Intrinsically localized vibrations and the mechanical properties of α-uranium

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Abstract

Recent experiments have indicated that the high-temperature properties of α-uranium may be strongly influenced by the formation of randomly distributed intrinsically localized vibrational modes, just a few atoms across in size. One observation was a loss of mechanical ductility that coincided with the formation of the intrinsically localized mode (ILM). Here, we consider this observation in more detail. In particular, we use the anisotropic thermal expansion behaviour to estimate the strains associated with each ILM and consider the implications for the forces between ILMs and the defects responsible for mechanical deformation. In the process we also suggest that an unusual transition from positive to negative thermal expansion along the [0 1 0] direction may be caused by the formation of ILMs.
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Non-linearity refers to a situation where perturbations of the system cause large shifts in the frequency spectrum. By this definition the lattice dynamics of α-uranium is highly non-linear; the phonon density of states soften by as much as 10% when the temperature changes by as little as 100 K [1]. Although thermal softening is an expected consequence of anharmonicity, α-uranium is unusual in that it does not show behavior typically associated with a strongly anharmonic solid [1]. Calculations and some experiments have shown, however, that non-linear dynamics can also lead to the spontaneous formation of intrinsically localized vibrations [2–4], and recent measurements using both inelastic X-ray scattering (IXS) and inelastic neutron scattering (INS) have revealed that at least some of the phonon softening in α-uranium is associated with a new mode forming [5].

As shown in Fig. 1a 14.3 meV mode appears at high temperatures at a Q-position on the [0 1 ζ] zone boundary near the Y high symmetry point. Also appearing in Fig. 1, a phonon branch softens at an energy just below the new mode energy. A more detailed view of the dispersion curves (not shown here) indicates

that other branches also soften, which are mainly along the zone boundary near the Y high-symmetry point [5].

Ref. [5] provides detailed arguments supporting the hypothesis that the new mode shown in Fig. 1 is an intrinsically localized mode (ILM) [2–4]. Briefly, the five main points presented are:

(1) New mode forms without a long-range crystal structure change, indicating that the required symmetry breaking must be local.
(2) New mode appears confined to a zone boundary, implying that its spatial periodicity does not extend much beyond the lattice spacing.
(3) Ductile deformation is reduced in the presence of the new modes while the long-range elastic moduli are not affected.
(4) The mode forms in the presence of a strong non-linearity in the dynamical behavior.
(5) An excess in the heat capacity is found to be consistent with the configurational entropy of having randomly distributed intrinsically localized modes on the lattice.

Interestingly many of the effects of having these new modes resemble the effects of adding impurities; a reduction in mechan-

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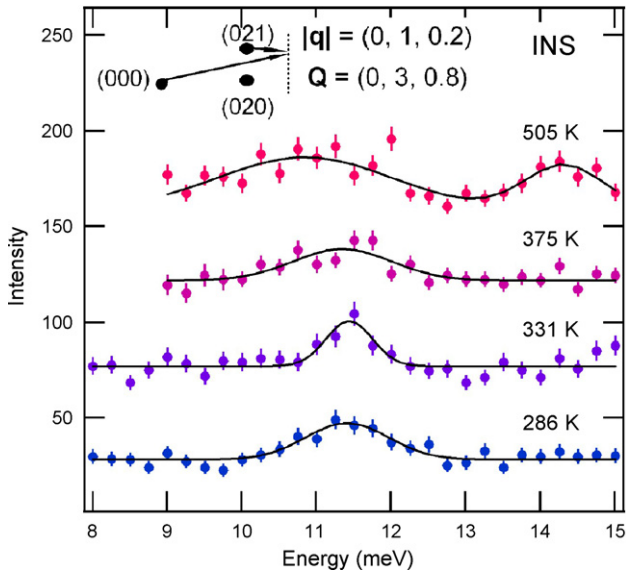* Corresponding author. Tel.: +1 505 690 8862.

Fig. 1. Data showing a new mode emerge near 14.3 meV at high temperature, together with the softening of the mode at about 11 meV. Data are offset for clarity. The scattering vector, Q, is in the b–c plane. The phonon wave vector, q, is at a zone boundary. Data was collected using inelastic neutron scattering (INS) at the HFIR facility of Oak Ridge National Laboratory using the procedure described in Ref. [5].

ical ductility and the appearance of mixing entropy [4,5]. This is expected for ILMs because, much like impurities, ILMs are distinguishable within the crystal and they have associated strain fields [4]. Depending on the details of the strain-field interactions ILMs can either be attracted to or repelled by dislocations responsible for deformation. Furthermore, since it takes energy

to move an ILM [4] these interactions can create drag forces on mobile dislocations as they push and/or drag ILMs around, thereby increasing the Peierls stress. Vacancies also play a role in deformation, assisting in dislocation climb [6]. ILMs are expected to complicate these processes as well since they are expected to interact with vacancies [4]. Therefore, understanding the anomalous mechanical-deformation behavior of uranium in the presence of ILMs requires a detailed picture of the ILM strain fields. Here, after a discussion of the anomaly in the mechanical deformation [7] and its coincidence with ILM formation, we attempt to obtain information on the ILM strains by looking at the anisotropic thermal expansion behavior [8,9]. By extension we also argue that a transition from positive to negative thermal expansion along [0 1 0] is caused by the ILM strains.

Accompanying the formation of the new mode shown in Fig. 1 is a loss of intensity in the longitudinal-optic-phonon branch along [0 0 1]. Fig. 2a shows the integrated intensity for two positions on this branch corrected for temperature by dividing out the thermal occupation factor ($\langle n \rangle + 1$), where $\langle n \rangle$ is the Bose–Einstein thermal factor [10]. There is a clear drop in intensity for both positions on the branch near 450 K, although the drop is larger at $|q| = (0\,0\,0.4)$ than it is at the zone boundary, $|q| = (0\,0\,0.5)$. The temperature at which this intensity loss occurs and the new mode appears coincides with an anomalous plateau in the plastic deformation behavior, Fig. 2b. Normally with increasing temperature the amount of deformation that can be imparted increases monotonically, but for uranium there is an unexplained loss of ductility above about 450 K [7]. As discussed above this might be explained if the new mode, shown in Fig. 1, is interpreted as resulting from a random distribution of ILMs on the lattice. Implicit in
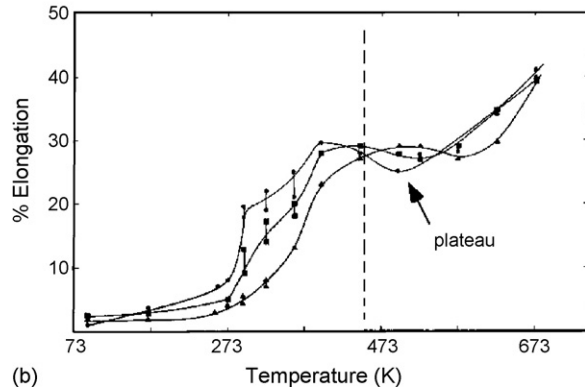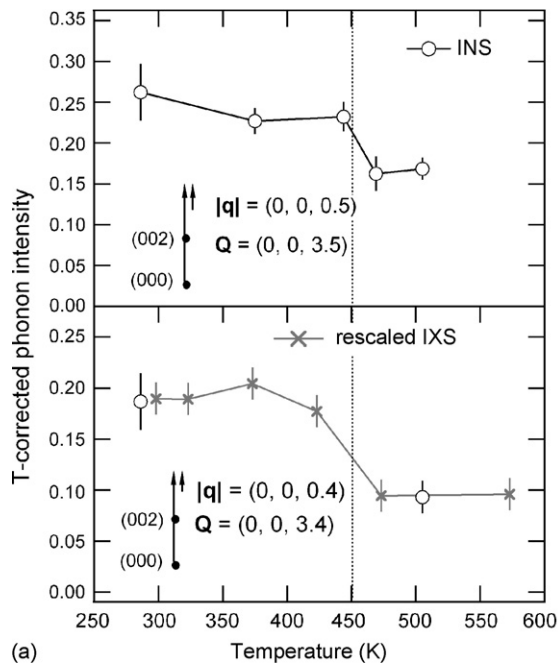

Fig. 2. This figure shows the coincidence of the anomalies in the phonons and mechanical deformation: (a) inelastic intensities derived from fits to raw phonon data, and corrected for the thermal factor as described in Ref. [3] (INS indicates inelastic neutron scattering data and IXS indicates inelastic X-ray scattering data); (b) Maximum amount of deformation imparted on a tensile test specimen at failure, measured as percent elongation (taken from Ref. [6]). The three curves correspond to three different heat treatments; (▲) brine quench, (■) Hg quench and (●) recrystallized (see Ref. [6] for details).
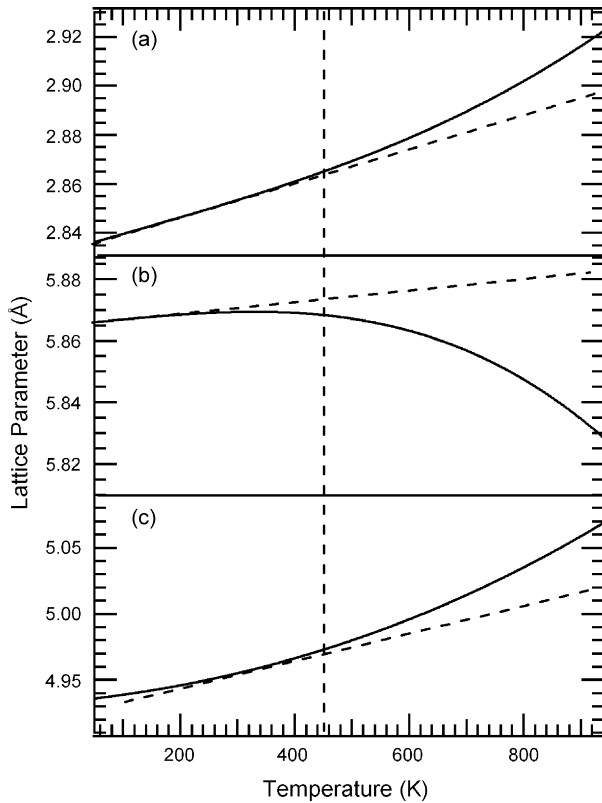
Fig. 3. Temperature-dependent lattice parameters of α-uranium calculated from polynomial fits to single-crystal data by Lloyd and Barrett [9]. The vertical dashed line indicates the temperature where the phonon and mechanical deformation anomalies occur in Figs. 1 and 2. The dashed lines tangent to the curves are used to estimate excess changes in the lattice parameters, see text.

this argument is that the local strain associated with the ILM is large enough to create a barrier to the movement of the defects responsible for deformation. A corollary to this argument is that the aggregate effect of having these distorted regions in the crystal should produce anomalies in the anisotropic thermal expansion behavior. These anomalies, in turn, should reflect the strains and symmetry of the individual ILMs.

Fig. 3 shows the temperature dependence of the α-uranium orthorhombic unit cell lattice parameters calculated from polynomial fits to single-crystal data by Lloyd and Barrett [9]. Indeed anomalous behavior does occur near and above the temperature where the new mode appears, 450 K. The *a*-axis dimension changes from well-behaved linear thermal expansion to an enhanced non-linear thermal expansion above 450 K. The *b*-axis dimension shows the most dramatic change, going from positive to negative thermal expansion. Interestingly the *b*-axis direction is close to the direction to which the new mode is displacing atoms. As shown in the inset of Fig. 1, the direction that momentum was transferred to the neutron that scattered from the new mode, $Q = [0\,3\,0.8]$, had a large component along the [0 1 0] direction, indicating that the new mode displaces atoms in this direction [10]. This suggests that the lattice contracts in the direction the ILM is vibrating. By extension this implies that ILM formation is driving negative thermal expansion in the [0 1 0] direction. Interestingly, a recent model proposed by Lawson et al. [11] for the negative thermal expansion of plu-

tonium makes use of a mixture of two-states, with the excited state having a lower volume per atom than the ground state. Like uranium, plutonium also shows anomalous softening of the phonons [12–15]. Perhaps the anomalies in both uranium and plutonium are related to the thermal activation of excited states with ILM-like characteristics.

The *c*-axis dimension changes in a way that is similar to the *a*-axis dimension except that there is no clear transition from linear to non-linear behavior at 450 K. This may be the result of an additional non-linearity caused by the depopulation of phonons at the lowest temperatures. The *c*-axis phonons have the highest frequencies [16] and are therefore depopulated first (at near 14 meV they have a characteristic temperature of about 160 K). This depopulation of phonons should reduce the usual anharmonic thermal expansion, giving an additional non-linearity at low temperatures.

To determine the amount of strain per ILM we first need to estimate the concentration of ILMs at a given temperature. As pointed out by Sievers and Takeno [4], because they form randomly throughout the lattice, ILMs have configurational entropy associated with them. Therefore, there should be a contribution to the heat capacity above the ILM formation temperature ($\sim$450 K) that cannot be accounted for by the phonon and electronic contribution, and this excess heat capacity should be relatable to the ILM concentration. Such an analysis was presented in Ref. [5]. In summary, the phonon contribution was estimated from the temperature-dependent phonon DOS measured by Manley et al. [1] using the procedure described by Nagel et al. [17]. The electronic contribution was determined from low-temperature heat-capacity data, where the electronic coefficient is $\gamma = 9.13\,\mathrm{mJ\,K^{-2}\,mol^{-1}}$ [18]. Combining the phonon, C_{ph}, and the electronic, C_{el}, contributions and comparing the result to the measured heat capacity [19] reveals the excess above 450 K, Fig. 4. This excess heat capacity, C_{ex}, implies excess entropy according to:

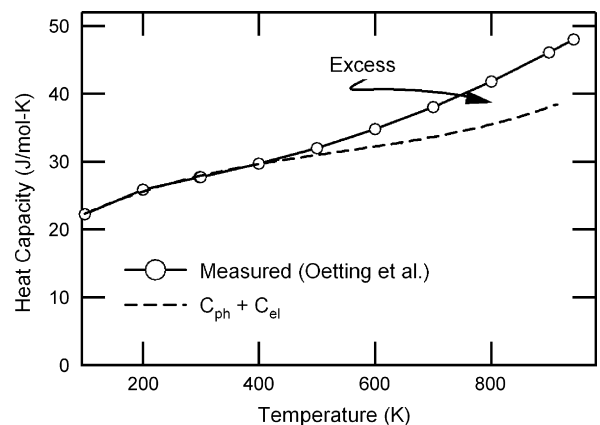$$S_{ex}(T) = \int_0^T \frac{C_{ex}(T')}{T'}\,dT'. \tag{1}$$

Fig. 4. The heat capacity of α-uranium determined by measurement [14] and calculated by summing the contribution from the phonon density of states [1] and the electronic heat capacity [16] ($C_{el} + C_{ph}$), see text. This figure was taken from Ref. [5].

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

$$S_c = -k_B(f \ln f + (1 - f) \ln(1 - f)), \qquad (2)$$

where f is the number of local modes per atom. Setting the excess entropy at 850 K equal to the configurational entropy provides an estimate of the ILM concentration, $f(850\,K) = 0.077$. This implies that a volume containing about 13 atoms, on average, contains one ILM. Therefore, the strain of one ILM on each volume element of this size is equal to the total strain on the bulk due to all the ILMs at 850 K.

The total strain from ILMs at 850 K can be estimated by taking the difference between what the extrapolated (dashed tangent lines) and actual thermal expansion shown in Fig. 3. This assumes that the non-linearity in the anisotropic thermal expansion behavior above 450 K is caused by ILMs. The resulting strains at 850 K are:

$$\varepsilon_{11} = \frac{\Delta a}{a_0} = 0.007, \quad \varepsilon_{22} = \frac{\Delta b}{b_0} = -0.007, \quad \text{and}$$

$$\varepsilon_{33} = \frac{\Delta c}{c_0} = 0.01. \qquad (3)$$

These are remarkably small strains given that they are over a distance of only about $13^{1/3} = 2.35$ atomic distances (concentration of 7.7%). For comparison an edge dislocation embedded in a volume of this size produces a strain of order $1/2.35 = 0.43$; the extra half plane wedge is approximately one atomic distance, and the displacement is over a reference length of 2.35 atomic distances. Experimentally, these differences are what distinguish the ILM from a structural defect. For a structural defect the strains are the main observable (e.g. TEM imaging of dislocations [20]) and any changes in the dynamics would be difficult to observe. For the ILM it is just the opposite, large changes in the dynamics are the main observable (e.g. with inelastic neutron scattering [2,5]) and changes in the average structure are difficult to observe. Nonetheless, these entities should interact and for what the ILM lacks in the magnitude of its strain field it more than makes up for in numbers. Structural defects such as dislocations and vacancies typically involve of order 1 in 10^6 atoms while, as discussed above, the ILMs appear to affect several percent. Therefore, structural defects experience a cloud of ILMs around them.

The large number of ILMs around an individual defect should behave in ways similar to solute atoms in a substitutional alloy. In equilibrium, solute atoms rearrange themselves around dislocations in such a way that small atoms collect in compressive regions and large atoms collect in tensile regions, forming the dislocation atmosphere. This problem was worked out by Larche and Cahn [21] by introducing the concept of open-system elastic constants. Alternatively the solute or vacancy problem can be treated by superimposing a chemical force on the dislocation [6]. The distribution of ILMs around a dislocation can be treated using similar approaches except that the anisotropy of the ILM has to be accounted for. In the [1 0 0] or [0 0 1] directions, the ILMs appear to expand the lattice and will therefore collect in regions with large tensile stresses along these directions.

On the other hand, along the [0 1 0] direction the ILMs appear to contract the lattice and will therefore collect in regions with compressive stresses along this direction. A complete model requires an analysis of interaction of the fully anisotropic strain tensor of the ILMs with that of all the defects responsible for α-uranium's cataloged deformation mechanisms [22].

The formation of intrinsically localized vibrations presents a new kind of point defect with a large degree of mechanical anisotropy. These new modes further complicate the already complicated process of mechanical deformation in α-uranium. Furthermore, the spontaneous formation of large concentrations of these modes with their associated strains also appear to produce anomalies in the anisotropic thermal expansion behavior, including negative thermal expansion along the [0 1 0] direction. These observations may help shed light on the anomalous properties of other highly non-linear solids, including plutonium, which also exhibits non-linearity [12] and negative thermal expansion [11].

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