ZrW$_2$O$_8$ has attracted considerable attention recently due to its large isotropic negative thermal expansion (NTE) over a wide range of temperature (from 10 to 1050 K) [1]. This behavior appears to be driven [2–4] by two optical modes with extraordinarily low energy that have been observed in specific heat measurements [2] and have a negative Grueneisen parameter [3,5]. It was proposed that the rotations of rigid WO$_4$ and ZrO$_6$ polyhedra are responsible for NTE in ZrW$_2$O$_8$, which involve a large transverse motion of the O atom in the W-O-Zr linkage [1,6,7]. However, the unusually low energy of the modes suggests that heavy atoms must be involved, not just O motion. In addition, this model does not provide any explanation as to why a soft-mode displacive transition where its NTE vanishes [8]. The absence of such a phase transition in ZrW$_2$O$_8$ is a question of fundamental significance, and one of us has argued for its connection to the problem of geometrical frustration in triangular magnets [9]. Here we use the x-ray absorption fine structure (XAFS) technique to investigate the local structure in this material, and from that we can extract important information about the low-energy vibration modes and therefore address the origin of NTE in this material.

XAFS data at the W $L_{III}$- and Zr $K$ edges were collected as a function of temperature at the Stanford Synchrotron Radiation Laboratory (SSRL) using a powder ZrW$_2$O$_8$ sample. The energy-space data were reduced using standard procedures and the resulting $k$-space data were Fourier transformed (FT) to $r$ space to show the peaks that correspond to different shells of neighbor atoms (see Fig. 1). The amplitude of the nearest neighbor W-O peak in $r$ space has almost no temperature dependence from 20 to 315 K which supports the concept of a rigid unit for the WO$_4$ tetrahedra. However, the nearest Zr-O peak amplitude decreases about 10% at 300 K; consequently, the ZrO$_6$ octahedra are stiff but clearly not rigid. A more surprising result is that the W-O-Zr linkage is also quite stiff with almost no drop in amplitude from 20 to 160 K and only a small drop in amplitude ( ~ 25%) as the temperature is increased to 315 K. In striking contrast, the $r$-space peak amplitudes for both the shortest W(1)-W(2) and the Zr-Zr atom-pair linkages decrease rapidly with temperature ( > 60% decrease at 300 K).

Quantitatively the width $\sigma$ of the atom-pair distribution function provides information about local distortions, including thermal vibrations and static distortions. $\sigma$ is determined by fitting the $r$-space data to a sum of theoretical functions calculated using the FEFF7 program [10]. The $\sigma^2$ vs $T$ plots (Fig. 2) confirm the above qualitative observations. $\sigma^2_{Zr-O}$ for the Zr-O bond increases about 50% at 300 K (ZrO$_6$ octahedra are stiff but non-rigid) and $\sigma^2_{W-Zr}$ for the W-Zr linkage (including multiple scattering paths) shows a comparable temperature dependence. Clearly, however, the large increase of $\sigma^2$ between 20 and 300 K for the nearest W(1)-W(2) and Zr-Zr atom pairs shows that these heavy atom vibrations have lower energies (Einstein temperature from XAFS ~46 K). A very important additional feature in Fig. 2 is the cusp above 100 K for the W-W and Zr-Zr pairs; this indicates a hardening of the dominant vibration frequency above 100 K and serves as a signature to connect these vibrations with the lowest Einstein mode observed in the phonon density of states [5]. Since the nearest W(1)O$_4$-W(2)O$_4$ pair is oriented along a (111) axis, there must be significant translations of the WO$_4$ unit (a correlated motion of W and O atoms) along this axis.

Because the transverse O model has been invoked by several groups [1,6,7] to explain NTE, we consider in detail the implications of this motion for the XAFS analysis. We first assume that the W-O and Zr-O bonds are completely rigid. Then to achieve the required NTE ( ~ 9 x 10^{-6} K^{-1}) via a transverse O vibration would...
require a large O vibration amplitude (about 0.20 Å; rms 0.15 Å [7]) at 300 K. Under the above assumptions, this transverse O vibration would produce a significant fluctuation of the W(1)-Zr distance $\Delta \sigma_{W(1) \cdot Zr}^2 \sim 0.0035 \text{ Å}^2$; W(1)-O-Zr bond angle $\sim 154^\circ$, and a large change in the multiple-scattering contribution which dominates [11] for the nearly collinear linkage W(2)-O-Zr (bond angle $\sim 173^\circ$). As a result, this would lead to a $\sim 27\%$ amplitude reduction for the W-Zr peak. However, the Zr-O bond length fluctuation will also broaden the W-Zr peak and reduce the amplitude. If we assume the transverse O vibration amplitude is zero, then the observed fluctuation of the Zr-O bond alone would reduce the W-Zr peak amplitude by $\sim 17\%$–$20\%$. If the transverse O vibration and the stretching of the Zr-O bond are uncorrelated (i.e., $\sigma_{W \cdot Zr}^2 = \sigma_{\text{stretch}}^2 + \sigma_{\text{transverse}}^2$), the overall amplitude reduction of the W-Zr peak would be $\sim 50\%$ when we include both effects, which is far too large comparing to the observed 25% reduction. This means that the atomic motions must be correlated. Since the XAFS results show that fluctuations of the W-Zr distance are small, the W and Zr motions must be partially correlated (i.e., the W-Zr pair moves as a stiff dumbbell).

Three important points emerge from the above analysis. (i) The ZrO$_6$ is not a rigid unit and the Zr-O and W-Zr distances have comparable stiffness, thereby invalidating the purely rigid unit model for ZrW$_2$O$_8$. (ii) The large thermal changes in $\sigma^2$ for both the nearest W-W and Zr-Zr pairs (Fig. 2) are good evidence that the vibrations of these atom pairs are responsible for the observed low-energy modes. (iii) The cusp above 100 K for $\sigma_{W \cdot Zr}^2$ and $\sigma_{Zr \cdot Zr}^2$, indicative of a hardening of the mode, confirms this identification (details in a longer paper).

We now construct a simplified local model for the low-frequency vibrational eigenmodes that not only explains the above XAFS data, but also accounts for the NTE. First note that the stiff W-O-Zr linkage connects the motions of a WO$_4$ tetrahedron and its three nearest ZrO$_6$ octahedra which lie in a plane perpendicular to the (111) axis.

FIG. 1. XAFS r-space data for both W L$_{III}$- and Zr K-edge data up to 7 Å. Data at 20 K (solid line), 160 K (dotted line), and 315 K (dashed line) are shown for each edge. The Fourier transform (FT) range is from 3.3 to 13.5 Å$^{-1}$, with 0.3 Å$^{-1}$ Gaussian broadening. The high frequency curve inside the envelope is the real part of the Fourier transform ($F_{R}$). The envelope is defined as $\pm \sqrt{F_{R}^2 + F_{I}^2}$, where $F_{I}$ is the imaginary part of the transform. There is a well-defined XAFS phase variation of the W(1)-Zr distance [7] at 300 K. Under the above assumptions, this result shows that fluctuations of the W-Zr distance are $\sim 25\%$ reduction. This means that the atomic motions must be correlated. Since the XAFS results show that fluctuations of the W-Zr distance are small, the W and Zr motions must be partially correlated (i.e., the W-Zr pair moves as a stiff dumbbell).

FIG. 2. $\sigma^2$ vs temperature. The W L$_{III}$-edge data are plotted in the upper panel: the open triangles represent the nearest neighbor W-O bonds; the solid squares show $\sigma^2$ for the W-Zr pair including W-O-Zr multiple-scattering effects; the open circles represent the nearest W(1)-W(2) atom pair. In the lower panel, $\sigma^2$ for three atom pairs are shown: the nearest neighbor Zr-O bond (open triangle), the nearest Zr-W pair including the Zr-O-W linkage (solid square), and the nearest Zr-Zr pair (open circle). Note the unusual cusp for the W-W and Zr-Zr pair data near 100 K.
We use a simplified model (with O omitted) to explain the correlated motions of W and Zr based on the stiffness of W-O-Zr [Fig. 3(b)]. Consider the Watom to be at the top of a small triangular tent (but initially in the plane of the Zr) with rigid poles connected to the three Zr atoms on the base. When W moves out of the plane [as in Fig. 3(b)], then, due to the three rigid legs, the Zr-Zr distance $D_{Zr-Zr}$ will decrease and the base area must shrink while preserving the equilateral shape. A similar contraction occurs if the W moves down out of the plane. The lattice constant of $\text{ZrW}_2\text{O}_8$ ($a = 9.1494 \text{ Å}$ [12]) is directly related to $D_{Zr-Zr}$ ($a = \sqrt{2}D_{Zr-Zr}$) since the Zr atoms occupy the fcc positions in a cube. As the temperature increases, $D_{Zr-Zr}$ will on average become shorter due to the increased vibration amplitude of $\text{WO}_4$ along a ⟨111⟩ axis; thus, we expect to have a net lattice contraction.

A natural question that arises out of the above discussion is why does a low-energy optical mode not soften (vibration frequency goes to zero) such that a soft-mode displacive phase transition takes place? For a cubic system, there should be four equivalent vibrational modes (per unit cell) in the above model, oriented along each of the possible ⟨111⟩ axes. However, such a fourfold degeneracy is inconsistent with cubic symmetry and the actual eigenmodes must therefore be linear combinations of displacements along different ⟨111⟩ axes. This implies that the motion of the W and Zr for vibrations of the W along a given ⟨111⟩ axis are coupled to other ⟨111⟩ axes. This frustrates a possible soft-mode transition. Using group theory, we can write down the local modes that are consistent with space group $P2_13$. Let $a_{111}$ represent a vibration amplitude of W-W along the [1, 1, 1] axis. Then under the 12 symmetry operation for $P2_13$, this amplitude will be transformed to a vibration along one of the other three ⟨1, 1, 1⟩ axes (or remain unchanged). There are four possible linear combinations of these amplitudes—three of which are degenerate and transform into each other.

Singlet:

$$\Psi_1 = 0.5(a_{111} + a_{-1,1,1} + a_{1,-1,-1} + a_{-1,1,1}).$$

Triplet:

$$\Psi_2 = 0.5(a_{111} + a_{-1,1,1} - a_{1,-1,-1} - a_{-1,1,1}),$$
$$\Psi_3 = 0.5(a_{111} - a_{-1,1,1} - a_{1,-1,-1} + a_{-1,1,1}),$$
$$\Psi_4 = 0.5(a_{111} - a_{-1,1,1} + a_{1,-1,-1} - a_{-1,1,1}).$$

For each mode $\Psi$, there are equal amplitudes along each of the ⟨1, 1, 1⟩ axes and hence equal contractions in all directions. Thus, if one of these modes were to become frozen it would not change the symmetry—that is, there is no preferred direction. The analysis of David et al. [3] indicates that the lowest mode at 3.3 meV (singlet) has by far the most negative Gruneisen parameter [a factor of 20 larger in magnitude than that for the 5.8 meV mode (triplet), and hence dominates for NTE].

The coupling between different axes which frustrates a soft-mode transition can be understood geometrically. In Fig. 3 we showed that the triangles around each W atom would shrink uniformly as W vibrates transversely; we now consider the consequences of such displacements for the entire lattice. Figure 4 shows three (of the four possible) planes which are perpendicular to different ⟨111⟩ axes. First let us focus on the white plane in panels 1 and 2. Note that the structure contains both filled Zr triangles (with W atoms in the center) and nonfilled Zr triangles. The latter form hexagons (panel 2 of Fig. 4) in this kagome lattice; similar patterns are found for other ⟨111⟩ planes. If the W atoms vibrate transversely to the white plane, then each of the filled triangles will contract uniformly (panel 2 of Fig. 4). This will in turn contract the hexagon in the center and preserve its equilateral shape as the central Zr is constrained by the lattice against a large vertical displacement, although the Zr atom can move within the planes. Consequently, the non-filled triangles also shrink, which then drives vibrations of the W atoms perpendicular to other ⟨111⟩ planes as depicted in panel 3 of Fig. 4. Thus, a shrinkage in one plane is coupled to a local shrinkage on each of the other ⟨111⟩ planes.

The interconnectivity of the ⟨111⟩-type motions illustrates why these displacements can be soft locally, yet resist a symmetry-lowering phase transition. An analogy to this local motion is found in the ‘‘Hoberman’’ sphere, a children’s toy which retains its spherical shape while changing size in response to a uniaxial force. The dynamics of a related two-dimensional version of this model are discussed by Simon and Varma [13]. A similar mechanism seems to be operative in $\text{ZrW}_2\text{O}_8$ on the nanometer scale and explains how $\text{ZrW}_2\text{O}_8$ retains its cubic...
structure. Presumably, further neighbor interactions limit the size change in response to thermal vibrations. Interestingly, the Hoberman™ sphere is an example of a system with a negative Poisson ratio, a quantity which measures the transverse expansion in response to a uniaxial compression. It remains to be seen whether or not the local motion found in ZrW2O8 is manifested as a negative Poisson ratio in the bulk.

In conclusion, the WO4 tetrahedra are essentially rigid over a wide temperature range (5 to 315 K) but the ZrO6 octahedra are not, although the Zr-O bonds are quite stiff. Importantly, the W-Zr linkage between these two types of polyhedra has a comparable stiffness to Zr-O and the W-Zr pair will move as a unit to the same extent as the ZrO6 unit; consequently, some of the O motion must be related to translations of WO4 and ZrO6. Thus, transverse vibrations of O in the W-O-Zr linkage cannot be the primary origin of NTE in this material. The XAFS results indicate that the vibrations of the nearest W and Zr atom are correlated with a translation of WO4 along a ⟨111⟩ axis; the W(1)-W(2) and Zr-Zr pairs have the lowest vibrational energy with a hardening of the vibration frequency near 100 K. These correlated displacements suggest the form of the eigenmodes that lead to NTE. The coupled motions along different ⟨111⟩ axes also frustrate the formation of a soft-mode transition; consequently, the lattice shrinks uniformly along all four ⟨111⟩ axes, which maintains the cubic lattice structure.

This work was supported by NSF Grant No. DMR0071863 and was conducted under the auspices of the U.S. Department of Energy (DOE). The experiments were performed at SSRL, which is operated by the DOE, Division of Chemical Sciences, and by the NIH, Biomedical Resource Technology Program, Division of Research Resources.