Vibrational Softening in α-Uranium

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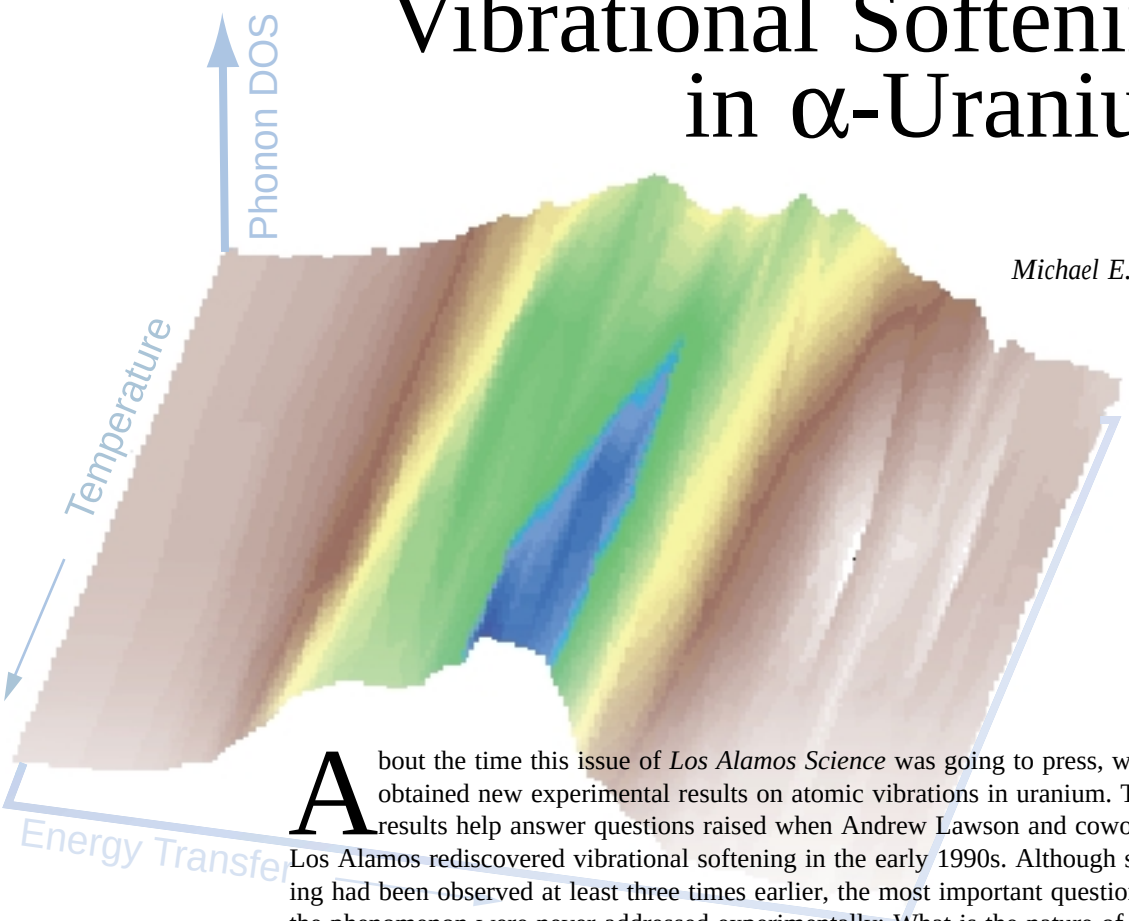


About the time this issue of *Los Alamos Science* was going to press, we obtained new experimental results on atomic vibrations in uranium. These results help answer questions raised when Andrew Lawson and coworkers of Los Alamos rediscovered vibrational softening in the early 1990s. Although softening had been observed at least three times earlier, the most important questions about the phenomenon were never addressed experimentally: What is the nature of vibrational softening? Is it an anharmonic or electronic effect? This article summarizes preliminary inelastic neutron-scattering results that address both questions. Our full results will be published in a journal article (Manley et al. 2000a).

Lawson's measurements of Debye-Waller factors—mean-square atomic displacement, $\langle u^2 \rangle$—suggest that the average phonon frequency decreases by about 40 percent as the temperature is raised from room temperature (300 kelvins) to uranium's β-phase transition temperature (940 kelvins), a much larger decrease than the quasi-harmonic theory of anharmonicity would normally predict (see the article "Atomic Vibrations and Melting in Plutonium" on page 190). In the quasi-harmonic approximation, anharmonic vibrations are assumed to be independent harmonic modes whose frequencies are not fixed but, instead, depend on volume (V). In this approximation, the vibrational entropy S of a collection of vibrational modes can be written as

$$S(V,T) = \sum_j -3k_B \ln\left(\frac{\hbar\omega_j(V)}{k_B T}\right) \quad , \tag{1}$$

where ω is the frequency of the quasi-harmonic mode. Using this expression, we can determine the entropy difference between a constant-pressure (changing ω) and a constant-volume (fixed ω) experiment. Specifically, for the 40 percent decrease in frequency implied by the results of Lawson, Equation (1) would predict that $(S_p - S_V)_{940\ K} - (S_p - S_V)_{300\ K} = -3k_B \ln(0.6) = 1.5k_B$/atom, which is about 5 times larger than the total entropy change of the α-β transition.

On the other hand, if we neglect the electronic entropy, we can also determine this vibrational-entropy difference directly from classical thermodynamics. Using the

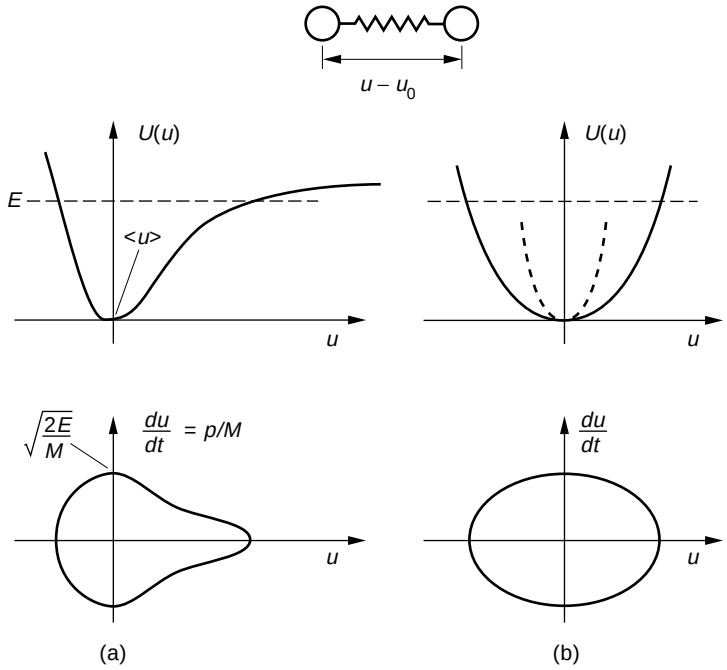


Figure 1. Anharmonic vs Harmonic Oscillators

Potentials (top) and phase space (bottom) are shown for (a) anharmonic and (b) harmonic oscillators with the same mean square displacement $\langle u^2 \rangle$ and energy *E*. The dashed lines in (b) represent the effective potentials seen at low energy. The anharmonic phase space contains a smaller area and hence has a lower vibrational entropy.

classical expression relating the specific heats at constant volume and constant pressure, $C_p - C_V = 9B_T v\alpha^2 T$, and the well-known values for bulk modulus B_T, molar volume v, and thermal expansion coefficient α, we obtain

$$(S_P - S_V)_{940\text{K}} - (S_P - S_V)_{300\text{K}} = \int_{300\text{K}}^{940\text{K}} \frac{C_p - C_v}{T} dT = 9B_T v\alpha^2 (640\text{ K}) = \frac{0.16\, k_B}{\text{atom}} , \qquad (2)$$

which is nearly an order of magnitude smaller than the quasi-harmonic value derived from Equation (1). Clearly, a greater understanding of vibrational softening is needed.

Equation (1) is based on the usual assumption that phonon softening comes from anharmonicity. That is to say, the softening is assumed to come from higher-order terms (higher than quadratic) in a temperature-independent interatomic potential. A simple analog of this potential is the pair potential shown in Figure 1(a). In this case, the increase in the average interatomic separation $\langle u \rangle$ with increasing temperature can be related directly to the softening (or flattening) of the potential. In other words, as the masses, or atoms, are pulled farther apart by thermal motion, the potential has less restoring force than is expected from a linear spring (hence, the term softening). But what if the potential is not fixed? Could the interatomic potential remain harmonic and soften because the electronic contribution to the potential changes with temperature? If true, this fact would have profound implications on the way we think about the electronic structure and equation of state for uranium.

Figure 1 shows the potentials and phase-space trajectories for an anharmonic (a) and a harmonic (b) oscillator, both having the same energy E and mean-square displacement $\langle u^2 \rangle$. Note that the phase-space trajectory of the anharmonic oscillator has a smaller area than that of the harmonic oscillator. In the classical limit ($k_B T >>$ the energy spacing of quantum states), a unit of phase-space area of size $\Delta p \Delta u \sim \hbar$ (set by the uncertainty principle) contains one quantum state. So, a smaller area accesses fewer quantum states. Because entropy is proportional to the log of the number of accessible quantum states, the anharmonic oscillator with its smaller

phase-space area must have less vibrational entropy. A similar argument can be made for harmonic and anharmonic oscillators at equal temperatures, but in that case they would have equal entropies, and the energy of the anharmonic oscillator would be larger. Either way, the vibrational free energy ($F = E - TS$) is larger for the anharmonic oscillator. Thus, determining whether anharmonic or harmonic models describe the vibrational modes of uranium is essential to understanding the equation of state for uranium.

Most standard measurements of vibrations in solids are immediately interpreted in terms of harmonic models. However, it is possible to take a more general view. In particular, for inelastic neutron scattering, the dynamic-structure factor can be interpreted in terms of the mean-square power spectrum. The dynamic-structure factor $S(Q, \omega)$ gives the scattering intensity as a function of momentum transfer Q and energy transfer $\hbar\omega$. The limiting case of zero-energy transfer (elastic scattering), $S(Q, \omega = 0)$, gives the usual diffraction pattern used for structural determination. The limiting case of $Q = 0$ can be measured by various vibrational spectroscopies such as infrared. But neutrons are unique in their ability to accurately probe both the dynamics and positions of atoms in solids simultaneously. This is because, as if by some lucky twist of fate, neutrons with energies on the order of the vibrational energies also have wavelengths similar to the spacing between atoms.

For a Bravais lattice, the polycrystalline averaged incoherent dynamic scattering function is given by

$$S_i(Q,\omega) = \frac{1}{2\pi\hbar}\int^{\infty} \left\langle e^{-iQr(0)} e^{iQr(t)} \right\rangle e^{-i\omega t}\, dt \quad , \tag{3}$$

where the brackets imply a thermal and powder average. Expanding Equation (3) in powers of Q gives the following:

$$\left\langle e^{-iQr(0)} e^{iQr(t)} \right\rangle \cong 1 + iQ\left(\left\langle r(t)\right\rangle - \left\langle r(0)\right\rangle\right) - \tfrac{1}{2}Q^2\left(\left\langle r^2(t)\right\rangle + \left\langle r^2(0)\right\rangle\right) + Q^2\left\langle r(0)\, r(t)\right\rangle + \ldots \ .$$

Substituting this expansion into Equation (2) and simplifying in the classical approximation gives

$$S_i(Q,\omega) \cong \frac{\delta(\omega)}{\hbar}\left(1 - Q^2\left\langle r^2(0)\right\rangle\right) + \frac{Q^2}{2\hbar}\left|R(\omega)\right|^2 + \ldots \quad , \tag{4}$$

where $R(\omega)$ is the Fourier transform of the atomic motion given by

$$R(\omega) = \int_{-\infty}^{\infty} r(t)\, e^{-i\omega t}\, dt \quad . \tag{5}$$

The first term in Equation (4) gives the elastic line, and the second gives the modulus-square power spectrum. The average potential energy per oscillator can then be determined from

$$\left\langle U\right\rangle = \frac{1}{2} M \int \omega^2 \left|R(\omega)\right|^2 d\omega \quad , \tag{6}$$

where M is the mass of the vibrating atom.

In the case of harmonic phonons in the high-temperature limit, the power spectrum can be related to the phonon density of states $Z(\omega)$ by the relation

$$\frac{1}{2} M\omega^2 \left|R(\omega)\right|^2 = \frac{1}{2} k_B T Z(\omega) \quad . \tag{7}$$

Integrating both sides with respect to ω gives the expected classical result, $\langle U \rangle_h = k_B T/2$. Note that this result holds true even if the harmonic potential is temperature dependent. On the other hand, if the potential is fixed and the softening comes from anharmonicity, the potential energy is given by

$$\langle U \rangle_{anh} \cong \frac{1}{2} k_B T + A(k_B T)^2 + B(k_B T)^3 + \ldots \quad , \tag{8}$$

where the A and B coefficients can be related to true anharmonic terms in the interatomic potential.

In recent experiments, we took inelastic neutron-scattering spectra of uranium at several temperatures from 50 to 913 kelvins. Measurements at room temperature and below were taken on the Low-Resolution Medium-Energy Chopper Spectrometer (LRMECS) at the Intense Pulsed Neutron Source at Argonne National Laboratory. Spectra at room temperature and above were taken on the Fermi-Chopper Spectrometer (FCS) at the Center for Neutron Research at the National Institute of Standards and Technology. Both spectrometers are time-of-flight instruments. We used these instruments with polycrystals to obtain the best average over the phonon spectrum. Because uranium scatters coherently, interference modulates the inelastic scattering intensity as a function of momentum transfer Q. Thus, to determine a phonon density of states, we must sum over all Q in the Brillouin zone.

We extracted the phonon density of states from data taken over a wide range of momentum transfers using a procedure described in Manley et al. 2000b. The results, shown in Figure 2, do indeed indicate the phonon softening with increasing temperature predicted by Angus Lawson and coworkers. That is, the average phonon frequency decreases as the temperature is increased. But the data show another surprise. The phonon density-of-state features sharpen with increasing temperature. Normally, the features broaden with increasing temperature if the potential is anharmonic. The reason is that the anharmonicity becomes more pronounced at high temperatures, causing phonon-phonon scattering and thereby reducing the lifetimes of the phonons. Because of the wave nature of neutrons, shortened phonon lifetimes result in broadened phonon energy line widths according to the time-energy relationship $\Delta E \Delta t > \hbar$. Thus, the sharpening of the phonon density-of-state features with increasing temperature does not indicate anharmonicity. More likely, the low temperature broadening is a result of increased electron-phonon coupling associated with the charge density wave that occurs at ~43 kelvins.

A result that contradicts the fixed anharmonic potential model is the linear increase with temperature of the average potential energy

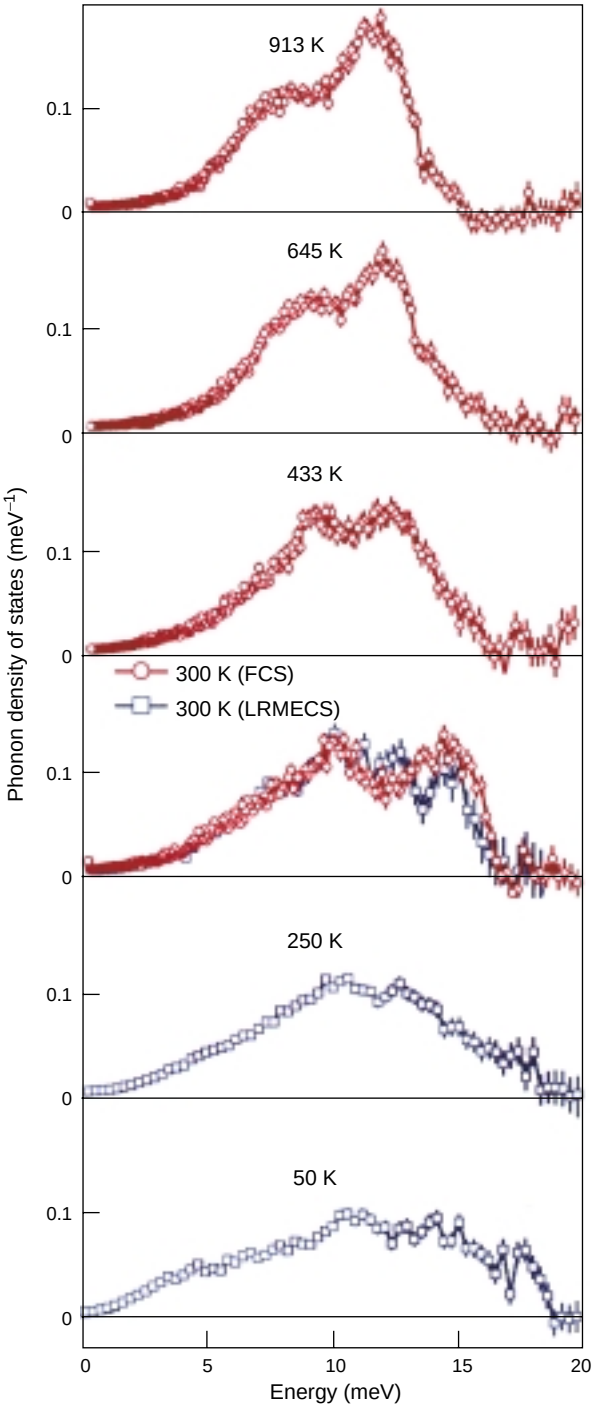
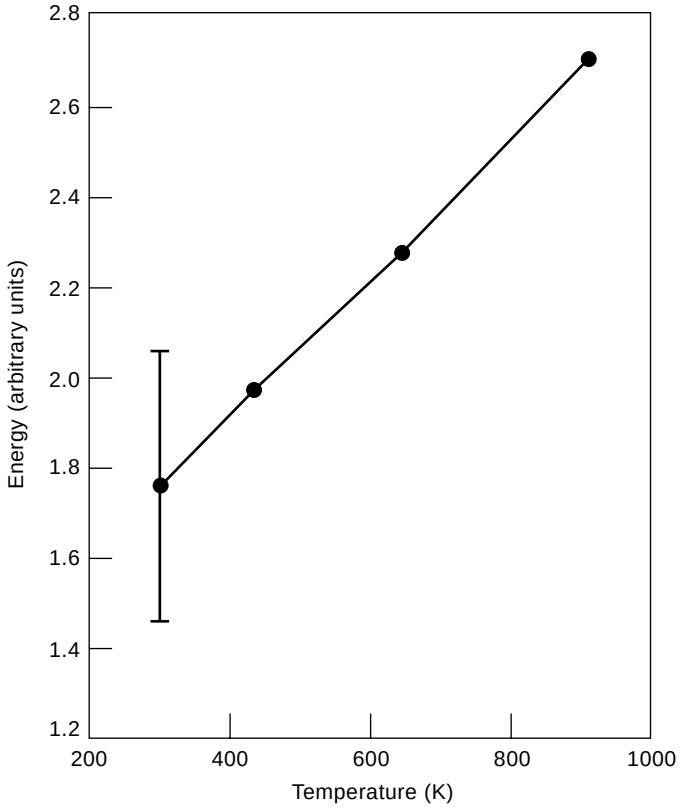


Figure 2. Phonon Density of States for α-Uranium
Our data from the Fermi-Chopper Spectrometer (FCS) at the National Institute of Standards and Technology are shown in red and those from the Low-Resolution Medium-Energy Chopper Spectrometer (LRMECS) at Argonne National Laboratory are shown in blue. They both indicate phonon softening.

Figure 3. Vibrational Potential Energy of α-Uranium

The average vibrational potential energy calculated from the mean-square power spectrum increases linearly with temperature. The linear increase implies that the thermal vibrations obey harmonic statistics.



(see Figure 3), which we calculated by substituting our measurements of the mean-square power spectrum into Equation (6). The linear increase implies that the motion obeys harmonic statistics and that the higher-order terms in Equation (8) are zero. Therefore, although the phonon density of states is softening, the underlying potential must be harmonic in this temperature range (consistent with the sharper features). Evidently, the potential is temperature dependent, and the simple model given in Figure 1(b) best describes the nature of the phonon softening. Because the potential originates with the sensitivity of the electronic energy to atom displacements, it follows that thermal excitations of the electronic states are altering the potential.

Although uranium has temperature-dependent phonon frequencies, the vibrational part of the equation of state of uranium can be treated with the well-understood harmonic statistics. Therefore, preliminary phonon density-of-states data measured near the α-β transition and the β-γ transition in uranium, shown in Figure 4, were used to estimate the vibrational entropies of these transitions. The change in phonon density of states at each phase transition accounted for vibrational entropy changes of $(S^{\beta} - S^{\alpha})_{\text{vib}} = +(0.15\pm0.01)k_B$/atom and $(S^{\gamma} - S^{\beta})_{\text{vib}} = +(0.36\pm0.01)k_B$/atom. Both these values are significantly smaller than the total entropy obtained from latent heat measurements: $(S^{\beta} - S^{\alpha})_{\text{tot}} = 0.37k_B$/atom and $(S^{\gamma} - S^{\beta})_{\text{tot}} = 0.55k_B$/atom. The remaining entropy increases of the phase transitions must be electronic in origin. This is quite a surprise because vibrations by far make up the largest contribution to the total entropy (see the article "Elasticity, Entropy, and the Phase Stability of Plutonium" on page 208). The total electronic entropy is smaller because the Pauli exclusion principle restricts the number of countable electronic states. Another important observation is that the large thermal softening observed in α-uranium did not occur in the high-temperature γ-uranium (bcc) phase.

These results are most interesting because they challenge the way we think about the strength of bonding. With very few exceptions, changes in the stiffness of a bond between two atoms or a collection of atoms in a crystal are related to atomic

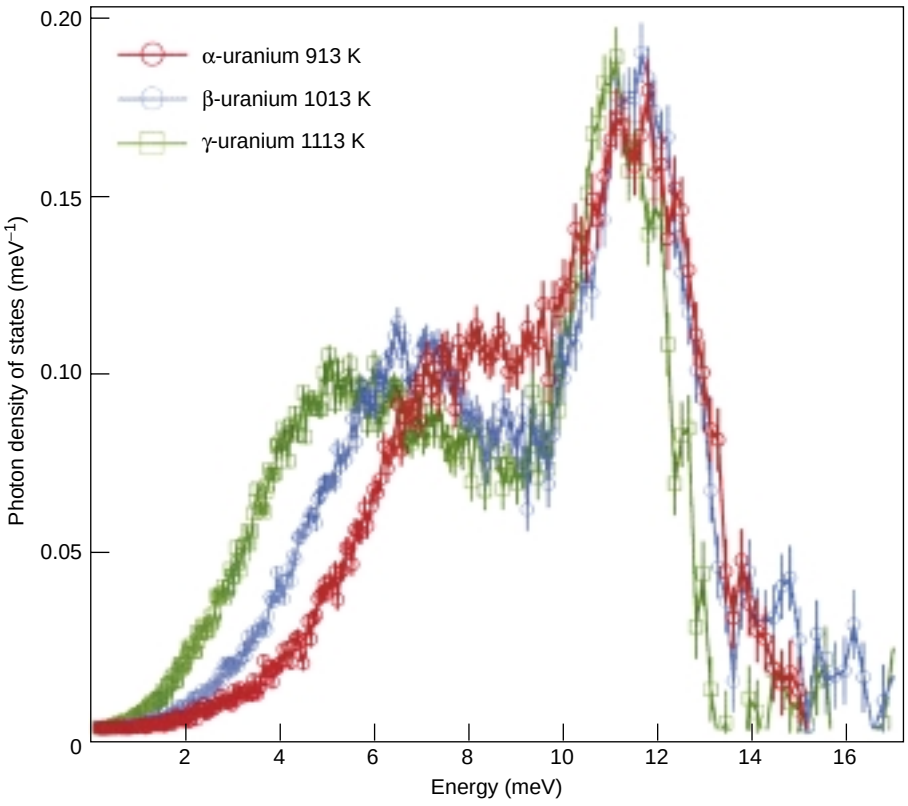


Figure 4. Phonon Density of States of the Three Solid-State Phases

The plot shows our results for the phonon density of states of the three solid-state phases of uranium: α-uranium (orthorhombic), β-uranium (tetragonal), and γ-uranium (bcc). The shifting of the peaks to lower energies for the higher-temperature phases implies an increase in vibrational entropy with each phase transition.

distances and/or the symmetry of the arrangement in the case of a crystal, and the effects of electronic thermal excitations are usually ignored. The results presented here suggest the opposite and therefore should be of considerable interest to those studying electronic structures and related issues, such as the equation of state. Quantifying and understanding the vibrational and electronic parts of the equation of state of uranium as well as the other actinides are our primary objectives in the near future.

Further Reading

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Michael E. Manley is currently pursuing a Ph.D. in materials science at the California Institute of Technology, but he spends a large part of his time working at the Los Alamos Neutron Science Center (LANSCE). His research focuses on the entropies of elementary excitations in metals and alloys. He is also studying how mechanical properties and microstructure affect the thermodynamics of metals and alloys. He is a member of the LANSCE User Group Executive Committee for 2000.