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 ZrW₂O₈. 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 ZrW₂O₈ 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 ZrW₂O₈ 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 ZrW₂O₈ 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:

$$\alpha = \frac{1}{3B} \sum \gamma_i c_i$$

(1)

The summation is over normal vibrational modes, $B = -dP/d \ln V$ is the bulk modulus ($B = 4.8 \times 10^{10}$ Nm⁻² for ZrW₂O₈), $c_i$ is the specific heat contribution of a single mode, and $\gamma_i = - (\partial \ln \omega / \partial \ln V)$ 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 ZrW₂O₈, 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 ZrW₂O₈.

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 Al₂O₃ by approximately 30 meV and this reflects the strong covalent bonding of oxygen in WO₄ tetrahedra and ZrO₆ 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 $\gamma = 0$ 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 ZrW₂O₈.
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 \( \frac{\partial \omega}{\partial T} \bigg|_P = -3 \gamma \alpha \) 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\(_2\)O\(_8\) 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\(_2\)O\(_8\) 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.

REFERENCES