The Nature of Vibrational Softening in α-Uranium

The standard textbook explanation for phonon softening with increasing temperature in a single phase is that the interatomic potentials are not perfectly harmonic, but it has been suggested that phonon softening can also occur if the potential itself can change with temperature, while remaining harmonic. For example, a large softening of the vibrational properties of α-uranium has been observed [1] that cannot be explained in terms of the anharmonic lattice contribution alone. In the present work a harmonic contribution to the phonon softening is made evident by treating inelastic neutron scattering spectra as an expansion of the vibrational power spectrum of the atomic motion.

Earlier diffractometry measurements by Lawson *et al.*, [2] suggested that the Debye temperature decreased by 40 % in going from 300 K to the β-phase transition temperature at 940 K. In terms of entropy this corresponds to an additional $\Delta S = -3k_B ln(0.6) = 1.5\ k_B$/atom. The usual thermodynamic argument is that this increase in vibrational entropy compensates for the elastic energy generated by thermal expansion. However, from heat capacity data, the entropy needed to compensate for the elastic energy is nearly an order of magnitude too small at 0.16 k_B/atom.

All experiments used uranium powder. High temperature measurements were made using the Fermi-Chopper Spectrometer (FCS) at the NCNR. Low temperature measurements were performed with the Low Resolution Medium Energy Chopper Spectrometer (LRMECS) at Argonne National Laboratory. Figure 1 shows the phonon density of states obtained from the measured spectra, corrected for the incoherent multiphonon scattering using a procedure described elsewhere [3]. There is a redistribution of intensity in the main features at ≈ 8 meV and ≈ 12 meV, with the higher energy peak gaining extra weight with increasing temperature. These features also show an overall softening of around one meV for every 200 K increase in temperature.

The Q-summed one phonon scattering function was used to calculate a quantity proportional to the square of the power spectrum and hence to the average potential energy per oscillator, $\langle U \rangle$. In Fig. 2 we show $\langle U \rangle$ for α-uranium at the four highest temperatures scaled so that the lowest point is at the harmonic energy $k_B T/2$. The effects of anharmonicity on $\langle U \rangle$ would be evident as a nonlinearity in

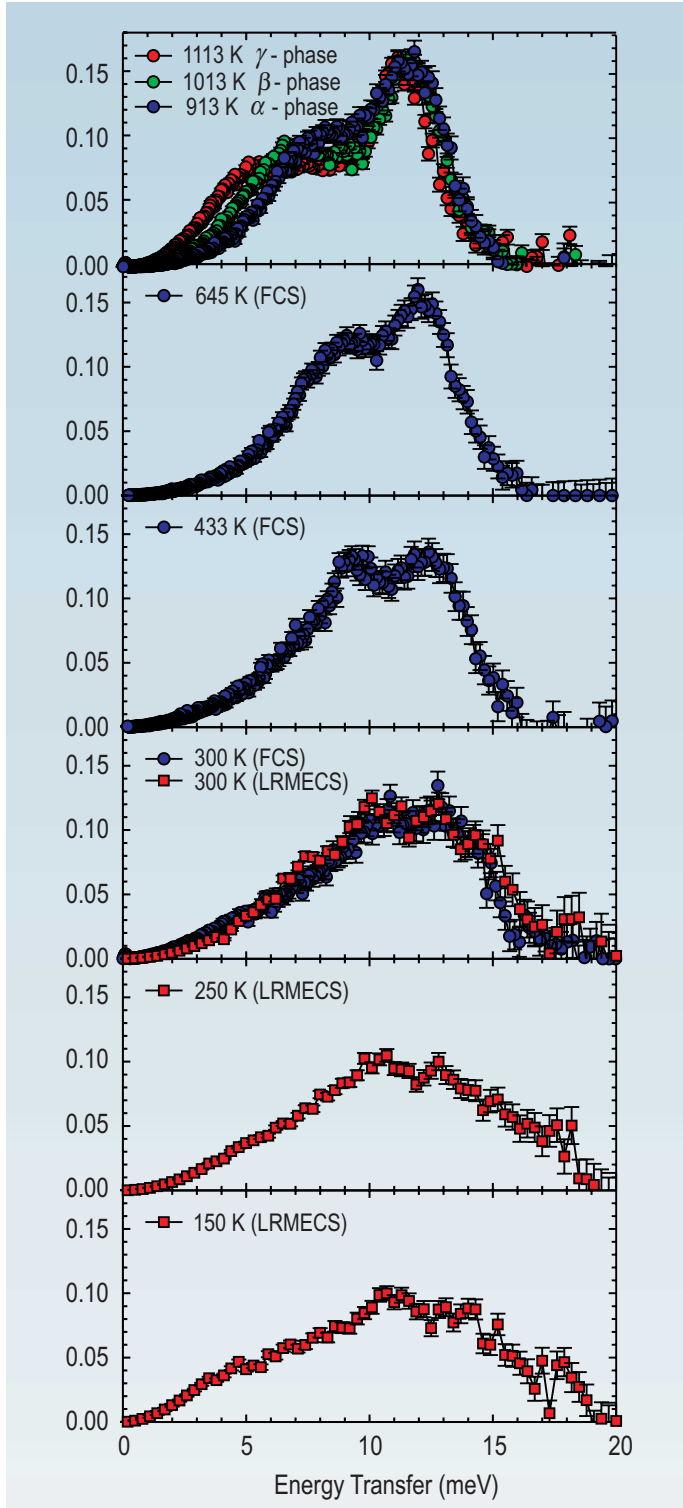

FIGURE 1. The phonon density of states of uranium. Data from 300 K and above were obtained from spectra acquired with FCS. Data from 300 K and below were measured on LRMECS.

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the plot of <*U*> vs. temperature. For comparison, attempts were made to calculate the temperature dependence of the potential energy of Morse and Lennard-Jones potentials with the appropriate vibrational softening for uranium [1]. The result shown in Fig. 2 indicates that, in the high temperature limit, the potential energy has nearly a linear dependence on temperature, i.e., the phonon softening in α-uranium occurs while the potential remains primarily harmonic. Evidently the interatomic force constants are decreasing with increasing temperature. Since the force constants originate from the change of the electronic energy with atom displacements, it must be that thermal excitations of the electronic states are altering the force constants.

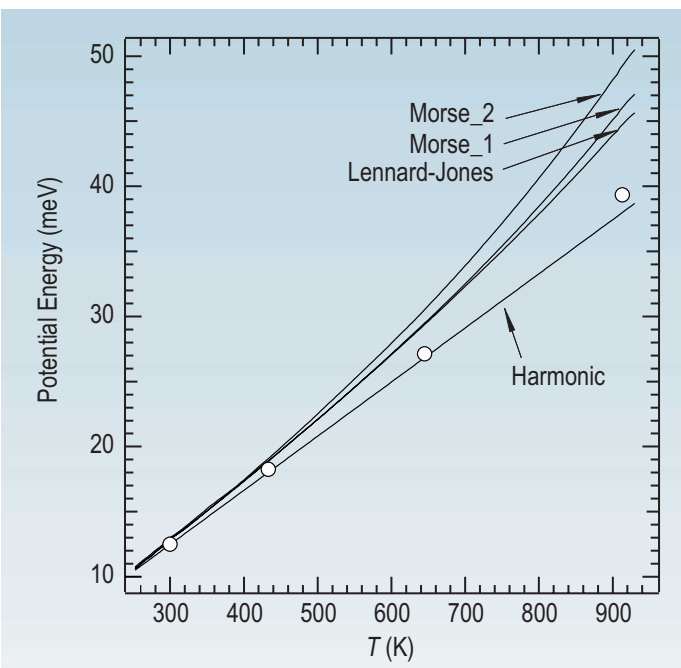

FIGURE 2. Vibrational potential energy of α-uranium (open circles). The Lennard-Jones, Morse_1 and Morse_2 curves were calculated from potentials described in the text. The Harmonic curve is the result for a harmonic potential in the classical limit.

The phonon density of states of the three solid state phases of uranium, orthorhombic (α), tetragonal (β) and body centered cubic (γ) are compared in the top panel of Fig. 1. The γ-uranium phonon density of states was statistically identical at 1113 K and 1213 K. Evidently, the thermal softening mechanism seen in α-phase does not operate in the γ-phase. The β-phase was not stable over a wide enough temperature range to obtain a reliable temperature dependence. The phonon softening between each phase accounted for vibrational entropy changes of 0.15 ± 0.01 k_B/atom and 0.20 ± 0.01 k_B/atom for the α to β and β to γ transitions, respectively. Both of these values make up only about 35 % to 40 % of the total entropy changes predicted from latent heat measurements: $(S^{\beta}-S^{\alpha})_{tot} = 0.37\ k_B$/atom and $(S^{\gamma}-S^{\beta})_{tot} = 0.55\ k_B$/atom. The remaining 60 % of the entropy increases must be electronic in origin. So not only does the phonon softening disappear in the high temperature γ-phase, but also it does so with a large increase in electronic entropy.

Electronic band structure calculations used to predict phonon frequencies are based on the assumption that thermal effects can be neglected when compared to volume effects. The actinides, however, show the need for more sophisticated treatments of the role of temperature on interatomic interactions.

References

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