Correlated atomic motions in the negative thermal expansion material ZrW$_2$O$_8$: A local structure study

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Recent studies of zirconium tungstate, ZrW$_2$O$_8$, show an isotropic negative thermal expansion (NTE) over a wide temperature range. It has been proposed that the low-energy phonon vibrational modes, observed in both specific heat and phonon density-of-states measurements, are responsible for this unusual NTE. We have carried out x-ray-absorption fine-structure (XAFS) experiments at both the W L$_{III}$ edge and Zr K edge to study the detailed local structure in ZrW$_2$O$_8$. Our XAFS results show a very small temperature dependence of the broadening parameter, $\sigma$, for the W-Zr atom pair and the W-O-Zr linkage; consequently, the displacements of the W, O, and Zr atoms must be correlated. The data show a much larger temperature dependence of $\sigma$ for the nearest W$_1$-W$_2$ pair as well as for the nearest Zr-Zr pair. These combined results indicate that it is the correlated motion of a WO$_4$ tetrahedron and its three nearest ZrO$_6$ octahedra that leads to the NTE effect in this material instead of primarily transverse vibrations of the middle O atom in the W-O-Zr linkage. The data for both W-W and Zr-Zr atom pairs also indicate a hardening of the effective spring constant near 100 K, which is consistent with the shift of the lowest mode with $T$ in the phonon density of states. A simple model is developed to explain the NTE in terms of the local structure results; it also provides a natural explanation for the lack of a soft-mode phase transition.

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I. INTRODUCTION

The negative thermal expansion (NTE) in ZrW$_2$O$_8$ was discovered long ago by Martinek and Hummel$^1$ and has attracted considerable attention recently due to its isotropic nature over a wide range of temperature (from 10 to 1050 K).$^{2,3}$ NTE has been studied in several different systems,$^{4-6}$ but most of them only show a small and anisotropic NTE effect over a small temperature range. The unusual NTE features of ZrW$_2$O$_8$ make it potentially useful in developing composites with easy-to-control thermal properties.

The crystal structure of zirconium tungstate, ZrW$_2$O$_8$, is cubic with the space group $P2_13$ at temperatures from 0 to $\sim$430 K, while the space group changes to $Pa\bar{3}$ as the temperature passes $\sim$430 K, with an order-to-disorder phase transition due to the disordering of the WO$_4$ tetrahedra.$^{2,7}$ An interesting feature of the ZrW$_2$O$_8$ crystal structure is that it consists of ZrO$_6$ octahedra and WO$_4$ tetrahedra which are connected via the corner O atoms. An important exception is that one O atom on each WO$_4$ tetrahedron is not connected to another unit and is therefore considered to be unconstrained. This O is located on a WO$_4$ vertex oriented along one of the (111) directions. Figure 1 shows the details of this structure.

It was first suggested by Mary et al. that a large transverse vibration of the oxygen in the middle of the W-O-Zr linkage, which requires corresponding rotations of the polyhedra, is the primary origin of NTE in this material due to the unconstrained feature of the structure.$^2$ A similar idea was used to explain the isotropic NTE in ZrV$_2$O$_7$ as temperature increases above 373 K,$^8$ i.e., the transverse vibration of the central O atom in the middle of the O$_3$V-O-VO$_3$ group.

ZrV$_2$O$_7$ has a similar structure to ZrW$_2$O$_8$ consisting of ZrO$_6$ octahedra and VO$_4$ tetrahedra. Three corners of a VO$_4$ tetrahedron are shared with ZrO$_6$ octahedra, but the fourth corner of each VO$_4$ tetrahedron is shared with another VO$_4$ tetrahedron and is therefore more highly constrained.

The calculation of rigid unit modes (RUMs) in these two materials, carried out by Pryde et al.,$^9$ pointed out that

![Image](http://example.com/figure1.png)

**FIG. 1.** The cubic unit-cell structure for ZrW$_2$O$_8$. The white polyhedra are the ZrO$_6$ octahedra; they occupy the corner and face-centered positions of the unit cell. The four gray and four black polyhedra are the W(1)O$_4$ and W(2)O$_4$ tetrahedra, respectively. Each tetrahedron shares its three corners with three other white octahedra while the last unshared corner is pointing along one of the four (111) axes. One of these (111) axes is between two isolated octahedra in this figure (the two octahedra marked Zr1 and Zr2); there are two tetrahedra on this (111) axis with their unshared corner pointing towards Zr1.
RUMs are only possible in \( \text{ZrW}_2\text{O}_8 \). A comparison of the calculated vibration density of states for these two materials shows that many more low-frequency modes occur in \( \text{ZrW}_2\text{O}_8 \) than in \( \text{ZrV}_2\text{O}_7 \). Since \( \text{ZrW}_2\text{O}_8 \) exhibits NTE at very low temperatures, Pryde et al. suggested that the low-frequency rotations of rigid units contribute mainly to the NTE in this material, and the mechanism for NTE in \( \text{ZrW}_2\text{O}_8 \) and \( \text{ZrV}_2\text{O}_7 \) should be qualitatively different.\(^9\)

The thermodynamics of this unusual system have been investigated by several groups in recent years.\(^3,10–14\) In specific-heat data there is a very large contribution at low temperatures. To model these results, Ramirez and Kowach\(^10\) used two low-energy Einstein modes (near 38 and 67 K) with a ratio of 1:3, respectively, in their density of states, plus smaller contributions from Debye modes with much higher Debye temperatures. Ernst et al.\(^11\) measured the low-energy density of states using neutron scattering and found similar low-energy modes. In addition, using the modes below 8 meV they estimated the effective Grüneisen parameter and found it to be large and negative (\(-14\)). David et al.\(^3\) also estimated the Grüneisen parameters but did so for each of the modes separately—in this analysis the two lowest modes both have negative Grüneisen parameters but the magnitude of the lower mode is roughly 20 times larger, while the higher-energy Debye modes have very small positive Grüneisen parameters. Recently Mittal et al.\(^14\) investigated the change in phonon frequency with applied pressure and found that the low-frequency modes softened, hence the lowest modes have a negative Grüneisen parameter in agreement with the earlier work.\(^3,11\) These studies clearly show that the low-energy optical modes play a dominant role in the NTE but detailed information about the atomic vibrations is not yet available, particularly information explaining which atoms are principally involved. In order to investigate the local structure of \( \text{ZrW}_2\text{O}_8 \) in detail, we have carried out x-ray-absorption fine-structure (XAFS) measurements as a function of temperature. From these data we obtain plots of \( \sigma^2 \) vs \( T \) from which an Einstein or Debye temperature can be extracted. This enables us to connect the local structure results to the modes found in the above studies. Some preliminary results have recently been published.\(^27\)

The XAFS data show that the \( \text{WO}_4 \) tetrahedra are rigid from 5 up to \( \sim 320 \) K. The \( \text{ZrO}_6 \) octahedra are softer, although still quite stiff over the same temperature range, but they are not rigid. Surprisingly, the data analysis shows that the W-O-Zr linkage is also quite stiff, comparable to the \( \text{ZrO}_6 \) octahedra.

The data for the W(1)-W(2) and Zr-Zr atom pairs show much larger temperature dependencies, which are associated with low-frequency optical vibrational modes. These combined results indicate that the Zr, O, and W atomic motions are highly correlated; such correlations must be recognized in discussions of the low-energy vibrational modes. Based on these results, we propose a modified model for the eigenmodes that includes translations of the \( \text{WO}_4 \) as a rigid unit and leads to NTE in this material. This model also provides an explanation for both the unusually low energy of the optical modes and the lack of formation of a soft-mode dispersive transition.

![FIG. 2. \( k\chi(k) \) vs \( k \) for both the W \( L_{III} \) and Zr \( K \) edges to show the quality of the XAFS data.](image)

The experimental details and the sample information are given in Sec. II. Section III shows the XAFS data and analysis, while the discussion is presented in Sec. IV. The conclusions are summarized in Sec. V.

### II. EXPERIMENT DETAILS

XAFS experiments were carried out at the Stanford synchrotron-radiation laboratory (SSRL) on beam line 10-2 with silicon (220) monochromator crystals. W \( L_{III} \)-edge and Zr \( K \)-edge data were collected as a function of temperature from 5 to 350 K.

The sample used in this experiment was a \( \text{ZrW}_2\text{O}_8 \) powder, which was prepared from high-purity Alfa AESAR Pruratonic grade \( \text{ZrO}_2 \) (99.978%) and \( \text{WO}_3 \) (99.998%) in a stoichiometric ratio. The powders were vibratory milled in methyl ethyl ketone to reduce the particle size. After drying, the powder mixture was uniaxially pressed into pellets and heated in an oxygen atmosphere to 1470 K for 4 h and quenched to room temperature. The sample was reground and passed through a 400-mesh sieve to obtain a fine powder. The fine powder was then brushed onto Scotch tape in order to make samples for XAFS measurements.

### III. XAFS DATA AND ANALYSIS

#### A. XAFS data

The x-ray-absorption data were reduced using standard procedures.\(^15,16\) The XAFS \( k \)-space data are shown in Fig. 2 for the W \( L_{III} \) and Zr \( K \) edges at 20 K. Both sets of data show very good quality. Here \( k \) is the wave vector and \( \chi \) is the XAFS function, which is defined as \( \chi = (\mu / \mu_0) / \mu_0 \), where \( \mu \) is the absorption coefficient and \( \mu_0 \) is the background (embedded atom) function.\(^17\)
XAFS \( r \)-space data [the Fourier transform (FT) of the \( k \)-space data] are shown in Fig. 3 for the W \( L_{III} \)-edge data. The \( r \) space data show peaks which correspond to different atomic shells around the central atom. The position of each peak is shifted slightly in \( r \) space as a result of a well-known phase shift. The temperature dependence of each peak provides information about the relative (correlated) vibrations of the corresponding atomic shell. A reduced amplitude of a peak indicates a larger width, \( \sigma \), and hence a larger local distortion of that atomic shell. Detailed discussion about the XAFS technique and data analysis can be found in Refs. 15–19.

The FT of \( k^3 \chi(k) \) is plotted in Fig. 3 instead of \( k \chi(k) \) to enhance the change in the amplitude of peaks at longer distance (from 3 to 6 Å). The upper panel shows that the first W-O peak (at \( \sim 1.4 \) Å) has very little temperature dependence, which indicates that the W-O bonds in the WO\(_4\) tetrahedra [for both W(1) and W(2)] are very rigid and essentially undistorted as the temperature increases to 315 K. In the expanded view (lower panel of Fig. 3), the peak near 3.5 Å, corresponding to the W-Zr atom pair, also shows little change in the amplitude from 20 to 120 K, while the amplitude of this peak drops about 25% when the temperature reaches 315 K. In contrast, the peak near 4.0 Å, which is mainly due to the nearest W\(_1\)-W\(_2\) atom pair, changes about 60% from 20 to 315 K. This much larger amplitude decrease with temperature near 4.0 Å indicates that the vibrations between the nearest W(1) and W(2) are much softer than that between the nearest W-Zr atom pair. These soft vibrational modes can be excited at much lower temperatures. The peak near 5.6 Å includes several single- and multiple-scattering peaks, and also has a large change in amplitude with temperature.

To show the temperature dependence more clearly, difference data are shown in Fig. 4. These plots are the difference in the FT of \( k^3 \chi(k) \) data between 20 and 315 K, 20 and 160 K, as well as 20 and 5 K. Figure 4 clearly illustrates that significant changes only occur beyond 3.5 Å as the temperature is increased. The bottom panel indicates almost no change to 20 K; the middle panel shows little change up to 3.5 Å, however, several significant peaks near 3.9, 4.5, 5.0, and 5.6 Å appear. This indicates that large local distortions for atom shells at these distances are present at 160 K. These distortions become even larger when the temperature is increased to 315 K as indicated in the top panel. An additional contribution develops near 3.6 Å for \( T \) at 315 K, which is due to a change in the amplitude for the W-Zr peak. A small peak also develops at 2 Å (see top panel of Fig. 4); it arises from a large change in the fluctuations of the long W(1)-O(3) distance between the two WO\(_4\) tetrahedra.
The first peak near 1.6 Å is the nearest Zr-O peak, and shows a small change with temperature (20 to 315 K), which is a surprisingly large effect.

### B. Fitting procedures

The XAFS equation we use is given by

$$k\chi(k) = \sum_i k\chi_i(k)$$

$$= \text{Im} \sum_i A_i \int_0^\infty F_i(k,r) \frac{g_i(r_0,r) e^{i(2kr + 2\delta_i(k) + \delta_i(k))}}{r^2} dr,$$

where \(\chi_i\) is the XAFS function for shell \(i\), \(F_i(k,r)\) is the back-scattering amplitude of the photoelectron from neighbors \(i\) (it includes mean-free-path effects), \(g_i(r_0,r)\) is the pair distribution function for the atoms at a distance \(r_0\)—assumed to be Gaussian for most of this work—and \(\delta_i(k)\) and \(\delta_i(k)\) are the phase shifts of the central and backscattered photoelectron waves. The amplitude factor \(A_i\) is given by

$$A_i = N_i S_0^2,$$

where \(N_i\) is the number of equivalent atoms in shell \(i\), and \(S_0^2\) is the effective “amplitude reduction factor” that accounts primarily for many-body effects such as shake-up or shake-off, but also includes small corrections to the mean free path in the theoretical functions. In this equation, the photoelectron wave vector \(k\) is defined by \(k = \sqrt{2m(E-E_0)/\hbar^2}\), where \(E_0\) is the binding energy for the absorption edge under study.

A detailed fit was carried out for W \(L_{III}\) and Zr \(K\)-edge data in \(r\) space using theoretical functions for \(\chi_i\) calculated using the FEFF7 code, which has been developed by Zabinsky and co-workers. \(^{20}\) \(S_0^2\) was found to be 0.99 for the W \(L_{III}\)-edge and Zr \(K\)-edge data. Each peak in the \(r\)-space data was fit with a Gaussian distribution function, and the width of this function, \(\sigma\), was extracted. \(\sigma\) also called the Debye-Waller factor, is a measure of the local distortions of a shell of neighboring atoms. The fit range is 1.0–5.8 Å for the W \(L_{III}\)-edge and 1.2–6.2 Å for the Zr \(K\)-edge data.

Details about the crystal structure can be found in Refs. 21 and 25. Briefly, each W(1)O(4) tetrahedron (gray areas in Fig. 1) is surrounded by three O(1) and an O(4)—the latter is located on a \(\langle 111 \rangle\) axis; each W(2)O(4) tetrahedron (black areas in Fig. 1) is surrounded by three O(2) and an O(3) [O(3) is also located on the \(\langle 111 \rangle\) axis]. Therefore there are four short W-O bonds [W(1)-O(1), W(1)-O(4), W(2)-O(2), and W(2)-O(3)] distributed from 1.7 to 1.8 Å (see Table I) plus one long bond at 2.41 Å [W(1)-O(3)]. However, XAFS cannot differentiate between \(W_1\) and \(W_2\) in this material and it is impossible to distinguish such small distances between the nearest W-O bonds. Therefore the theoretical standard for the first W-O peak in \(r\) space is a sum of the peaks for the four short W-O bonds, and the bond distance is averaged to be 1.7752 Å. Since all W-O bonds within one \(WO_4\) tetrahe-
dra are included in this standard, it is easy to tell whether the bonds within the tetrahedra became distorted as the temperature increases. The octahedra surrounding each Zr are composed of three O(1) and three O(2), so that the theoretical standard for the nearest Zr-O peak in r space includes two Zr-O bonds, at 2.03 Å [Zr-O(1)] and 2.09 Å [Zr-O(2)], due to similar constraints.

In extended XAFS (EXAFS) analyses the maximum number of parameters is given by

$$P_{max} = \frac{2 \Delta k \Delta r}{\pi} + 2,$$

where $\Delta k$ is the Fourier-transform $k$ range and $\Delta r$ is the fitting $r$ range. From the above discussed $k$ and $r$ ranges, $P_{max}$ corresponds to 33 and 34 parameters for the W $L_{III}$- and Zr $K$-edge data, respectively. To minimize the number of parameters used, the peaks for distances that are nearly the same are summed as described above. In addition, the number of neighbors in each shell/multiple-scattering path is constrained from the known crystal structure.

In our fitting procedure, 12 theoretical standard peaks were used to fit the W $L_{III}$-edge data. These 12 include the nearest W-O peak (combination of all four nearest W-O bonds), the W-Zr peak (combination of both single- and multiple-scattering effects), the nearest and second-nearest W-W peaks, plus eight other multiple-scattering peaks with smaller amplitudes. For the Zr $K$-edge data, eight theoretical standard peaks were used in the fit. They include the nearest Zr-O peak (a combination of the two short Zr-O bonds), the Zr-W peak (combination of both single- and multiple-scattering effects), the nearest Zr-Zr peak (combination of the two shortest Zr-Zr atom pairs), and five other multiple-scattering peaks with small amplitudes.

There are in general four parameters associated with each peak: $\sigma$, $\Delta r$, amplitude, and $\Delta E_0$ [there can also be higher cumulants, $C_3$ (asymmetry) and $C_4$ (kurtosis); these are discussed in the following paragraph]. $\sigma$ is the width of the pair distribution function (PDF). $\Delta r$ is the change of the bond (atom-pair) distance from the starting value, the amplitude is a measure of $S_0^2$ [see Eq. (2)], and $\Delta E_0$ is a shift of the absorption binding energy. An initial step, for both the W $L_{III}$ and Zr $K$ edges, was to determine the amplitude and $\Delta E_0$ for each peak using low-temperature data for which the signal-to-noise ratio is highest. In subsequent fits of the data at various temperatures, $S_0^2$ and $\Delta E_0$ were fixed, and $\Delta r$ and $\sigma$ were allowed to vary. In order to further reduce the total number of free parameters during fitting the W $L_{III}$-edge data, only $\Delta r$’s for the single-scattering peaks—the nearest W-O and W-Zr, and the nearest and second-nearest W-W peaks—were allowed to vary; the $\Delta r$’s for the eight small multiple-scattering peaks were determined at low temperature and fixed. Note that the small thermally induced changes in $\Delta r$ for these contributions, estimated from the known thermal contraction, are $\approx 0.015$ Å. This is at most comparable to the error in $\Delta r$ for these small peaks. Allowing these $\Delta r$’s to vary from the low-$T$ values did not significantly improve the quality of the fit parameter. For the Zr $K$-edge fit, $\Delta r$ was allowed to vary for all peaks. As a result, the number of free parameters in the fit procedure is 16 for both edges, much less than $P_{max}$ mentioned above.

A few fits were also carried out in which the $C_3$ or $C_4$ parameter was varied for the W-O, Zr-O, W-W, and Zr-Zr peaks. $C_4$ fluctuated in sign and its average value was close to zero. $C_3$ was slightly negative for W-O ($\sim -4.0 \times 10^{-5}$ Å$^3$), and positive and slightly larger in magnitude for Zr-O ($\sim -0.00016$ Å$^3$), but with little temperature variation. The $C_3$ results for Zr-O suggests that this bond expands asymmetrically with $T$. For W-W, $C_3$ is negative and increases in magnitude with $T$ (from $-3E$–5 to $-0.0006$ Å$^3$ as temperature increases from 5 to 315 K), however, the errors are large, about 0.0003 Å$^3$ at 315 K, because of the overlap of this peak with the W-Zr peak, and the effect is small below 300 K.

In the following fits, the theoretical standards for W-Zr (Zr-W) are a sum of both the W-Zr (Zr-W) single scattering and the W-O-Zr (Zr-O-W) multiple scattering since the theoretical standards overlap in $r$ space and have similar distances. The same procedure was used to obtain the theoretical standard for the W(1)-W(2) atom pair. See Table II for detailed information about all the single and multiple paths. In these fits the amplitude $NS_0^2$ was kept constant to reduce the relative error in $\sigma^2$. Absolute errors in $S_0^2$ are of order 10% and shift the $\sigma^2$ vs $T$ plots vertically. The error bars show the relative error; several traces are collected at each temperature and analyzed independently. The error bars indicate the rms variation in the values of $\sigma^2$ obtained at each temperature.

Table 2 shows $\sigma^2$ as a function of temperature. In the upper panel, $\sigma^2$ for the nearest W-O bond is nearly independent of temperature—the WO$_4$ tetrahedra are very rigid up to 315 K. The small change in $\sigma^2$ with temperature for the nearest Zr-O peak (Fig. 6, bottom panel) shows that the ZrO$_6$ octahedra are not rigid although quite stiff within this temperature range.

The $\sigma^2$ curves for W-Zr (black square in Fig. 6, upper panel) and Zr-W (black square in Fig. 6, bottom panel) are nearly parallel with only a tiny vertical shift between each other. This is not surprising because both curves measure the

<table>
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<tr>
<th>Path</th>
<th>Degeneracy</th>
<th>Path distance (Å)</th>
</tr>
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<tbody>
<tr>
<td>W$_1$-Zr</td>
<td>3</td>
<td>3.745</td>
</tr>
<tr>
<td>W$_2$-Zr</td>
<td>3</td>
<td>3.870</td>
</tr>
<tr>
<td>W$_1$-O-Zr</td>
<td>6</td>
<td>3.793</td>
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<tr>
<td>W$_2$-O-Zr</td>
<td>6</td>
<td>3.875</td>
</tr>
<tr>
<td>W$_1$-O-Zr</td>
<td>3</td>
<td>3.841</td>
</tr>
<tr>
<td>W$_2$-O-Zr</td>
<td>3</td>
<td>3.880</td>
</tr>
<tr>
<td>W$_1$-W$_1$</td>
<td>1</td>
<td>4.128</td>
</tr>
<tr>
<td>W$_1$-O-W$_2$</td>
<td>2</td>
<td>4.128</td>
</tr>
<tr>
<td>W$_1$-O-W$_1$</td>
<td>1</td>
<td>4.128</td>
</tr>
</tbody>
</table>
same local structure from two different perspectives. The very small vertical shift comes from the fit procedure and the different edges. In Figure 7, we show on an expanded scale that the temperature dependence of $\sigma^2$ for the Zr-W and W-Zr peaks are essentially the same and only slightly larger than that for the Zr-O peak.

Another fit was carried out, in which the $\sigma$'s for the single- and multiple-scattering peaks were fit separately for the W-Zr atom pair; the fit result shows that $\sigma^2$ for each contribution is about the same—see Fig. 8. However, the data do not support further attempts to extract separate $\sigma$'s for the W-Zr and W-O-Zr single- and multiple-scattering peaks (i.e., a fit of four independent peaks) because these peaks are too close together and there would be too many free parameters for this $r$ range.

It is surprising that $\sigma^2$ for the W-Zr (Zr-W) pair shows only a small temperature dependence, comparable to that for the nearest Zr-O bond. This indicates that the nearest W-O-Zr linkage is quite stiff—the W-Zr distance does not fluctuate much with temperature up to 300 K, although the distance between the nearest W and Zr atoms is more than 3.7 Å with an oxygen in between. In contrast, the nearest W-W pair [a W(1)-W(2) pair along a (111) direction] with only a slightly longer pair separation, 4.128 Å, shows a much larger temperature dependence of $\sigma^2$, as does the second-nearest W-W pair [also a W(1)-W(2) pair at 4.621 Å]. The change in $\sigma^2$ with temperature for W-W is more than five times larger than that for the W-O-Zr linkage. The nearest Zr-Zr atom pair has the largest change in $\sigma^2$ with temperature. Note that the much larger error bars for the Zr-Zr peak (Zr K-edge data) at high temperature are due to the weak XAFS signal for peaks with a large $\sigma$ at large distances (near 6.5 Å). The amplitude of the Zr-Zr peak at high temperature (above 280 K) is approaching the noise level. Error bars for $\sigma^2$ in this temperature range are quite large for the W-W and Zr-Zr pairs as indicated in Fig. 6.

An important feature of Fig. 6 is that the $\sigma^2$ curves for both nearest and second-nearest W-W pairs are almost paral-
TABLE III. Estimated Einstein temperatures for each mode.

<table>
<thead>
<tr>
<th>Atom pair</th>
<th>$\Theta_E$ (K)</th>
</tr>
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<tbody>
<tr>
<td>W-O</td>
<td>962(50)</td>
</tr>
<tr>
<td>Zr-O</td>
<td>493(50)</td>
</tr>
<tr>
<td>W-Zr</td>
<td>470(50)</td>
</tr>
<tr>
<td>Zr-W</td>
<td>459(50)</td>
</tr>
</tbody>
</table>

level, which indicates correlated vibrations between these two sets of atom pairs. A break point or cusp clearly exists for both plots near 100 K. Furthermore, the temperature dependence of $\sigma^2$ for the Zr-Zr pair is also similar, with the same break point present near 100 K. To check that this is not an artifact, a second data set was collected for each edge as a function of temperature; the data yield the same result. A detailed discussion of the interpretation of this break point will be given in the next section.

**IV. ADDITIONAL ANALYSIS AND DISCUSSION**

**A. Einstein temperatures**

The specific-heat measurements of Ramirez and Kowach show that low-energy Einstein modes ($\Theta_E \sim 38$ and 67 K) associated with optical phonons dominate and are overwhelmingly responsible for NTE in this material. Similar results were also obtained by phonon density-of-states measurements and theoretical simulations. However, the calculations suggest a larger contribution for low-frequency transverse-acoustic modes than had been assumed in the experiments. To have a large contribution to NTE, the entire band of such transverse-acoustic modes must be below $\sim 8$ eV.

In crystals, the temperature dependence of $\sigma^2$ for optical modes can be modeled with a sum of Einstein contributions:

$$\sigma^2 = \frac{\hbar^2}{2M_R k_B \Theta_E} \coth \frac{\Theta_E}{2T},$$

where $M_R$ is the reduced mass and $k_B$ is Boltzmann's constant. The high-temperature approximation (when $\Theta_E/T \approx 0.3$) of Eq. (4) can be written as

$$\sigma^2 = \frac{\hbar^2 T}{M_R k_B \Theta_E^2}.$$  

Thus we can extract an estimate of the Einstein temperature for vibrations of various atom pairs from the $\sigma^2$ vs $T$ plots (Fig. 6) for the purpose of comparing with the specific-heat results (for the W-O and Zr-O peaks, a Debye approximation is normally a better model). The results are given in Table III for the three nearest atom pairs. All $\Theta_E$ are larger than 450 K; in particular, $\Theta_E$ for the W-Zr pair is comparable to that for the Zr-O bond. This is another way of quantifying that the W-Zr pair distance is very stiff. The high Einstein temperature for W-Zr (Zr-W) means that the vibration of O in the W-O-Zr linkage does not correspond to the low-frequency modes observed in the heat-capacity measurements. Results of the Einstein temperature for the W-W and Zr-Zr pairs are discussed in the next subsection.

**B. Further identification of the low-energy modes in ZrW$_2$O$_8$**

The low-energy phonon density of states determined by Ernst et al. show that the lowest mode frequency remains unchanged as temperature increases from 50 to 100 K but clearly increases (hardens) by 7% between 100 and 300 K as shown in Fig. 3 of Ref. 11. This means that the effective spring constant $\kappa$ must increase significantly. Such a change should be observed in XAFS data if the atomic displacements are driven by this mode since at high temperature

$$\sigma^2 \sim k_B T/\kappa$$

FIG. 9. Fit results to $\sigma^2$ vs $T$ data for the W-W and Zr-Zr atom pairs. The solid lines are the fit results and were carried out up to 250 K because the data at higher temperatures have very large error bars. The temperature dependence of $\Theta_E$ is plotted in the inset of the figure. The dotted and dashed lines in the bottom panel are the fit results for a fixed $\Theta_E$ at low $T$ (dotted) and high $T$ (dashed).
TABLE IV. The fit results with temperature dependent Θ_E using Eq. (4) and Eq. (7). In these final fits, $T_0$ and $\delta$ in Eq. (7) were fixed at 115 and 12 K, respectively.

<table>
<thead>
<tr>
<th>Atom pair</th>
<th>Reduced mass (g/mol)</th>
<th>$\Theta_{E0}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-W (4.1282 Å)</td>
<td>750(50)</td>
<td>46(10)</td>
</tr>
<tr>
<td>W-W (4.6210 Å)</td>
<td>550(50)</td>
<td>47(10)</td>
</tr>
<tr>
<td>Zr-Zr (6.4696 Å)</td>
<td>580(50)</td>
<td>46(10)</td>
</tr>
</tbody>
</table>

spring constant were to increase just above 100 K. To represent this mode hardening we define $\Theta_E$ to be a function of temperature:

$$\Theta_E = \Theta_{E0} + 0.07 \times \Theta_{E0} \times \left[ 1 - \frac{1}{e^{(T-T_0)/\delta+1}} \right].$$  (7)

Here, $\Theta_{E0}$ is the Einstein temperature at low $T$. $T_0$ is the temperature at which $\Theta_E$ increases, and $\delta$ is the width of this step function. We used the small 7% mode hardening as reported by Ernst et al., and found $T_0$ and $\delta$ to be $\sim 115$ K and 12 K to fit the data. $\Theta_E$ at low temperature is $\sim 46$ K for the W-W and Zr-Zr pairs (see Table IV for details) consistent with the heat-capacity and phonon measurements. The fit results are reasonable as shown in Fig. 9, where solid lines are the fit results and the circles are the data. $\Theta_E$ as a function of temperature is shown in the inset. Separate fits to the low-$T$ and high-$T$ parts of the $\sigma^2$ vs $T$ curve show that the average static distortion, $\sigma^2_{\text{static}}$, is very large for the W-W and Zr-Zr atom pairs (0.0032 Å$^2$ for the nearest W-W, 0.0069 Å$^2$ for the second-nearest W-W, 0.0034 Å$^2$ for the nearest Zr-Zr). We therefore use these values of the static distortions in the overall fit for each atom pair, respectively.

The fit results in Table IV show very large reduced masses for these modes compared to the W-O or Zr-O reduced masses used in Table III. This indicates that the low-energy vibration modes must involve several large rigid units which include the heavy metal atoms, W and Zr. Part of the reason for the very large value of the reduced mass in this fit is that we have used an equation for a single type of mode; in fact we should sum over the four lowest modes that are clearly present from the specific-heat analysis. To do so we would need the projections of the phonon modes onto the W motions along the (1,1,1) directions. A crude approximation is that Eq. (4) should be multiplied by a number between 1.5 and 2.5; then $M_2$ is about 350 g/mol for W-W, which is still very large. The clear indication of a small hardening of the effective spring constant for only the W-W and Zr-Zr pairs completes our identification of the low-energy modes in this system as being vibrations of W(1)-W(2) along the (111) axes, which are coupled to the Zr-Zr motions as described below.

An unanswered question is why does the mode harden near 100 K? The answer may be related to the amplitude of the W-W vibration. For small amplitudes, nearly rigid unit modes may be possible at low temperature with only a small flexing about the O atoms that connect the WO$_4$ and ZrO$_6$ units. However, at larger amplitudes, the angles within the units (i.e., the O-W-O and/or O-Zr-O angles) may also need to change slightly and the Zr-O bond to stretch, to keep the units connected; this would stiffen the vibration. A review of the supplementary data of Ref. 25 also indicates that on average the O1-W1-O1 angle decreases with temperature by roughly 0.4°, while the O2-W2-O2 decreases by 1.0° up to 293 K, which is comparable to the estimated angle change required in our tentpole model (below) for the vibration amplitudes at 300 K.

Such a possibility is also consistent with the results for the W-Zr and Zr-O peaks. As discussed earlier, $\sigma^2_{W-Zr}$ changes very little below 120 K but changes rapidly at higher $T$. In Fig. 10, which involves no analysis, the amplitude of the W-Zr peak is plotted as a function of $T$. There is a break in the slope of the curve near 120 K (close to the cusp in the $\sigma^2$ vs $T$ plots for W-W), and the amplitude decreases more rapidly for $T > 120$ K. $\sigma^2_{W-Zr}(T)$ for this peak increases too rapidly above 120 K (see Fig. 7) to fit a Debye model well. The behavior for Zr-O is similar. Although both can be fit by an Einstein model with a large $\Theta_E$ (see Table III), that is surprising since one expects these vibrations to involve the acoustic modes at these temperatures and hence to follow a Debye model. If, however, the small stretching of the Zr-O bond (and the transverse O motion, see Sec. IV C 2) is a by-product of low-energy Einstein modes, driven by the large inertia of the massive WO$_4$ tetrahedra, then the simple Einstein mode equation above no longer applies—the resulting Zr-O vibration amplitude would be much smaller than expected for a low $\Theta_E$. Within this model the Zr-O bond begins to fluctate and the O to move transversely at a low frequency once the W amplitude reaches a critical value (near 120 K).

C. Transverse vibration of O in W-O-Zr

The above results show that the temperature dependence of the W-Zr pair (and W-O-Zr) is weak. Because the origin
of the NTE effect in ZrW2O8 has long been thought to be a large-amplitude low-energy transverse vibration of the O atom in the middle of the W-O-Zr linkage, 3 we address the analysis of the W-Zr peak in more detail. The results depend on assumptions about the atomic correlations; we consider uncorrelated and correlated situations separately.

1. Uncorrelated motions

We first note that if the transverse O vibration in the W-O-Zr were solely responsible for the NTE of 9 × 10^-6 K in ZrW2O8, the required O vibration would need to have an rms transverse displacement of at least 0.15 Å (σ2 ~ −0.02 Å2) to produce the observed thermal contraction at 300 K. 7 Here both the W-O and Zr-O bonds are assumed to be rigid. Then the distance between the nearest W and Zr atoms must fluctuate significantly (Fig. 11). For example, the W(1)-Zr pair (single scattering) would have a contribution to σ2 of 0.003 Å2 from this O thermal vibration, while for the W(2)-Zr pair (bond angle of 173°) the contribution to σ2 is −0.0006 Å2. However, the total thermal change in σ2 for the W-Zr pairs is only about 0.0015 Å2 (Fig. 7).

More importantly, the multiple-scattering contribution to the amplitude of the W-O-Zr peak is also very sensitive to the displacement of the O atom. 19 It dominates when the bond angle is nearly colinear, since its amplitude can decrease by a factor of 3–4 when the bond angle changes from 180° to ~ 150° (see upper panel of Fig. 12). For large bond angles, the single-scattering peak starts to dominate.

For W(2), the O is displaced about 0.14 Å (see Fig. 12) which corresponds to a bond angle of 173°, and in this case the multiple-scattering peak dominates. The average amplitude of the W(2)-O-Zr multiple-scattering peak is decreased by 25% as the rms oscillation amplitude of the central O atom reaches 0.14 Å. For W1, the O displacement is ~0.42 Å (bond angle of 155°), and the change of the amplitude of the multiple-scattering peak is considerably smaller. In this case, the W(1)-Zr single-scattering peak is the dominant contribution.

The measured stretching vibration of the Zr-O bond must also be included in the analysis. In general, σ2 for the W-O-Zr (or Zr-O-W) linkage can be expressed as follows when the various motions are not correlated:

\[ \sigma^2 = \sigma_{\text{static}}^2 + \sigma_{\text{stretch}}^2 + \sigma_{\text{trans}}^2. \]

Here \( \sigma_{\text{static}}^2 \) is the contribution for a static distortion, which does not have a temperature dependence; \( \sigma_{\text{stretch}}^2 \) is the contribution from the change in the W-Zr distance caused by a stretch of the Zr-O and W-O bonds; and \( \sigma_{\text{trans}}^2 \) comes from the transverse vibration of the O atom in the middle of the W-O-Zr linkage. Since \( \sigma_{\text{static}}^2 \) doesn’t change with temperature, we neglect it in the following discussion. \( \sigma^2 \) for the W-O bond is nearly independent of temperature up to 300 K and is also neglected. Therefore, \( \sigma_{\text{trans}}^2 \) can be represented by \( \sigma^2_{\text{Zr-O}} \). Note that the total change in \( \sigma^2 \) of the W-Zr and Zr-W peaks are about 0.0015 Å2 and 0.0020 Å2, respectively as the temperature increases from 5 to 315 K, while the change of \( \sigma^2_{\text{Zr-O}} \) over the same temperature range is about 0.0013 Å2 (Fig. 7). The remaining contribution from the O transverse vibration, \( \sigma_{\text{trans}}^2 \), would not be large enough under the above assumptions to account for the total NTE in ZrW2O8 at 300 K. Below 100 K the changes in \( \sigma^2_{\text{W-Zr}} \), \( \sigma^2_{\text{Zr-W}} \), and \( \sigma^2_{\text{Zr-O}} \) are nearly identical, thus any O transverse oscillation must be negligible over this temperature range (see Fig. 7).

The net effect when the Zr-O stretching vibration and transverse O motions are included is that the total amplitude reduction would be too large as shown by the solid square at 315 K in Fig. 10. The open squares are the amplitudes of the W-Zr peak in the raw data and do not involve any detailed analysis. These data cannot be explained in terms of a transverse O vibration when the Zr-O bond stretches and the atomic motions are uncorrelated.

2. Correlated motions

Correlated motions of atoms occur in a variety of situations. When acoustic phonons dominate, the motions of the nearest neighbors are in the same direction—the motions are positively correlated. In more complex crystals there can be several other types of correlated motions. For example, in ZrW2O8 the very small value of \( \sigma^2 \) for the W-O bond, even at 300 K, means that the WO4 tetrahedra move as a rigid unit—the O must follow the W motion. Similarly, although the Zr-O bond is not completely rigid, the small value of \( \sigma^2 \) for Zr-O indicates that the ZrO6 octahedra are quite stiff—

![FIG. 11](https://example.com/figure11.png)

FIG. 11. This plot shows in general how the transverse vibration of the middle O atom will affect the distance between two metal (M) atoms in a M-O-M linkage for rigid M-O bonds. The solid line shows the equilibrium position, and the dotted lines show the status of the M-O-M linkage during an O transverse vibration when the O atom reaches the rms vibration amplitude at \( h_1 \) and \( h_2 \). Note \( \sigma \) is the half width for the M-M pair distribution function.
served in diffraction 2,7,25 for the O atoms indicate that the
contraction extreme case would be if the W and Zr were fixed
the stretching of the Zr-O bond are not independent. An ex-
more subtle correlation in that the transverse O motion and
that the fluctuations of the W-Zr distance are small. This is a
motions of the atoms in this linkage must be correlated such
linkage in ZrW2O8. The small value of
These types of correlated motions are quite common.
changes in the W-Zr distance and the rms variation of this
distance under different conditions.

the O in these units must approximately follow the Zr atom. These types of correlated motions are quite common.

More surprising are the correlations within the W-O-Zr
linkage in ZrWO3. The small value of \( \sigma^2 \) for the W-O-Zr
and Zr-O-W linkage plus the large thermal parameters ob-
erved in diffraction27,25 for the O atoms indicate that the
motions of the atoms in this linkage must be correlated such that
the fluctuations of the W-Zr distance are small. This is a
more subtle correlation in that the transverse O motion and
the stretching of the Zr-O bond are not independent. An ex-
treme case would be if the W and Zr were fixed (no length
contraction) and the Zr-O bond stretched as the O vibrated
transversely. Here we consider the thermally induced changes in
the W-Zr distance and the rms variation of this distance under different conditions.

\[
A = A_o + A_1(t),
\]

\[
H = H_o + H_1(t),
\]

\[
A_1(t) = a_1 \cos(\omega_A t),
\]

\[
H_1(t) = h_1 \cos(\omega_H t + \theta),
\]

where \( A_o \) and \( H_o \) are the static values, \( a_1 \) and \( h_1 \) are the
vibration amplitudes, and \( \omega_A \) and \( \omega_H \) are the corresponding
frequencies for the stretching and transverse motions. The
total Zr-W distance, \( L \), is given by

\[
L = \sqrt{A^2 - H^2} + \sqrt{B^2 - H^2}.
\]

To simplify the final results we set \( B = A_o \). Substituting
for \( A \) and \( H \), expanding the square roots to second order, and
keeping terms up \( A_1 \) in the previous section. To calculate these aver-
ages, we need to know how \( A_1 \) and \( H_1 \) are correlated.
Using Eq. (10) we show that

\[
\langle A_1(t) \rangle = \langle H_1(t) \rangle = 0,
\]

\[
\langle A_1^2(t) \rangle = A_o^2/2; \quad \langle H_1^2(t) \rangle = h_1^2/2,
\]

and

\[
\langle A_1(t)H_1(t) \rangle = \int A_1(t)H_1(t)dt.
\]

If \( \omega_A \neq \omega_H \), then \( \langle A_1(t)H_1(t) \rangle = 0 \); for \( \omega_A = \omega_H = \omega \),

\[
\langle A_1(t)H_1(t) \rangle = \frac{A_o h_1}{\omega^2} \sin(\omega t + \phi).
\]

In Fig. 13 we show the arrangement of the atoms and
define the parameters. Here \( A \) is the time-dependent length
of the Zr-O bond, \( B \) is the length of the W-O bond which will
be held constant, and \( H \) is the time-dependent transverse po-
sition of the O atom. We model the time dependencies of \( A \)
and \( H \) using cosine functions:
where $\Phi = \cos \theta$ is called the correlation parameter and can vary from $-1$ to $1$. After simplification,

$$
\langle A_1(t)H_1(t) \rangle = \frac{1}{T} \int_0^T h_1 a_1 \cos(\omega t) \cos(\omega t + \theta) dt = \frac{h_1 a_1}{2} \Phi,
$$

(15)

and

$$
\langle \Delta L \rangle = -\frac{1}{L_o(A_o^2 - H_0^2)} \left[ A_o^2 h_1^2 + H_0^2 a_1^2 / 2 - A_o H_0 a_1 h_1 \Phi \right]
$$

(16)

and

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

(17)

If $A_1$ and $H_1$ are uncorrelated this reduces to

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

(18)

while for positively correlated motions

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

(19)

Under the assumption that $a_1$ is very small (i.e., Zr-O is rigid), $\langle \Delta L \rangle \sim -h_1^2 / L_o$, as used earlier to estimate the magnitude of the transverse vibration amplitude required to produce a Zr-W length contraction corresponding to the bulk value. When $a_1$ is finite and the motions correlated ($\Phi > 0$) then the net contraction is smaller. However, for the value of $a_1$ obtained from $\sigma_{Zr-O}$ at 300 K ($a_1 ~ 0.08 \ \text{Å}$), this correction is small, $\sim 8\%$.

In contrast, the effects of correlations on $\sigma^2_{thermal}(\Phi)$ are large. Using $a_1 \sim 0.08 \ \text{Å}$, $h_1 = 0.21 \ \text{Å}$, $H_0 = 0.4 \ \text{Å}$ for W(1)-O-Zr, and $A_1 \sim 2 \ \text{Å}$, then $\sigma^2_{thermal}(0) \sim 7.0 \times 10^{-3} \ \text{Å}^2$, while $\sigma^2_{thermal}(1) \sim 8.3 \times 10^{-6} \ \text{Å}^2$. Thus $\sigma^2_{thermal}(\Phi)$ can have a wide range of values depending on the value of $\Phi$.

In the above discussion we have used a value of $h_1$ obtained from the oxygen thermal parameters in diffraction experiments. This is an overestimate of the transverse motion, since part of the O displacement must correspond to the rotations/translations of the W-O-Zr linkage (which includes translations of the WO$_4$ and ZrO$_6$ units). Ideally a determination of $\Phi$ would provide a measure of the transverse motion within the W-O-Zr linkage. However, in Eq. (17), $\Phi$ and $h_1$ are coupled. An approximate determination can be obtained by using the results of the fits for the W-O-Zr linkage to the sum of the single-scattering and multiple-scattering peaks as shown in Fig. 8. Using the effective value of $\sigma^2$ obtained for W-O-Zr at 300 K, the dominant W(2)-O-Zr multiple-scattering peak amplitude should drop by $\sim 25\%$ from 20–300 K. Using the measured value of $\sigma^2$ for the Zr-O component accounts for $17\%$–$20\%$ of this drop, leaving $5\%$–$8\%$ from changes in the multiple-scattering peak as a result of the transverse vibration. From Fig. 12, lower panel, this yields rms values ($h_1 / \sqrt{2}$) for the transverse O motion (within the linkage) of 0.067–0.092 Å, considerably smaller than the total O motion determined from the diffraction thermal parameters.

D. Possible transverse motions of O(3) in W(1)-O(3)-W(2) linkage

In the above discussion, we showed that for a nearly colinear three-atom linkage, the amplitude of the multiple-scattering XAFS peak is strongly dependent on transverse vibrations of the middle atom. Since O(3) is located between W(1) and W(2), we need to consider the same possibility for the W(1)-O(3)-W(2) peak. If the transverse vibration of O(3) dominates, there should not be a large W motion. However, the second-nearest W-W pair also has a very large change in $\sigma^2$ with temperature and there is no atom between this pair. This suggests that it is the W atom that is moving significantly rather than the transverse motion of the O(3).

Another way to address the question is to look at the temperature-dependent broadening of $\sigma$ for the long W(1)-O(3) pair. Because the W-O bonds within the tetrahedra are very rigid, the change of $\sigma^2$ for the W(1)-W(2) pair must be comparable to that for the W(1)-O(3) if transverse oscillations of O(3) are not large. Although the W(1)-O(3) peak is difficult to observe in the regular data because it has an amplitude of $\sim 1/15$ for the short W-O bond, it is clearly observed in the difference data of Fig. 4: a peak develops at 2 Å for the difference data between 20 and 315 K. The amplitude for the main W-O peak in the difference data is about 40% smaller. In order to estimate the broadening of the W(1)-O(3) peak with temperature, we used a method of fitting $r$-space difference data recently developed in our magnetic-field modulation experiments.

Briefly, this method is as follows. The XAFS function $\chi(k)$ can be written as

$$
k\chi(k) = \sum_i e^{-2\sigma_i^2k^2} \text{func}(k, r_i) = \sum_i k \chi_i.
$$

(20)

Here $r_i$ is the distance from the central atom to the $i$th atom shell; $k$ is the wave vector and $\sigma_i$ is the width of the PDF of the $i$th atom shell. Note func($k$, $r_i$) is a function which has no $\sigma_i$ term in it. Assuming $\sigma_i$ is the only parameter changing with temperature ($r_i$ also varies with $T$, but is a very small effect compared to the change in $\sigma_i$), then we get

$$
\frac{\partial [k \chi(k)]}{\partial \sigma} = -4\sigma \frac{\partial \sigma}{\partial \sigma} k^3 \chi(k).
$$

(21)

Thus the amplitude in the difference data is proportional to $\sigma$,$\partial$.$\sigma$.$\partial$. The $r$-space data for the W $L_{III}$ edge is the Fourier transform of $k^3 \chi(k)$ data. Let $\sigma$ for the W(1)-O(3) peak be $\sigma_{20}$ at 20 K and $\sigma_{315}$ at 315 K, where $\sigma_{315} = \sigma_{20} + \delta\sigma$. Then we have the difference, $\delta(k^3 \chi)$:

$$
k^3 \chi(k)(315 \text{ K}) - k^3 \chi(k)(20 \text{ K}) = -4\sigma_{20} \delta\sigma [k^3 \chi(k)].
$$

(22)

We generated a $k^3\chi(k)$ standard for the W(1)-O(3) peak to fit the difference data of $k^3 \chi(k)$. The fit procedure is the same as a normal $r$-space fit. Once we extract the amplitude.
of the peak from the fit, we can obtain $\delta \sigma$, the increase of $\sigma$ with temperature. The result of the fit shows that $\delta \sigma$ is $\sim 0.045$ Å, and $\sigma_{215}^2 - \sigma_{20}^2 = 0.005$ Å$^2$ which is close to the $\sigma^2$ change for the nearest W-W peak, $\sim 0.0065$ Å$^2$, over the same temperature range. Such a large change in $\sigma^2$ with temperature for the W(1)-O(3) peak confirms that the W (and hence the rigid WO$_4$ tetrahedra) has significant translations along a $\langle 111 \rangle$ axis, in agreement with the large value of $\sigma^2$ for the W(1)-W(2) pair. Some diffraction data indicate that the W vibrations are nearly isotropic$^7$ while Fig. 7(a) of Ref. 25 shows prolate thermal ellipses oriented along $\langle 111 \rangle$. EXAFS analysis is not very sensitive to the motion perpendicular to a $\langle 111 \rangle$ axis and cannot distinguish between these two possibilities.

There is, however, a disagreement regarding the motions of the O3 atom. The thermal ellipses obtained from neutron-diffraction data at 293 K suggest that the O(3) atom [the unconstrained O atom for W(2)] has a motion mainly perpendicular to the $\langle 111 \rangle$ axis$^7,25$ which is in disagreement with our above analysis. [For the O(4) atom, the thermal ellipse is quite large in both directions, so the possibility of a large vibration along the $\langle 111 \rangle$ axis is not inconsistent. Although the thermal ellipse at 293 K is shown with the largest axis perpendicular to the $\langle 111 \rangle$ axis (oblate spheroid), the complete data set (supplementary data for Ref. 25) indicates that the thermal ellipse is a prolate spheroid with the long axis along the $\langle 111 \rangle$ axis for data at six out of eight temperatures. In a second paper with much poorer $S/N$ but many more temperatures,$^7$ Evans et al. also obtain an oblate thermal ellipsoid for O3. However, the oblate spheroid they obtain for O3 has a serious problem; for motion along the $\langle 111 \rangle$ axis, the W2 vibration is much larger than that for O3, i.e., the W is vibrating relative to the O3 atom along $\langle 111 \rangle$. This is inconsistent with the large mass difference between W and O. On the other hand, the prolate spheroid has the expected result that the O motion along $\langle 111 \rangle$ is larger than that of W.

E. Tent-pole model

Based on the analysis above, we develop a simplified local vibrational mode for the low-frequency optical phonons. We propose that this model contains the essential physics that leads to NTE in ZrW$_2$O$_8$. Figure 14 shows a simplified cutaway structure, which consists of three WO$_4$ tetrahedra (two W$_1$ and one W$_2$) and all their nearest ZrO$_6$ octahedra plus two isolated ZrO$_6$ octahedra which are aligned along one of the four $\langle 111 \rangle$ axes. Each tetrahedron is surrounded by three ZrO$_6$ octahedra which form a plane perpendicular to the $\langle 111 \rangle$ axis of the crystal. The unshared corner of each tetrahedron points along a $\langle 111 \rangle$ axis. As a WO$_4$ tetrahedron moves along this $\langle 111 \rangle$ axis, the three nearest ZrO$_6$ octahedra will move together due to the stiffness of the W-O-Zr linkage and rotate slightly because of the corner connections to other units. Note that for this motion the WO$_4$ is unconstrained along the $\langle 111 \rangle$ direction and can move into unoccupied space. Also, there are no atoms between any pair of ZrO$_6$ octahedra to constrain their translational motion.

![FIG. 14. A cutaway section of the unit cell after removing many of the polyhedra; it shows the remaining W(1)O$_4$ (gray) and W(2)O$_4$ (black) tetrahedra and ZrO$_6$ octahedra. From this point of view, each tetrahedron is connected to three ZrO$_6$ octahedra which form a plane perpendicular to a $\langle 111 \rangle$ axis. Each tetrahedron vibrates vertically to this plane.](image)

We now consider the motions of the three nearest Zr atoms while a W atom vibrates along a $\langle 111 \rangle$ axis. In Fig. 15, we present a "rigid-tentpole model" to show how the Zr-Zr distance changes with the W motion. The oxygen atoms are omitted for simplicity, the W-Zr linkages are assumed here to be rigid (the tent poles), and the W is initially in the plane of the Zr. When W moves away from the plane of the Zr atoms, either up (as in a tent) or down, the Zr atoms move closer together because of the stiff W-Zr link. Since such motions occur on all four $\langle 111 \rangle$ axes, we expect an isotropic contrac-

![FIG. 15. A plot to show the correlated motions between W and Zr atoms. The O atoms in between are neglected in order to make it clearer.](image)
tion which agrees with diffraction results. In the real lattice, the tetrahedra and octahedra must also tilt/rotate and the Zr-O bond stretch slightly to maintain the lattice structure. The motions are similar in some respects to the more complicated model presented in Ref. 25. There the focus was on rotations of the polyhedra, while vibrations that included translations of the polyhedra were not considered; the main modes in their model correspond to a transverse vibration of some of the O atoms. In our model the low-energy mode involves large motions of the heavy W and Zr atoms.

**F. Soft-mode frustration**

As illustrated in Fig. 1, the crystal structure of ZrW$_2$O$_8$ is open, and measurements of both the phonon density of states and specific heat show that there are very low-energy optical modes which are associated with the negative thermal expansion in this material. These low-energy modes are therefore candidates for a possible soft-mode phase transition in ZrW$_2$O$_8$. In many other systems a low-frequency optical-phonon mode can correspond to a particular local distortion of the lattice. If the frequency of this soft mode decreases (referred to as a mode softening) and goes to zero, the distortion then becomes static and leads to a symmetry-lowering phase transition. In fact, another high-temperature NTE material, ZrV$_2$O$_7$, a close structural relative of ZrW$_2$O$_8$, shows a symmetry-lowering phase transition as its isotropic NTE vanishes below 373 K. However, ZrW$_2$O$_8$ displays an isotropic NTE and remains a cubic lattice to very low temperature. Thus the answer to the question of why ZrW$_2$O$_8$ doesn’t undergo a soft-mode phase transition is important for understanding NTE in this system.

An important aspect of this problem concerns the degeneracy of the vibration modes that we have identified. The low-temperature specific heat indicates that there are four low-frequency modes per unit cell that contribute; fits to the specific-heat data show that there are two Einstein frequencies with amplitudes in the ratio of roughly 1:3. This amplitude ratio does not appear in the phonon density of states—the two lowest peaks overlap and appear to have similar peak heights. However, one needs the width of the dispersion for each mode before comparing with the delta-function Einstein modes used in the specific-heat analysis.

The EXAFS results indirectly support the 1:3 ratio of the mode intensities. There are four possible local vibrations of W$_1$-W$_2$ along the four equivalent ⟨111⟩ axes per unit cell. These modes appear to be degenerate because of the equivalency of the ⟨111⟩ axes; however, a fourfold degeneracy is not compatible with cubic symmetry. Using group theory and the 12 symmetry operations for this space group (P2$_1$3) these four modes break up into a singlet and a triplet and hence would have amplitudes in the ratio of 1:3. Thus the modes we have identified are also consistent with the specific-heat data. With the singlet as the lowest mode there is no degeneracy that can be lifted by a symmetry-lowering distortion at low temperatures and hence no reason for a displacive transition to occur.

A detailed examination of the lattice structure also suggests that the WO$_4$ vibrations along different ⟨111⟩ axes are coupled which leads to the splitting of the singlet and triplet discussed above. As a WO$_4$ tetrahedron translates, its three nearest ZrO$_6$ octahedra rotate slightly and move together (or apart) as described in the discussion of the tentpole model. These motions in turn drive the motions of other WO$_4$ tetrahedra through the relatively rigid W-O-Zr linkage. See Ref. 27 for further details. This coupling of W motions along different ⟨111⟩ axes leads to the prediction that if the correlated motions occur at $k = 0$, the application of a uniaxial pressure (for example, along the $x$ axis) to the ZrW$_2$O$_8$ unit cell will lead to a contraction along the other two axes as well. This effect is called a “negative Poisson ratio” (NPR). Usually when uniaxial pressure is applied to a material (with a positive Poisson ratio) the material will expand along the other axes in order to keep its original volume. An example of a system with a NPR is the “Hoberman™ sphere”: the whole sphere will contract or expand symmetrically when a uniaxial force is applied upon it.

Figure 16 shows a simplified two-dimensional model of such a system with NPR: it consists of connected squares and triangles. All units are rigid and the triangles are constrained to not rotate. There are two sets of triangles in this system: triangles with two constrained corners along the $y$ axis (vertically) are called $T_1$, and those with two constrained corners along the $x$ axis (horizontally) are called $T_2$. When uniaxial pressure is applied along the $y$ axis, the squares $S$ will rotate and the $T_1$ triangles will translate along the $x$ axis as the system contracts along this axis. In addition, the rotations of each square also drive translations of $T_2$ along the $y$ axis, leading to a net contraction along the $x$ axis as well. In the ZrW$_2$O$_8$ system, due to the effect of further-neighbor interactions, the NPR might only occur within the
nanometer scale. Further experiments will be carried out to see if the ZrW$_2$O$_8$ bulk sample also displays a negative Poisson ratio.

V. CONCLUSION

The XAFS results clearly show that the WO$_4$ tetrahedra are rigid, while the ZrO$_6$ octahedra are stiff but not rigid as temperature increases from ~0 to 315 K. The small temperature dependence of $\sigma^2$ for the W-Zr peak indicates that the W-O-Zr linkage is quite stiff over the same temperature range, which therefore suggests the existence of an even larger quasirigid unit involving a WO$_4$ tetrahedron and its three nearest ZrO$_6$ octahedra. The small magnitude and weak temperature dependence of $\sigma^2_{W-Zr}$ shows that the motions of the W, O, and Zr atoms are correlated and therefore cannot be considered independently. Consequently the simple RUM models are not appropriate—at least at 300 K. The stiffness of the W-O-Zr linkage also indicates that the transverse vibrations of the O atom in the middle of the W-O-Zr linkage cannot be the primary origin of the negative thermal expansion in ZrW$_2$O$_8$.

The much larger temperature dependence of $\sigma^2$ for the nearest W$_1$-W$_2$ and Zr-Zr pairs indicates that vibrations of these atom pairs produce the low-energy optical modes in this system that are considered to be the origin of NTE in ZrW$_2$O$_8$. The cusp around 100 K on the $\sigma^2$ vs $T$ plot for the W-W and Zr-Zr atom pairs indicates a mode hardening just above 100 K while the temperature dependence of $\sigma^2$ yields an Einstein temperature of ~45 K at low temperatures. Both results agree with the measurements of the phonon density of states and therefore provide further confirmation that the W-W and Zr-Zr vibrations produce the low-frequency optical modes. A simplified rigid-tentpole model based on the XAFS results suggests the form of the local vibrational mode. The rigidity of the WO$_4$ units implies that the WO$_4$ tetrahedra must translate along the [111] directions.

The lack of a soft-mode phase transition in this system is due to a coupling of the vibrations of WO$_4$ tetrahedra along all four [111] axes which leads to the formation of singlet and triplet states. Each of these eigenmodes is a linear combination of vibrations along each of the [111] axes and consequently each would produce an isotropic thermal contraction. The overall contraction is constrained by the lattice structure. These modes should cover the entire range in $k$ space. If this is true for the $k=0$ mode then this system may exhibit a negative Poisson ratio. It remains to be tested whether or not bulk ZrW$_2$O$_8$ shows a NPR because of the further-neighbor interactions.

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23. The amplitude, $A$, of a peak in r-space XAFS data can be written as $A \propto D_i / r^7_i$, where $r_i$ is the distance from center atom to backscattering atoms in the $i$th shell, and $D_i$ is the degeneracy of this scattering path. For the nearest W-O bonds in ZrW$_2$O$_8$, $D_i$ is 4 and $r_i$ is ~1.75 Å, while for the longer W-O bond, $D_i$ and $r_i$ are 0.5 [only W(1) has this bond] and 2.4 Å, respectively. Therefore the amplitude of this longer W-O peak at 2.4 Å is about 1/15 of that for the shortest W-O peak in W L$_{III}$-edge r-space data for ZrW$_2$O$_8$.