Intrinsic nature of thermally activated dynamical modes in α-U: Nonequilibrium mode creation by x-ray and neutron scattering

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Inelastic x-ray and neutron scattering were used to measure two matching lattice excitations on the $[01\zeta]$ zone boundary in α-uranium. The excitations have the same polarization and reciprocal-space structure, but one has energy consistent with the thermal activation energy of the other, indicating that it creates the mode. The implied mechanism, where a mode is created by an amplitude fluctuation that mirrors the mode itself, is consistent with an intrinsically localized mode (ILM), and this is supported by thermodynamic data. The reciprocal-space structure, however, indicates a mode that is extended along its polarization direction, [010], and yet fully localized along a perpendicular direction, [001]. An enhancement of the thermal but not electrical conductivity with mode activation also suggests that these modes are more mobile than conventional ILMs. The behavior is, however, qualitatively similar to that predicted for ILMs on two-dimensional hexagonal lattices, where in-plane localization has been shown to be extended over more than ten discrete units, and the modes can be highly mobile.

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I. INTRODUCTION

In anharmonic crystals, nonlinear forces cause the frequencies of vibrating atoms to depend on amplitude. As a consequence, a large-amplitude local fluctuation can develop a frequency that does not resonate with the normal modes, causing energy to become trapped in an intrinsically localized mode (ILM)—also called "discrete breather" or "lattice soliton."[1–4] As temperature is increased, entropy is expected to stabilize increased concentrations of these random hotspots.[2] This mechanism has been observed in analogous systems on a larger scale,[5–10] but unambiguous sightings in atomic lattice vibrations, where quantum mechanics may play a role,[11,12] have proved difficult.[13–16] A major challenge has been separating ILMs from modes associated with defects.[17] In uranium, for example, random localized vibrations were reported to form above 450 K and manifest as an excess in the heat capacity.[16] This excess was attributed to ILMs and used to estimate that a fraction $c \approx 0.077$ of the lattice is occupied by these modes at 850 K.[16] An activation free energy $\Delta F_a \approx 180$ meV follows from the standard expression, $\Delta F_a = -k_B T \ln(c)$. This activation process, however, applies equally well to ILMs or to structural point defects, which can also lead to localized vibrations.[17] The distinction is further complicated by the fact that simulations of ILMs in realistic solids show that they are also accompanied by local structural distortions.[18] In this paper we address the "intrinsic" problem experimentally by noting that, unlike with structural defects, the atomic movement that forms these nonlinear modes is itself a vibration possessing the same polarization and spatial form as the mode vibrational quanta, only with an energy equal to the activation energy. We use x-ray and neutron scattering to induce mode-forming amplitude fluctuations in uranium at low temperatures, aiming to create nonequilibrium nonlinear modes. The creation excitation is then matched to the activation energy and structure of the vibrational quanta of the thermally activated mode. The results suggest an alternative way to identify ILMs and related nonlinear-lattice modes in materials.

II. SCATTERING EXPERIMENTS AND RESULTS

Inelastic x-ray scattering measurements were performed at energies near the local-mode activation energy (≈ 180 meV) on an α-uranium single crystal at room temperature using the 3IDC-C spectrometer at the Advanced Photon Source of Argonne National Laboratory with an incident x-ray energy of 21.657 keV. As shown in Fig. 1(a), a well-defined inelastic response is observed at 160.3 meV when the scattering vector is set to $\boldsymbol{Q}=(0,3,0.8)$ on the $[0,1,\zeta]$ zone boundary, but no response was detected at $\boldsymbol{Q}=(0,2.12,0.56)$ within the zone. Similar null results were found for $\boldsymbol{Q}=(0,2.41,0.64)$ and $\boldsymbol{Q}=(0,2.71,0.72)$ within the zone. These $\boldsymbol{Q}$ positions, folded into the first Brillouin zone, are indicated by diamond symbols in Fig. 1(c) and show that this 160.3-meV excitation is confined near the $[0,1,\zeta]$ zone boundary. Interestingly, the 14.3-meV mode that forms at high temperatures occurs at the same $\boldsymbol{Q}$ point [Fig. 1(b)] and was also found to be confined along this zone boundary, sitting near the top of the upper phonon branch.[16] Using the BT-7 triple-axis spectrometer at the NIST Center for Neutron Research, we measured two more temperatures [Fig. 1(b)] and also found that the excitation extends along the boundary with no energy change (dispersionless). This last detail is indicated with a shaded line along the zone boundary in Fig. 1(c). The dominant direction of $\boldsymbol{Q}$ for both of these excitations indicates that they are polarized largely along the [010] direction. Confinement along the zone boundary shows that

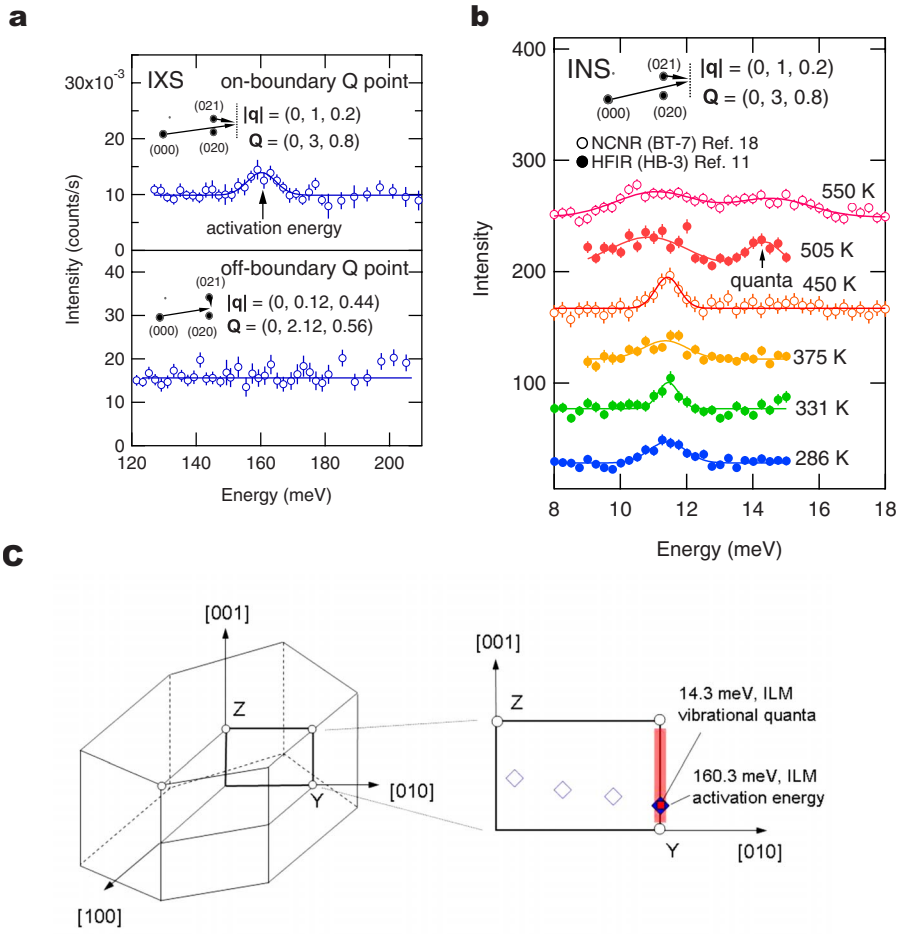

FIG. 1. (Color online) Two excitations on the $[01\zeta]$ zone boundary. (a) High-energy scattering measured on a cold (room temperature) crystal using inelastic x-ray scattering (IXS), both on and off the zone boundary. (b) Low-energy scattering showing the vibrational excitation observed forming at high temperatures using inelastic neutron scattering (INS); signals are offset for clarity and colors are to emphasize temperature. The scattering vector, $\boldsymbol{Q}$, is in the **b**-**c** plane. 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. (c) Locations of the measured $\boldsymbol{Q}$ points folded into the first Brillioun zone. Open diamond symbols within the zone indicate null high-energy results (see text), while the solid symbols indicate where signals were found. The square indicates where the thermally activated mode was found, and the shaded line (red) indicates the extension of this excitation on the $[01\zeta]$ zone boundary, which was found to be dispersionless along this boundary.

they are excited most effectively when $1/|\boldsymbol{Q}|$ (wavelength) matches a multiple of the atomic spacing, and it indicates a mode with atoms beating against each other, out of phase. This closely matching reciprocal-space structure indicates a direct relationship between these excitations. The fact that the 160.3 meV excitation energy is also consistent with the activation-energy scale of the process that produced the 14.3 meV mode provides strong evidence that the former creates the latter. The intensity of the 160.3 meV excitation is also consistent with the vibrational mechanism of nonlinear-mode creation. When corrected for width, it is a little more than an order of magnitude weaker than a 12-meV phonon in uranium, as expected since intensity for vibrations is inversely proportional to energy.[19] To definitively eliminate all possible electronic origins, however, we now turn to neutron scattering, a probe that does not interact with charge.

Inelastic neutron-scattering measurements were performed on polycrystalline uranium at room temperature using 250-meV incident-energy neutrons on the PHAROS time-of-flight spectrometer at the Los Alamos Neutron Science Center. Figure 2 shows the data summed over both high- and low-momentum transfers. Centered at zero energy is the elastic peak, negative energies indicate neutron energy gain, and positive energies indicate neutron energy loss. At high-momentum transfers a weak excitation at the expected energy of ~160 meV appears in the neutron energy-loss side, indicating that this energy is being deposited in the crystal. The feature is much harder to detect at low-momentum transfers. This is consistent with the behavior of lattice excitations, which scale as the square of momentum transfer Q^2, while magnetic excitations are cut off at high values of Q because of a form factor.[19] For uranium in particular, the magnetic-form-factor cutoff is around 1 Å^{-1}, so the observation above 9.5 Å^{-1} clearly rules out a magnetic origin,[20] leaving only lattice dynamics. Neutron detection of this feature alone might be dismissed as a hydrogen-impurity mode, as hydrogen has a large cross section and can produce vibrations in this energy range. However, observation of the

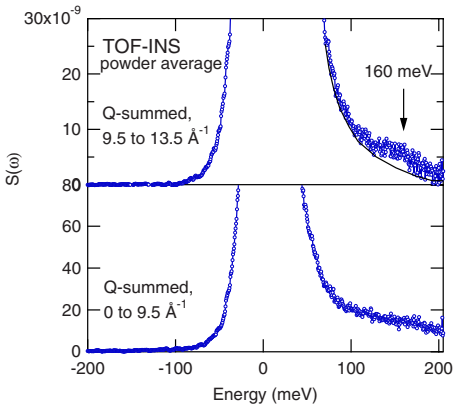

FIG. 2. (Color online) Time-of-flight (TOF) inelastic neutron scattering (INS) spectra collected using 250-meV incident-energy neutrons on polycrystalline uranium at room temperature. The top panel shows the data summed over the highest-momentum transfers (Q), while the lower panel shows the data summed over the lower values of Q.

same energy excitation in the inelastic x-ray scattering data [Fig. 1(a)] rules out this possibility; hydrogen is essentially invisible to x rays when compared to uranium. We therefore conclude that this excitation is a lattice dynamical feature of uranium with an energy a full order of magnitude higher than the highest phonon excitation. This energy cannot be explained in terms of conventional lattice dynamics, but it is consistent with the energy of forming the high-temperature mode. This, combined with the matching reciprocal-space structure, leads us to conclude that we are observing the formation mechanism of a nonlinear mode. It follows that 160.3 meV is the activation energy while 14.3 meV is the vibrational quanta energy of the thermally activated mode.

III. DISCUSSION

This mechanism, where a mode is created by an amplitude fluctuation that mirrors the mode itself, is consistent with the formation mechanism of an ILM[1–4] The confinement of the mode to a zone boundary in reciprocal space, however, indicates that it is not well localized in real space along the direction perpendicular to the boundary (direction atoms are displaced by mode). On the other hand, the lack of any change in the excitation intensity or energy along the [001] direction on the boundary [Fig. 1(c)] indicates that the mode is well localized along this perpendicular direction. Taken together these observations indicate a mode that is low dimensional and collapsed in the "basal" plane in real space.

The bulk properties of uranium also indicate similarities and differences with conventional ILM behavior. An excess heat capacity associated with the formation of these modes, reported in Ref. 16 and reproduced in Fig. 3(a), is consistent with the classic picture of an ILM,[2] where a random distribution of local states introduces configurational entropy (vibrational entropy is ruled out in this analysis[16]). The temperature dependence of the lattice parameters above the mode-activation temperature indicates a developing contraction along the mode polarization direction (b axis) and corresponding enhanced expansions in the orthogonal directions [Fig. 3(b)]. In classical simulations of ILMs in ionic crystals, local structural relaxations manifest in the same way; the lattice contracts along the mode polarization direction and expands in the orthogonal direction.[18] Transport properties, on the other hand, appear to contradict the classic ILM picture. A well-localized mode is not expected to move very easily through the lattice but rather acts as a scattering center for conduction electrons. With mode activation in uranium, however, it is just the opposite: there is an anomalous rise in the thermal conductivity [Fig. 3(c)] and yet no obvious effect on electrical resistivity [Fig. 3(d)].[22]

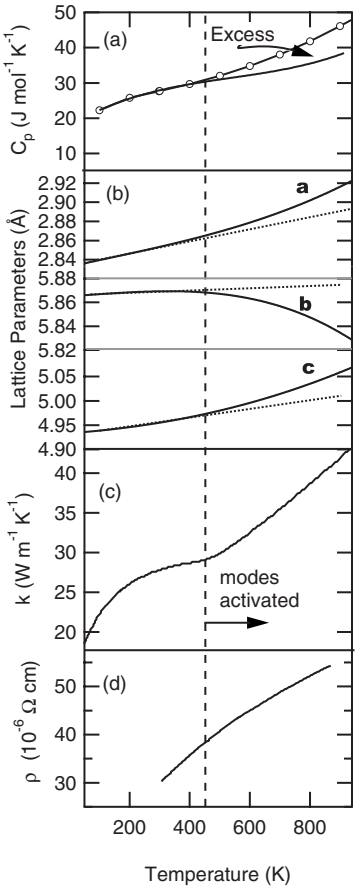

FIG. 3. Data from the literature on the temperature-dependent physical properties of uranium, with the mode-activation temperature [~450 K (Ref. 16)] indicated by a vertical dashed line. (a) Heat capacity from measurement (open circles) and calculation (line) indicating an excess above the mode-formation temperature (after Manley *et al.* Ref. 16). (b) Lattice parameters calculated from polynomial fits to dilatometry data by Loyd and Barrett (Ref. 21). (c) Thermal conductivity, k, and (d) electrical resistivity, ρ, from Holden (Ref. 22).

The apparent discrepancy between the excess configurational entropy and the "delocalized" nature of the in-plane Q dependence can be understood in terms of recent calculations of more extended ILMs propagating on a two-dimensional hexagonal plane. In the theoretical work of Butt and Wattis,[23] ILMs formed on two-dimensional Fermi-Pasta-Ulam (FPU) lattice, but were only localized to about ten periodic units in the mode polarization direction. The crystallographic situa-

tion for α-uranium is similar in that the plane perpendicular to the c axis is nearly hexagonal and becomes more so as the new mode develops.[24] A mode this spread out in real space could produce intensity localized in reciprocal space to about 1/10 of a reciprocal-lattice vector in the mode polarization direction, and the two-dimensionality would give no Q dependence in the perpendicular direction ("c axis"). This in-plane Q dependence is sharper than the Q resolution in the inelastic neutron-scattering measurements, and therefore cannot be confirmed from the Q scans alone. However, the size of the mode does have further implications: the number of the density of modes is not expected to exceed a concentration where all the modes overlap. For a mode that covers $10\times3\times1$ atoms, for example, the basal planes become saturated with modes when the concentration reaches $\sim$3.3%. From the thermodynamic assessment of the heat capacity of uranium, 7.7% was predicted at 800 K (Ref. 16) and using the same data, about 3.3% is expected around 650 K. Interestingly, recent high-temperature studies of the mode in uranium shows that it actually disappears just above 650 K.[24] It was argued that the loss of the mode was associated with orientation hopping on a nearly hexagonal-lattice plane,[24] but mode-mode interactions could also play a role at these temperatures. Thus, taking a saturation limit at 3.3% we estimate a size for the mode, about 30 atoms, which is similar to the ILMs on hexagonal FPU lattices.[23] Hence the idea of a "large" ILM resolves the contradiction between the existence of excess configurational entropy and the sharp Q dependence, at least up to 650 K. At temperatures above 650 K a more complex situation likely persists. Most of the physical property anomalies that are initiated with mode activation continue with increasing temperature, as shown Fig. 3 and discussed in Ref. 24.

The pronounced enhancement of the thermal but not electrical conductivity with mode formation [Figs. 3(c) and 3(d)] is surprising. The larger-sized ILMs are expected to be mobile[23] and therefore contribute to thermal conductivity. However, at these high temperatures normal phonon conduction is usually small compared to electronic thermal conduction because of the relatively short mean-free paths of the phonons. Normally, only at low temperatures, where the thermal resistivity causing umklapp processes become inhibited, does the phonon contribution overcome the electronic contribution in a metal.[25] One possible explanation is that the ILMs in uranium travel over large distances without losing energy. Interestingly, calculations indicate that ILMs can propagate over large distances along specific crystallographic directions at specific velocities on a two-dimensional hexagonal plane.[26] In addition, there have been speculative arguments suggesting a role for ILM in propagating energy in real materials. First, enhanced diffusion beyond an ion-irradiated region in stainless steel was attributed to the transmission of ILMs over a micron.[27] Second, it was argued that the ejection of atoms from the back side of an ion-irradiated layered muscovite crystal is caused by ILMs propagating over a macroscopic distance.[28] Alternatively, the presence of ILMs may have an indirect effect on the normal phonon conduction, perhaps by suppressing other phonon scattering channels. It is clear, for example, that certain phonons lose intensity (amplitude) when the ILMs form.[16] Either way, the implications for thermal transport are intriguing. As temperature is increased anharmonicity becomes more pronounced, resulting in an increased phonon-phonon scattering, which normally decreases thermal transport.[25] However in the case of uranium the anharmonicity seems to become strong enough to cause the phonons to coalesce into nonlinear modes, opening up a new lattice mechanism for thermal transport, and reversing the trend.

IV. CONCLUSIONS

A nonlinear-lattice dynamical mode in uranium has been created by inducing an amplitude fluctuation that mirrors the mode itself, providing direct evidence of its intrinsic nature. An assessment of the modes Q dependence, temperature evolution, and related thermodynamic properties suggests that it is more extended (larger) than a conventional ILM, but similar in size and shape with more extended ILMs predicted in some recent calculations.[23] This approach of identifying nonlinear modes by creating them with high-energy scattering suggests an alternative way to look for ILMs. It could be applied to many diverse areas of science where evidence for ILM formation has been indicated experimentally or theoretically, including complex biological materials,[14] ionic crystals,[18] covalent crystals,[29] quantum solids,[15] as well as other metals. Unlike with ILM vibrational quanta excitations above bands[2] or in gaps,[18] which could be mistaken for defect modes or lost within multiphonon excitations, the nonequilibrium-mode-creation energy is well outside that of conventional lattice dynamical processes. As a result, it can be detected in polycrystalline or powder materials. Furthermore, because mode creation occurs out of equilibrium, there is no need to know what temperature ILMs become thermally activated. Even in cases where the activation energy is too high for ILMs to be practically observed below the melting temperature, nonequilibrium-mode-creation experiments may still be possible.

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