SOLIDS THAT SHRINK WHEN HEATED

Thermal expansion is the reason that cracks between railroad tracks are largest in the winter and that the Sears tower grows by 15 cm in the summer. The reason that solids generally expand when heated is that atoms move apart to make room for each other when the amplitude of their thermal motion increases. There are however exceptions to this rule; i.e. solids that contract when heated. Such materials can be of great technological significance because they allow engineers to create composites that retain their dimensions irrespective of temperature. One example of a solid that contracts as temperature increases is ZrW_2O_8. Discovered by Martinek and Hummel in 1968 [1] this cubic material shrinks by 9 ppm/K from cryogenic temperatures until its decomposition temperature of $1050°C$ (see Fig. 1). Because the material is a transparent dielectric Lucent Technologies is using ZrW_2O_8 to compensate for thermal expansion of standard dielectrics in fiber optic gratings that must maintain their optical dimensions over a large range of temperatures. Before ZrW_2O_8 arrives at a telephone exchange near you we took it upon ourselves to understand this useful freak of nature through a series of neutron scattering experiments. [2]

Figure 1 shows the reduction of the lattice parameter of ZrW_2O_8 with increasing temperature as measured with cold neutron 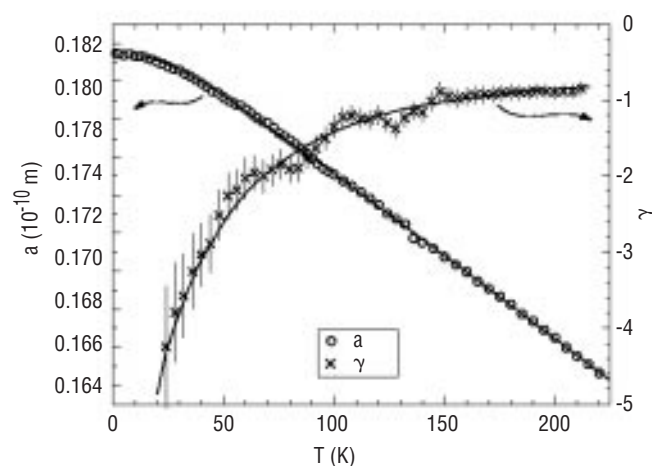diffraction. The Grüneisen theory of thermal expansion relates the linear thermal expansion coefficient $\alpha = d\ln a/dT$, to the specific heat as follows:

$$\alpha = \frac{1}{3B} \sum_i \gamma_i c_i \qquad (1)$$

The summation is over normal vibrational modes, $B = -dP/d\ln V$ is the bulk modulus (B = 4.8×10^{10} Nm^{-2} for ZrW_2O_8), c_i is the specific heat contribution of a single mode, and $\gamma_i = -(\partial\ln\omega_i/\partial\ln V)$ is the Grüneisen parameter which measures the contribution of each mode to thermal expansion. The overall Grüneisen parameter is defined as $\gamma(T) = 3B\alpha/C$ where $C = \sum_i c_i$ is the total lattice specific heat. Clearly, $\gamma(T)$ is temperature independent if all modes of vibration contribute equally to thermal expansion (or contraction). Figure 1 shows $\gamma(T)$ for ZrW_2O_8, which we determined by dividing the thermal contraction data in Fig. 1 by specific heat data [3]. $\gamma(T)$, is of course, negative at all T and its absolute value increases down to the lowest temperature probed. This indicates that low energy modes drive thermal contraction in ZrW_2O_8.

To quantify this statement we measured the phonon density of states (DOS) using inelastic neutron scattering and the result is shown in Fig. 2. The high energy modes correspond to librations of oxygen atoms. The top of the band at 140 meV lies higher than in Al_2O_3 by approximately 30 meV and this reflects the strong covalent bonding of oxygen in WO_4 tetrahedra and ZrO_6 octahedra (See inset to Fig. 2).

The low energy part of the spectrum is shown in Fig. 3. A large density of states remains down to 2.5 meV with a pronounced peak at 4 meV, which reveals low energy optical modes. Subsequent single crystal inelastic experiments have also identified several nearly dispersion-less modes around this energy.

To determine whether this DOS Peak could be important for thermal contraction we make the assumption that $\gamma(\hbar\omega) = \gamma_0 < 0$ for $E_0 < \hbar\omega < E_1$ and zero elsewhere as shown in the inset to Fig. 3. With $\gamma_0 = -14(2)$, $E_0 = 1.5(4)$ meV, and $E_1 = 9.5(2)$ meV and using the measured DOS, we obtain excellent fits to the data in Fig. 1 (solid lines). While the model is certainly not unique it establishes a range of energies for vibrations contributing to thermal contraction in ZrW_2O_8.
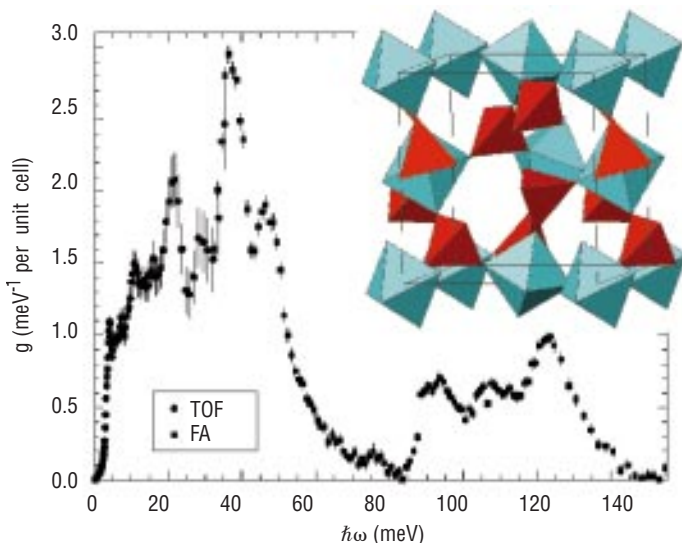

FUGURE 1. Temperature dependence of the cubic lattice parameter, a, and Grüneisen parameter γ(T) for ZrW_2O_8. Solid lines are based on a model described in the text.

G. Ernst, A. P. Ramirez and G. Kowach
Bell Laboratories, Lucent Technologies
600 Mountain Avenue
Murray Hill, NJ 07974

C. Broholm
Department of Physics and Astronomy
Johns Hopkins University
Baltimore, MD 21218

and

NIST Center for Neutron Research
National Institute of Standards and Technology
Gaithersburg, MD 20899

FIGURE 2. Density of states for ZrW_2O_8 at T=300 K measured using inelastic neutron scattering. For $0 < |\hbar\omega| < 40$ meV we used the TOF spectrometer with E_i=5 meV. For $\hbar\omega > 40$ meV we used BT4 with a polycrystalline Be filter analyser. Inset shows the structure with WO_4 tetrahedra in red and ZrO_6 octahedra in blue.

FIGURE 3. Low energy part of the phonon spectrum for ZrW_2O_8 and its temperature dependence. Inset shows our model for the energy dependence of the Grüneisen parameter.

An interesting aspect of these low energy modes is their temperature dependence shown in Fig. 3. There is a decrease in the frequency of the 4 meV optic mode as the temperature decreases and the unit cell volume increases. Naively this would appear to be in contradiction with a negative Grüneisen parameter because $(\partial\omega / \partial T)_P = -3\omega\gamma\alpha$ must be negative. But for an anharmonic vibration the mode frequency also depends on the amplitude and we propose that this non-linear effect which is not taken into account in the Grüneisen theory is responsible for the softening of the 4 meV optical mode.

What remains is to identify the microscopic nature of these modes. Single crystal phonon data will be required to accomplish this in earnest. Nonetheless inspection of the structure shown in Fig. 2 does provide important clues. ZrW_2O_8 consists of corner-sharing WO_4 tetrahedra and ZrO_6 octahedra. The unusual low energy optic modes are likely to correspond to twisting of these units with respect to one another and this twisting leads to contraction just as a vibrating guitar string tugs on its supports. What makes ZrW_2O_8 special is the unusually low energy of these twist modes which allows them to become highly excited and pull the structure together at temperatures far below those required to excite bond-stretching modes.
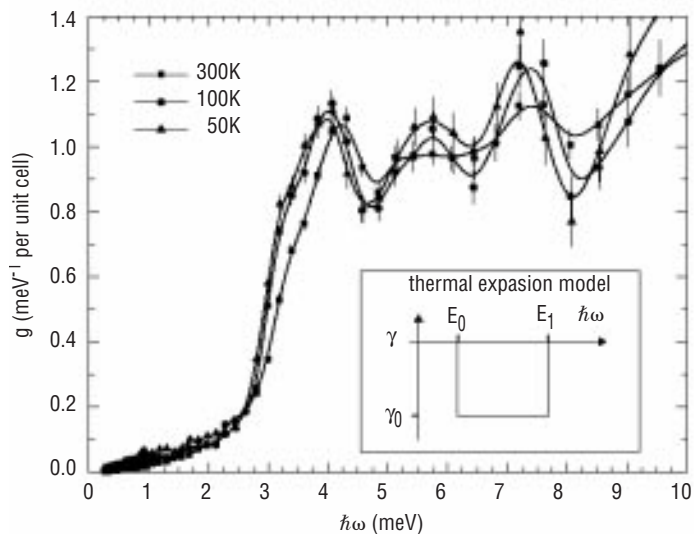
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