Formation of a New Dynamical Mode in α-Uranium Observed by Inelastic X-Ray and Neutron Scattering

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Phonon dispersion curves were obtained from inelastic x-ray and neutron scattering measurements on α-uranium single crystals at temperatures from 298 to 573 K. Both measurements showed a softening and an abrupt loss of intensity in the longitudinal optic branch along $[00\zeta]$ above 450 K. Above the same temperature a new dynamical mode of comparable intensity emerges along the $[01\zeta]$ zone boundary with energy near the top of the phonon spectrum. The new mode forms without a structural transition but coincides with an anomaly in the mechanical deformation behavior. We argue that the mode is an intrinsically localized vibration and formed as a result of a strong electron-phonon interaction.

Recent measurements revealed a large thermal softening of the phonon density of states (DOS) of α-uranium [1,2]. Although thermal phonon softening is normally attributed to anharmonicity, α-uranium is unusual in that it does not exhibit behavior typically associated with a strongly anharmonic solid. First, its thermal expansion [3]; the elastic energy of expansion can only account for about 10% of the entropy generated by the phonon softening [2]. Second, the energy derived from its vibrational power spectrum exhibits linear scaling with temperature, behavior consistent with classical harmonic vibrations [2]. Finally, features in the phonon DOS sharpen with increasing temperature, the opposite of what is expected from anharmonic lifetime broadening [2]. Based on these observations it has been argued that the temperature dependence in the phonon DOS of α-uranium is not entirely due to a classic anharmonic potential but largely results from changes in the electronic structure [2]. There is, however, another way in which nonlinear interatomic forces might be manifested; nonlinear dynamics can lead to the formation of extra dynamical modes [4–6].

For harmonic vibrations in a crystal the number of phonon branches is fixed by the number of atoms per primitive cell [7]. As a consequence, the appearance of extra modes is normally ascribed to a breaking of the crystal symmetry by a structure change. Nonlinearity, however, can also cause additional intrinsically localized modes [4–6]. Although it has been suggested that such modes may occur in conventional solids [6], experimental observations have been limited to quasi-one-dimensional solids [8], micromechanical systems, and magnetic analogs [9]. In this Letter, we report experimental evidence showing the formation of a new dynamical mode without a crystal structure change in α-uranium above 450 K. The effects appear in both high-purity and lower-purity single

crystals despite a large impurity effect on phonon energies [10,11]. This Letter also addresses two previously reported anomalies that coincide with the formation of the new mode: (1) a large change in the measured phonon DOS [2] and (2) an unexplained loss of mechanical ductility at the mode formation temperature [12].

All previous phonon dispersion curves measured on uranium were performed at room temperature [13] and below [3,10,14]. Measurements on other actinides have been more limited [10,15], but temperature-dependent measurements of Debye-Waller factors [1] and phonon DOS [16] indicate nonlinear behavior similar to that of uranium [1,2]. The present results, however, are the first phonon dispersion curves measured at high temperatures on an actinide element.

Inelastic x-ray scattering (IXS) measurements of the phonons were performed using SRI-CAT at the Advanced Photon Source of Argonne National Laboratory [17,18]. The spectrometer was operated with an incident energy of 21.657 keV. The crystals and the instrument configuration were the same as that used in an earlier measurement [10]. Inelastic neutron scattering (INS) measurements of the phonons were performed using the HB3 triple-axis spectrometer at the Oak Ridge high flux isotope reactor. The spectrometer was operated with fixed final neutron energy of 14.87 meV. The crystal and the instrument were the same as that used in the original room temperature INS work by Crummett *et al.* [13]. The crystal used in the IXS experiments was smaller but of higher purity than the crystal used in the INS experiments [3,10]. The constancy of the α-uranium crystal structure over the temperature range studied (298 to 573 K) [1,3] was confirmed for the IXS crystals by x-ray Laue diffraction.

The IXS measurement of the longitudinal optic (LO) mode at $[00\zeta = 0.4]$ showed a broadening and intensity
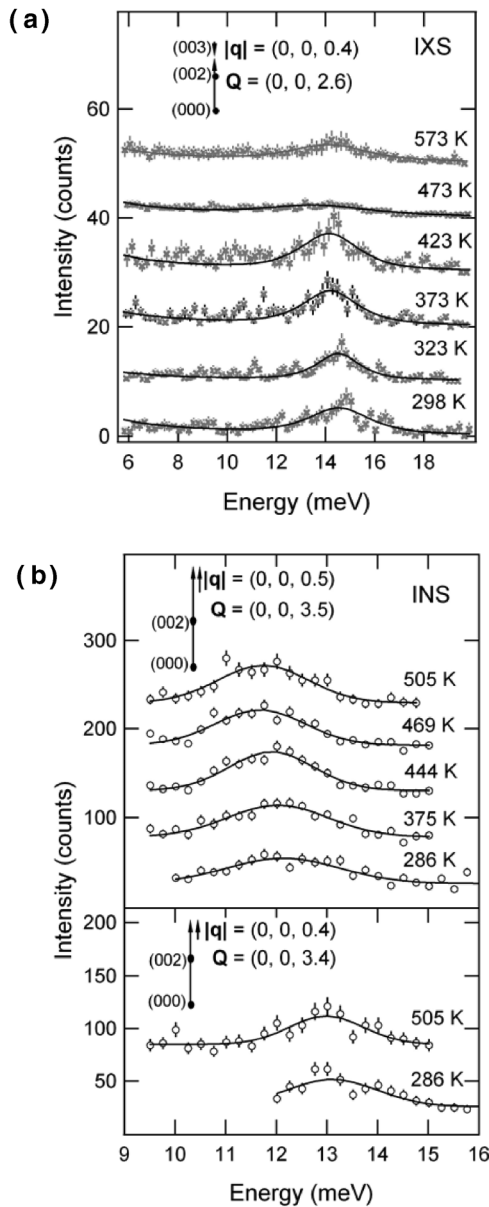
(a)

(b)

FIG. 1.   Raw data offset for clarity: (a) IXS and (b) INS. The geometry in reciprocal space is shown as an inset in each frame, with **Q** designating the scattering vector and **q** the phonon wave vector.

loss on heating from 423 to 473 K, Fig. 1(a). The broadening decreased on further heating but the loss of intensity persisted. Attempts to reproduce these observations with the INS measurement failed to reproduce the broadening but intensity losses across the same temperature range were observed, Fig. 1(b). The intensity losses were made more apparent by integrating phonon intensities and dividing out the thermal occupation factor, Fig. 2. The temperature-corrected integrated intensity losses in the LO mode at $[00\zeta = 0.4]$ showed good agreement between the IXS and INS measurements, both showing a 50% loss. Intensity loss in the LO optic mode at the zone boundary $[00\zeta = 0.5]$
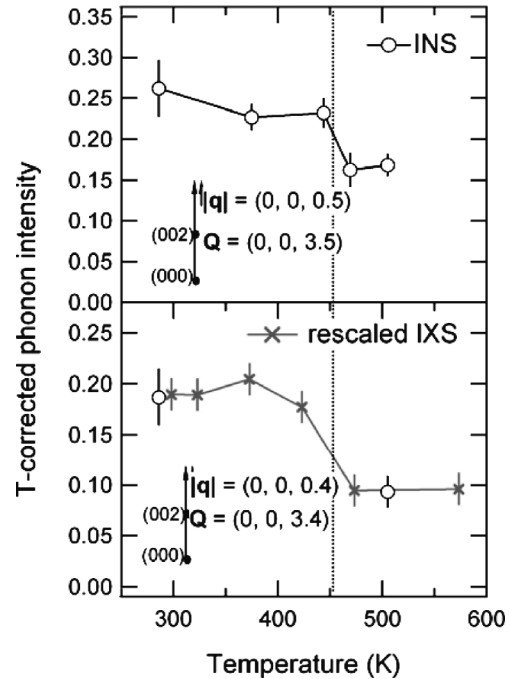

FIG. 2.   Inelastic intensities derived from fits to the raw data shown in Fig. 1, and corrected for the thermal factor ($\langle n \rangle + 1$), where $\langle n \rangle$ is the Bose-Einstein thermal factor. Each data set is normalized to the count time and the IXS data is multiplied by a scale factor for comparison with the relative changes in the INS data.

was less at 25%, but the loss occurred across the same temperature range, near 450 K. Also observed was a softening of the LO mode that diminished after the intensity loss, Fig. 2.

To reconcile the phonon intensity losses with changes observed in the phonon DOS [2], optic modes in the b-c plane were scanned with INS at several temperatures. The most distinctive change was the formation of a new 14.3 meV mode along the $[01\zeta]$ zone boundary, Fig. 3. Accompanying the new mode was a softening of the mode
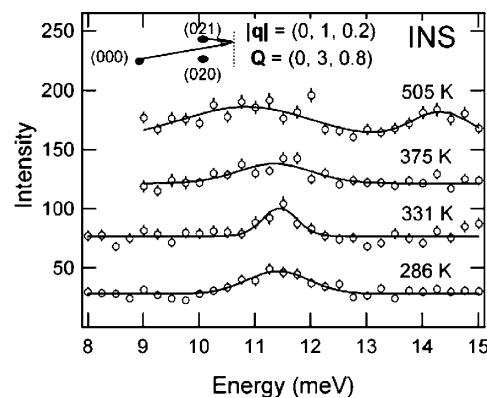

FIG. 3.   Data showing a new mode emerge near 14 meV at high temperature, together with the softening of the mode at about 11 meV. Data are offset for clarity. The phonon wave vector **q** is at a zone boundary.
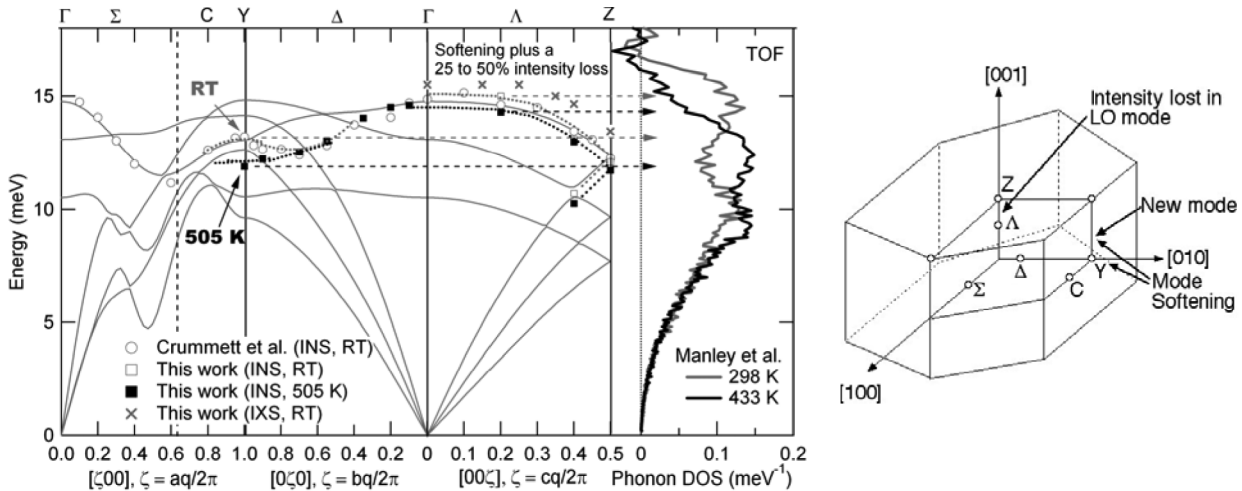
FIG. 4. Partial summary of the phonon dispersion data (left panels) with a comparison to phonon DOS extracted from a time-of-flight (TOF) neutron scattering measurement [2] (right panel). The dispersion data points shown are all from modes polarized along $[00\zeta]$. Right: Brillouin zone for α-uranium indicating the notation used for the high symmetry directions and the locations of the measured anomalies (see text).

along the same direction, also appearing in Fig. 3. The transverse optic mode propagating along $[0\zeta 0]$ and displacing atoms along $[00\zeta]$ also softened near the Y high symmetry point on the same zone boundary, Fig. 4. Viewing the optic mode displacing atoms along $[00\zeta]$ as it maps from a LO mode to a TO mode along $[0\zeta 0]$, Fig. 4, reveals some sources of the restructuring of the phonon DOS observed by Manley *et al.* [2]. Intensity loss in a feature of the phonon DOS around 15 meV coincides with the intensity loss in the LO mode along $[00\zeta]$, Fig. 4. The formation of a peak around 12 meV coincides with a flattening of the branch near Y owing to its softening at the zone boundary, Fig. 4. The new mode formed at 14.3 meV, however, does not contribute much intensity directly to the phonon DOS, presumably because it is confined a small region of reciprocal space.

Despite the obvious changes in the optic modes around 450 K, most properties of uranium show no anomaly near this temperature. The heat capacity [19] and elastic constants [3,20] vary smoothly across this temperature range, and Laue x-ray diffraction patterns performed in this study indicate no long-range structural transition, consistent with earlier diffraction work [1,3]. The implication is that changes are short range and that supporting evidence should be found in properties that depend strongly on short-range interactions. An example is the motion of defects responsible for mechanical deformation. Indeed, the ultimate amount of deformation that can be imparted in a tensile test of α-uranium, measured as percent elongation at failure, does show a dramatic change around 450 K [12]. Rather than increasing monotonically with temperature, the percent elongation decreases around 450 K and then increases again at higher temperatures. While known for more than 40 years [12], this mechanical anomaly has never been explained. The present observations suggest

that it may be related to changes in the local lattice dynamics.

The above observations suggest that the new mode is localized. First, no long-range structural change is associated with the appearance of the new mode, indicating that any symmetry breaking must be local. Second, many of the associated dynamical effects appear to be confined near a zone boundary, i.e., their spatial periodicity does not extend much beyond the lattice spacing. The intensity loss in the LO mode might also fit this picture since local modes take intensity from plane-wave phonons. Third, the property most strongly affected by the appearance of the mode, the motion of defects, is coupled to the local dynamics. Furthermore, the spontaneous formation of this mode in the absence of a structural transition, and in the presence of strong nonlinear dynamics [1,2], also suggests that it might be an intrinsically localized mode (ILM) [4–6,9].

As pointed out by Sievers and Takeno [6], because ILM's form randomly throughout a lattice, they give rise to additional configurational entropy. Therefore, if the new mode is an ILM then the heat capacity of α-uranium should show an excess above 450 K that cannot be accounted for by changes in the phonon DOS. To test this idea the measured heat capacity was compared to the known phonon and electronic contributions. The phonon contribution was estimated by interpolating the temperature-dependent phonon DOS measured by Manley *et al.* [2] using the procedure described by Nagel *et al.* [21]. The electronic contribution was estimated by extrapolating low-temperature heat-capacity data, where the electronic coefficient is $\gamma = 9.13 \text{ mJ K}^{-2} \text{mol}^{-1}$ [22]. Summing the phonon, C_{ph}, and the electronic, C_{el}, contributions and comparing the result to the measured heat capacity [19] reveals an excess above 450 K, Fig. 5. This
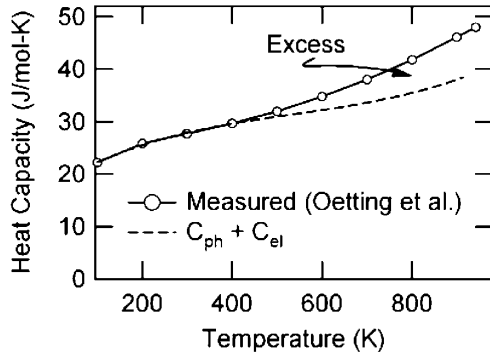
FIG. 5. Heat capacity of uranium determined by direct measurement [20] and calculated by summing the contribution from the phonon DOS and the electrons ($C_{el} + C_{ph}$), see text.

excess heat capacity, C_{ex}, implies excess entropy according to

$$S_{ex}(T) = \int_0^T \frac{C_{ex}(T')}{T'} dT'. \tag{1}$$

Integrating the excess heat capacity up to 850 K gives $S_{ex}(850\ \mathrm{K}) = 0.27 k_B/\mathrm{atom}$. For ILM's distributed randomly throughout the lattice, the configurational entropy is given by

$$S_c = -k_B[f \ln f + (1 - f) \ln(1 - f)], \tag{2}$$

where f is the number of local modes per atom. Setting the excess entropy at 850 K equal to the configurational entropy gives $f(850\ \mathrm{K}) = 0.077$. It is conceivable that concentrations of this order are responsible for the intensity of the new mode shown in Fig. 3. Vacancy formation also has this form but volume changes consistent with this many vacancies are not observed [3].

Although the above analysis indicates that the new mode may be an ILM, it does not specify whether the nonlinearity is from electron-phonon coupling or from nonlinear forces in a classic anharmonic potential. It has been argued that most of the nonlinearity in uranium is electron phonon [2] and this is consistent with soft-phonon modes associated with uranium's charge-density-wave transitions [3]. So perhaps the mode observed here is a three-dimensional version of electron phonon based ILM's observed previously in a quasi-one-dimensional charge-density wave system [8].

These results suggest that the physical properties of uranium are strongly influenced by the high-temperature formation of intrinsically localized vibrations [4–6,8,9]. Although such vibrations have been proposed as general phenomena [6], clear observations in three-dimensional solids have remained elusive. The observation in uranium is likely a consequence of strong nonlinear behavior leading to the stabilization of significant concentrations of ILM's at high temperatures.

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