^2 [1, 7, 8]. The interpretation of the

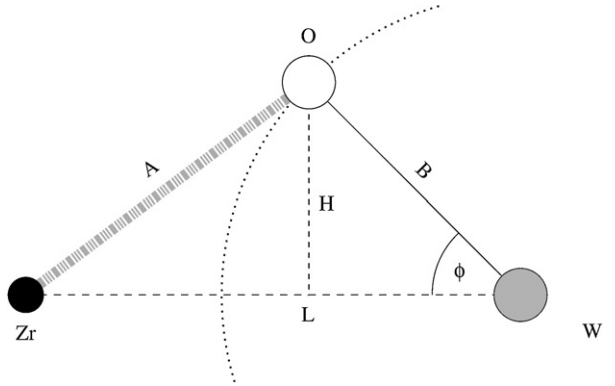

Fig. 2. The geometry of the Zr-O-W linkage; the angle ϕ is exaggerated to show the different distances. The W-O bond length B is rigid and the O would move on the dotted arc about the W atom. Between Zr and O there is a stiff spring (but the bond is not rigid).

diffraction data focused on the transverse vibrations of the O in the W-O-Zr linkage, and ignored stretching of the Zr-O bond and translations of the WO_4 tetrahedra as a rigid unit. (At least part of the O motion must correspond to the latter.) Under the assumption of rigid rotating units and uncorrelated displacements, a transverse O vibration would lead to a contraction of the Zr-W distance consistent with the observed macroscopic contraction. However it would also lead to a very large σ^2 for W-Zr or Zr-W which is not observed in the EXAFS data. If one includes the Zr-O bond stretching vibrations in the W-O-Zr linkage, but still assumes that the stretching vibration and the transverse O vibrations are uncorrelated, then the EXAFS data would imply that the transverse O vibration amplitude must be small, in conflict with the diffraction U^2 parameters. However, when correlations are included a significant transverse O vibration is possible with still only a weak temperature dependence for σ^2_{W-Zr}.

The W-O-Zr linkage is shown in Fig. 2; it is the important connection between a tetrahedron and an octahedron. The W-O bond B is taken to be rigid based on the EXAFS data, while the Zr-O bond A stretches as the W/Zr polyhedra units undergo thermal vibrations, a combination of translations and rotations. The O atom must move on an arc (to keep B rigid) and its motion is not completely transverse but includes a small component parallel to the Zr-W distance. This suggests a coupling between the rotations of the O about W and stretching of the spring A. Note that even if A were an ideal spring, the motions would not be harmonic. In the limit of no vibrations of the Zr-W distance (like the ends of a guitar string) the Zr-O bond would stretch completely in phase with the O transverse motion. For various assumptions about the stretching of A and the degree of correlation with the transverse O vibration, we need to consider the changes in the length L ($\Delta L = L - L_0$; L_0 is the length at low T) and the variance of the thermal fluctuations, $(\Delta L)^2$.

We initially allow the possibility that the motions involve two different modes – i.e. that the stretch of the Zr-O may arise from acoustic phonons while the transverse O motions might arise from low frequency optical modes. The time dependence of A and H are modeled as sinusoidal vibrations about the static values, A_0 and H_0.

$$\begin{aligned} A &= A_0 + A_1(t), \\ H &= H_0 + H_1(t), \\ A_1(t) &= a_1 \cos(\omega_A t), \\ H_1(t) &= h_1 \cos((\omega_H t + \theta). \end{aligned} \tag{1}$$

Here a_1 and h_1 are the vibration amplitudes and ω_A and ω_H are the frequencies for the stretching and transverse motions. The total Zr-W distance, L, is given by:

$$L = \sqrt{A^2 - H^2} + \sqrt{B^2 - H^2}. \tag{2}$$

To simplify the final results we will set $B = A_0$. Substituting for A and H, expanding the square roots to second order, and keeping terms up $A_1^2(t)$, $H_1^2(t)$ and $A_1(t)H_1(t)$, then

$$\begin{aligned} L = L_0 &+ \frac{1}{L_0}[2A_0A_1(t) + A_1^2(t) - 4H_0H_1(t) - 2H_1^2(t)] \\ &- \frac{1}{L_0^3}[4A_0^2A_1^2(t) + 8H_0^2H_1^2(t) - 8A_0H_0A_1(t)H_1(t)] \end{aligned} \tag{3}$$

where $L_0 = 2\sqrt{A_0^2 - H_0^2}$. Next we need to calculate the average length change $\langle \Delta L \rangle = \langle L - L_o \rangle$ and its variance, $\sigma^2_{thermal} = \langle (\Delta L)^2 \rangle$. To calculate these averages, we integrate each term over time, e.g. for $A_1^2(t)$:

$$\langle A_1(t)A_1(t) \rangle = \int A_1(t)A_1(t)\,\mathrm{d}t. \tag{4}$$

Using Eqn. (1) in this integral then:

$$\begin{aligned} &\langle A_1(t) \rangle = \langle H_1(t) \rangle = 0, \\ &\langle A_1^2(t) \rangle = a_1^2/2; \qquad \langle H_1^2(t) \rangle = h_1^2/2. \end{aligned} \tag{5}$$

The average of $A_1(t)H_1(t)$ depends on ω_A and ω_H; if $\omega_A \neq \omega_H$, then $\langle A_1(t)H_1(t) \rangle = 0$; for $\omega_A = \omega_H = \omega$,

$$\begin{aligned} \langle A_1(t)H_1(t) \rangle &= \frac{1}{T}\int_0^T h_1 a_1 \cos(\omega t)\cos(\omega t + \theta)\,\mathrm{d}t \\ &= \frac{h_1 a_1 \Phi}{2}, \end{aligned} \tag{6}$$

where $\Phi = \cos\theta$ is called the correlation parameter and can vary from -1 to 1. After averaging and simplification

$$\langle \Delta L \rangle = -\frac{1}{L_0(A_0^2 - H_0^2)}[A_0^2h_1^2 + H_0^2a_1^2/2 - A_0H_0a_1h_1\Phi]. \tag{7}$$

For $a_1 = 0$ (i.e. Zr-O is rigid), $\langle \Delta L \rangle \sim -h_1^2/L_0$ as used earlier [7]. For $a_1 \neq 0$ and Φ positive, $\langle \Delta L \rangle$ is reduced but for the relevant parameters the reduction is not large. In contrast the correlations have a very large impact on $\sigma^2_{thermal}(\Phi)$:

$$\sigma^2_{thermal}(\Phi) = \frac{2}{L_0^2}[A_0^2a_1^2 + 4H_0^2h_1^2 - 4A_0H_0a_1h_1\Phi]. \tag{8}$$

When A_1 and H_1 are uncorrelated ($\Phi = 0$) then

$$\sigma^2_{thermal}(0) = \frac{A_0^2}{2(A_0^2 - H_0^2)}\left[a_1^2 + 4\frac{H_0^2}{A_0^2}h_1^2\right]. \tag{9}$$

This is the typical results for two uncorrelated mechanisms; the contributions to the broadening add up in quadrature. For positively correlated motions, $\sigma^2_{thermal}$ is reduced because of the minus sign (Eqn. (8)). When $\Phi = 1$, Eqn. (8) simplifies to:

$$\sigma^2_{thermal}(1) = \frac{A_0^2}{2(A_0^2 - H_0^2)}\left[a_1 - 2\frac{H_0}{A_0}h_1\right]^2. \tag{10}$$

In this case, correlations effects are very large because $\sigma^2_{thermal}$ depends on the difference, $a_1 - 2H_0h_1/A_0$.

Using σ^2_{Zr-O} and U^2_O from diffraction to estimate the vibration peak amplitudes ($a_1 \sim 0.08$ Å, $h_1 = 0.21$ Å), $H_0 = 0.4$ Å for W(1)-O-Zr, and $A_0 \sim 2$ Å, then for $\Phi = 0$ $\sigma^2_{thermal}(0) \sim 7.0 \times 10^{-3}$ Å^2, while for $\Phi = 1$, $\sigma^2_{thermal}(1) \sim 8.3 \times 10^{-6}$ Å^2. For

negatively correlated displacements $\sigma^2_{thermal}$ can be very large, > 0.01 Å^2. Consequently, $\sigma^2_{thermal}(\Phi)$ can have a wide range of values depending on the value of Φ.

In this simplified discussion we have not accounted for any static distortions or zero-point motions and have not considered the multiple scattering contributions for W(2)-O-Zr. We have also used the maximum value of h_1 obtained in diffraction experiments, which assumed that the oxygen thermal parameter U^2_O arises solely from O transverse motion. This overestimates h_1, as part of the O displacement must correspond to translations of the WO_4 (and ZrO_6) units – i.e. rotations/translations of the W-O-Zr linkage. Unfortunately in Eqn. (8) h_1 and Φ are coupled and cannot be uniquely determined.

This work shows that in some cases it is crucial to recognize that atomic motions can be highly correlated and may involved quite large clusters of atoms. Although the O thermal parameters (U^2_O) from diffraction cannot be uniquely decomposed into two components – one corresponding to an O transverse motion and the other a translation of the WO_4 unit, including correlations in the atomic displacements essentially removes the discrepancies between the small value of σ^2_{W-Zr} and the relatively large values of U^2_O. The calculation also shows that in some cases, a small value of σ^2 does not necessarily mean that the thermal vibration causing the broadening has a high frequency. For the W-O-Zr linkage the Zr-O bond stretches slightly to accommodate the low frequency motions of the WO_4 and ZrO_6 units; the small stretch of the Zr-O bond is a *byproduct* of a low frequency mode and is not directly a measure of the Zr-O spring constant, κ (i.e. $\sigma^2 \sim kT/\kappa$ at high T) as is often assumed.

Acknowledgments

This work was supported by NSF grant DMR0071863 and was conducted under the auspices of the U.S. Department of Energy (DOE), Office of Basic Energy Sciences (OBES). The experiments were performed at SSRL, a national user facility operated by Stanford University on behalf of the DOE/OBES.

References

1. Mary, T. A., Evans, J. S. O., Vogt, T. and Sleight, A. W., Science **272**, 90 (1996).
2. David, W. I. F., Evans, J. S. O. and Sleight, A. W., Europhys. Lett. **46**, 661 (1999).
3. Ramirez, A. P. and Kowach, G. R., Phys. Rev. Lett. **80**, 4903 (1998).
4. Ernst, G., Broholm, C., Kowach, G. R. and Ramirez, A. P., Nature **396**, 147 (1998).
5. Cao, D., Bridges, F., Kowach, G. R. and Ramirez, A. P., Phys. Rev. Lett. **89**, 215902 (2002); Phys. Rev. B **68**, 180511 (2003).
6. Pryde, A. K. A. *et al*., J. Phys. Condens. Matter **8**, 10973 (1996).
7. Evans, J. S. O., David, W. I. F. and Sleight, A. W., Acta Cryst. **B55**, 333 (1999).
8. Evans, J. S. O., Mary, T. A., Vogt, T., Subramanian, M. A. and Sleight, A. W., Chem. Mater. **8**, 2809 (1996).

