Intrinsically localized mode in α-U as a precursor to a solid-state phase transition

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The high-temperature behavior of an intrinsically localized mode (ILM) in α-U was measured using inelastic neutron scattering. The mode, which forms above 450 K on the [010] boundary, becomes undetectable at 675 K. Thermodynamic and transport anomalies that develop with the ILM persist to temperatures above 675 K, but mechanical and electronic anomalies show changes at both 450 and 675 K. Anisotropic thermal expansion shows that ILMs drive the structure toward hexagonal symmetry. On the $[\frac{1}{2}\ \frac{1}{2}\ 0]$ zone boundary, which becomes equivalent to [010] under a hexagonal distortion, a normal mode shows a softening coincident with the disappearance of the ILMs. We argue that the symmetry local to the ILMs becomes hexagonal above 600 K, causing ILMs to hop between equivalent orientations and putting the structure on a path toward the high-temperature γ phase (bcc).

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When atoms interact with nonlinear forces, a local vibrational fluctuation is accompanied by a frequency shift. In a crystal, where the normal modes collapse into well defined frequency bands, these local fluctuations can develop frequencies that do not resonate with any normal modes, resulting in an intrinsically localized mode (ILM)[1–4] (also called discrete breather or lattice soliton). Inelastic scattering measurements using neutrons and x rays on α-U show strongly nonlinear lattice dynamics[5] and a new mode that develops above 450 K.[6] A matching "creation excitation" was also observed using high-energy scattering, providing direct evidence of the intrinsic nature of the mode.[7] The mode also forms without a change in the crystal structure or long-range elastic properties, but is accompanied by a loss of intensity in the $[00\zeta]$ longitudinal optic (LO) mode, an excess in the heat capacity,[6] and an anomalous decrease of the mechanical ductility.[6,8] The excess heat capacity has been accounted for by the configurational entropy of randomly distributed ILMs,[1,6] the loss of intensity in the LO mode from the redistribution of kinetic energy to form ILMs,[6] and the loss in ductility from the interactions of ILMs with the defects involved in deformation.[1,6,9] It was also suggested that the nonlinearity responsible for the ILM originates with electron-phonon coupling.[6] However, several earlier reports showed a sudden rise in thermal conductivity as ILMs formed[10] [above 450 K (Ref. 6)] but no corresponding change in the electrical resistivity,[10] suggesting that the ILMs assist in the transport of heat but not charge. Transport by ILMs (usually called lattice solitons in this context) has been considered theoretically for nonlinear lattices.[11] Here, we consider a potential role for ILMs: precursors to a solid-state phase transition.

Classically, vibrational instabilities can lead to displacive phase transitions by way of soft modes, where transition displacements are described in terms of plane waves achieving zero frequency (freezing) at a finite wave vector.[12,13] For uranium, such a mechanism was proposed for the transition from the high-temperature γ phase (bcc) to the low-temperature orthorhombic α phase (*Cmcm*) by passing through an hcp-like hexagonal phase ($P63/mmc$).[14] The proposed mechanism involves the softening of the [110] transverse acoustic mode in the bcc γ phase. However, subsequent measurements of the temperature-dependent phonon density of states of the γ phase showed no indications of softening,[5] while numerous anomalies appear in the α phase as it is heated toward the high-temperature γ phase (as well as an intermediate β phase at low pressures), the most prominent being the ILM.[6,7]

Evidence of the ILMs in α-U can be found in the temperature dependence of the lattice parameters calculated from fits to dilatometry data by Loyd and Barrett[15] and shown in Fig. 1. Above the temperature that ILMs become thermally activated [~450 K (Ref. 6)], the lattice parameter along the polarization direction of the ILM, the *b* axis,[6] begins to contract, while the two orthogonal directions show an

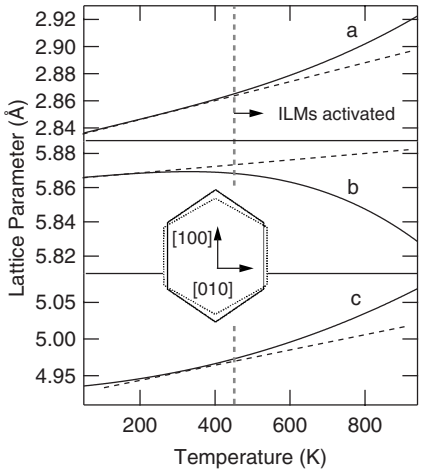

FIG. 1. Temperature dependence of the lattice parameters of α-U calculated from the polynomial fits of single-crystal dilatometry data by Lloyd and Barrett (1966). Intrinsically localized modes (ILMs) appear in the lattice vibrations above about 450 K (Ref. 6) indicated by the vertical dashed line.

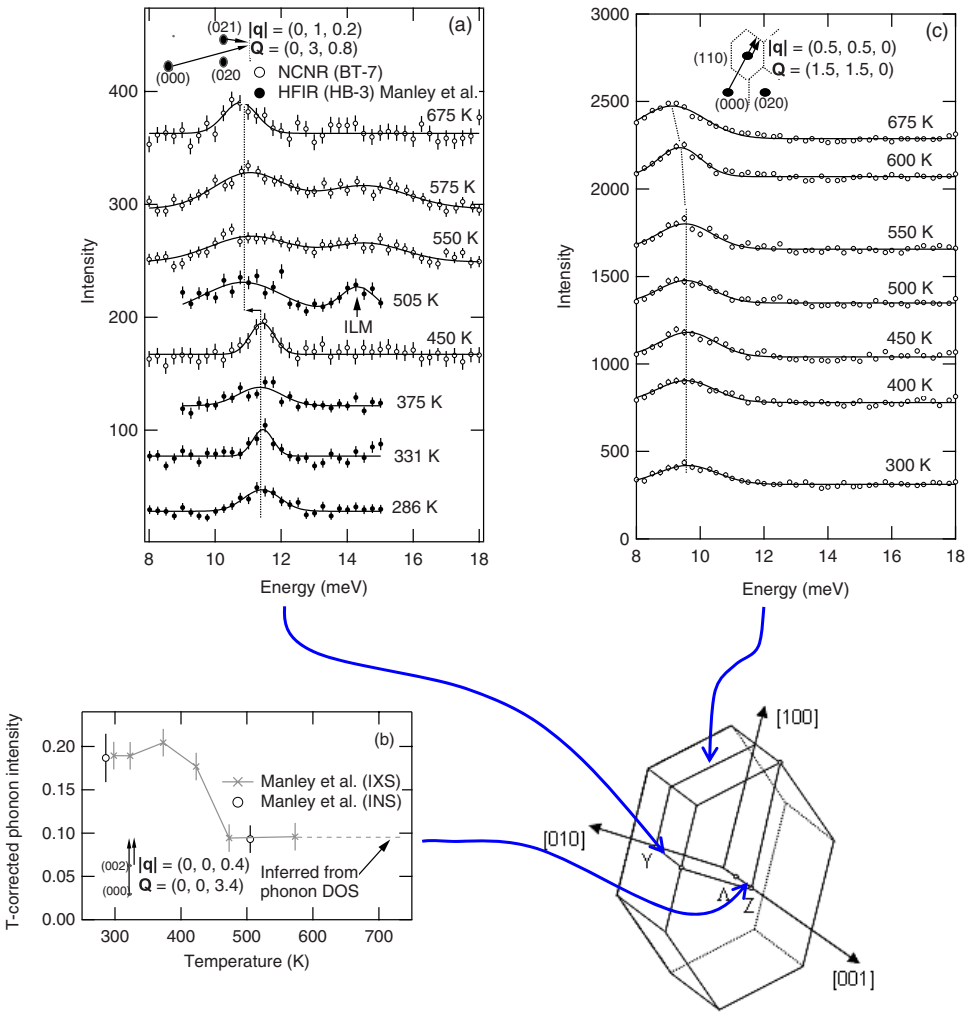

FIG. 2. (Color online) Temperature evolution of the lattice modes of α-U measured using triple-axis inelastic neutron scattering. The scattering vector is given by $\boldsymbol{Q}$, and the phonon wave vector $\boldsymbol{q}$ conserves momentum according to $\boldsymbol{Q}=\boldsymbol{G}+\boldsymbol{q}$, where $\boldsymbol{G}$ is a reciprocal lattice vector pointing to the nearest reciprocal lattice point. (a) Zone-boundary position where the mode was first discovered using the HB3 spectrometer at HFIR (from Ref. 6), with an extension to higher temperatures using the BT7 spectrometer at the NCNR (this work). (b) Loss of intensity in the LO mode extended to higher temperatures through inference to the phonon density of states in Ref. 5. (c) "Nearly equivalent" zone-boundary lattice modes measured using BT7 over the same temperature range as in (a).

enhanced expansion. This pattern of expanding and contracting is consistent with what is expected for the aggregate effect of forming ILMs. For both fcc and zinc-blende structures, molecular dynamic simulations of ILMs predict local dc contractions (local shortening of the lattice spacing) along the ILM polarization direction and local "dc" expansions (local lengthening of the lattice spacing) along the orthogonal directions.[16] However, unlike with these cubic structures, the distortions in orthorhombic α-U do not necessarily drive the local structure toward lower symmetry. This can be seen by looking down the c axis of the Brillioun zone, inset in Fig. 1, and noting that the symmetry is nearly hexagonal, requiring a small contraction along [100] (expansion of the real-space a-axis lattice parameter) and/or expansion along [010] (contraction of the real-space b-axis lattice parameter) to reduce b/a from about 2 to $\sqrt{3}=1.73$, the hexagonal condition. Figure 1 suggests that the ILMs induce a trend toward this condition through both the contraction of b and the accelerated expansion of a. While hexagonal long-range symmetry is never achieved in bulk uranium, it does appear in uranium thin films,[17] and an hcp-like structure ($P63/mmc$) is on a path from the α phase to the high-temperature bcc γ phase.[14] This suggests that the nonlinearity that causes the ILMs is a manifestation of existing instabilities in the crystal structure. Furthermore, since the distortions local to ILMs are expected to be larger, the local symmetry of the ILM may reflect a future phase, effectively preparing the crystal for a phase transition. We consider this possibility more directly by examining the temperature evolution of uranium's ILM and associated lattice dynamics.

Measurements were performed using the BT-7 triple-axis spectrometer at the NIST Center for Neutron Research (NCNR). The spectrometer was operated with fixed final neutron energy of 14.7 meV. The crystal used was about 0.1 cm^3 and was grown via a strain anneal process.[18] Data were collected along the $[01\zeta]$ zone boundary, where the ILM was originally found,[6] and on the $\left[\frac{1}{2}\ \frac{1}{2}\ 0\right]$ zone boundary, which becomes equivalent to the $[0\bar{1}0]$ boundary if the structure is distorted to the hexagonal symmetry (see inset in Fig. 1). Both regions were measured at temperatures ranging from 286 to 675 K, covering the temperature where the ILM was first observed[6] and extending to higher temperatures.

Figure 2(a) shows the temperature evolution of the modes located on the $[01\zeta]$ zone boundary and polarized along the [010] direction, a normal mode at around 11 meV, and the ILM that forms at 505 K near 14 meV.[6] At higher temperatures, the normal mode near 11 meV, which softens suddenly as the ILM forms, continues to soften with increasing tem-

perature to 675 K. The data also suggest that the ILM may broaden as the temperature is increased up to 575 K, but further experiments will be needed to confirm this. A clearer observation is that by 675 K, the ILM is no longer visible. This observation is surprising since many of the anomalies that develop with the ILM persist to higher temperatures, including the excess in the heat capacity,[6] an enhancement of thermal conductivity,[10] and the increased anisotropy in the thermal expansion[15] (Fig. 1). Furthermore, as indicated in Fig. 2(b), the loss of intensity in the longitudinal optic mode along [001] that coincides with the ILM formation[6] also appears to persist. The effect manifests as a large loss of intensity at high energies in the measured phonon density of states,[6] which does not reform at higher temperatures (up to 913 K in Ref. 5). On the other hand, mechanical deformation does show an additional change around 600 K (Ref. 8); the loss of deformability incurred as the ILMs form just above 450 K subsides near 600 K. These changes in deformability are also matched by changes in the electronic work function from the [001] surface of α-U crystals.[19] Compared to the other indicators, however, mechanical deformation and single-crystal work function are expected to be particularly sensitive to the crystallographic orientation of the ILMs, indicating the possibility that the ILMs do not disappear at high temperatures but rather change orientation.

Given that the average structure is moving toward hexagonal symmetry (Fig. 1), the hexagonally equivalent $[\frac{1}{2}\ \frac{1}{2}\ 0]$ zone boundary seems the most likely destination for a reoriented ILM. Figure 2(c) shows the temperature evolution of the modes on this boundary that are polarized along [110]. In contrast to the [010] boundary, only the normal phonon appears, and it shows no significant temperature dependence on heating from room temperature to 600 K. It does, however, show a sudden softening between 600 and 675 K, the temperature range where the ILM on the [010] boundary disappeared [Fig. 2(a)]. Thus, above 600 K, the zone-boundary softening appears on all the boundaries in the crystallographic a-b plane, intensity loss persists in the [001] LO mode, and yet the ILM excitation is not found. For clarity, all these anomalies are mapped onto the Brillouin zone, as viewed down the c axis in Fig. 3.

These puzzling observations might be understood in terms of ILM orientational hopping, where an ILM is able to move between "equivalent" polarizations. This effect was observed in molecular dynamic simulations of ILMs in cubic ionic crystals, where they hop between equivalent [111] polarizations.[16] For α-U, however, equivalent orientations only exist if the local symmetry is somehow increased by the presence of the ILM. The temperature dependence of the lattice parameters shown in Fig. 1 indicates that the average structure is moving toward hexagonal symmetry. Furthermore, the drive toward higher symmetry is precipitated by the formation of the ILM, suggesting that the local change may be larger. Assuming nearly hexagonal local symmetry, we can understand the sequence of events with the following picture. First, the ILM becomes thermally activated above 450 K, introducing a new mode, redistributing phonon intensity, and softening the mode just below the ILM. Next, as the structure moves toward hexagonal symmetry, somewhere between 600 and 675 K, the ILM begins to rotate among the

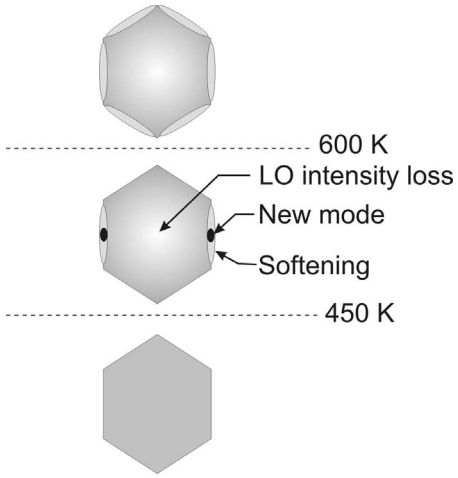

FIG. 3. Simplified schematic of the three stages in the temperature evolution of anomalies in the lattice dynamics of α-U as viewed down the c axis, projected onto the first Brillouin zone.

nearly equivalent orientations. This has the effect of smearing out the intensity of the mode in reciprocal space and introducing lifetime broadening but maintains the redistribution of phonon intensity from the LO mode to the ILM, consistent with the observations [Fig. 2(c)]. Also, it causes a softening all around the regions where the ILM rotates, giving the sixfold softening at the boundaries depicted in Fig. 3. Third, since the ILM persists above 600 K in this picture, it naturally follows that the anomalies in the thermodynamic properties also persist. Finally, orientational-sensitive measures, such as mechanical deformation and single-crystal work function, do show changes above 600 K.[8,19]

This interpretation supports the idea that the ILM is a precursor to a phase transition. The trend toward hexagonal local symmetry in the vicinity of the ILM provides a path towards the hexagonal phase observed in thin films[17] and also toward the high-temperature γ phase (bcc) (since hexagonal is intermediate between the α phase and γ phase[14]). As a lattice dynamical transition mechanism, this reverses many of the notions associated with the conventional soft-mode mechanism. A soft mode develops in a high-temperature phase as it is cooled and ultimately breaks the symmetry resulting in a lower symmetry, lower energy phase. By contrast, the ILM in uranium develops in the low-temperature phase, is stabilized by configurational entropy with increasing temperature,[2,6] and foreshadows higher symmetry, higher entropy phases. The introduction of random local states dispersed within the crystal is more reminiscent of the pseudobinary solid-state solution model developed by Aptekaŕ and Ponyatovskii,[20] and likely has similar thermodynamic implications. The Aptekaŕ-Ponyatovskii model, however, assumes a substitutional solid solution where the components are atoms with different electronic configurations. Intrinsically localized modes, which simply follow from nonlinearity and periodic discreteness,[1–4] have a much broader range of applicability. A more closely related model is that proposed for relaxor ferroelectrics by Bussmann-Holder *et al.*,[21] where ILMs are coupled to the soft matrix producing an intrinsic inhomogeneity and explaining the re-

laxor ferroelectric behavior. In this model, however, there is a direct coupling to long-range elastic properties, whereas the ILMs in uranium produce no anomalies in the elastic properties.[6] This difference is likely related to the origins of ILMs; in the ferroelectric case, the ILM forms via a soft nonlinearity where the ILM drops down from an optic branch toward an acoustic branch,[21] whereas in uranium, the ILM forms above the upper optic branch and only affects the optic modes.[6] Nevertheless, these two phenomena likely belong to the same class in that both involve dynamic nonlinear localization precipitating a phase transition.

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