Phonon dispersion in uranium measured using inelastic x-ray scattering

M. E. Manley,[1] G. H. Lander,[1,2] H. Sinn,[3] A. Alatas,[3] W. L. Hults,[1] R. J. McQueeney,[1] J. L. Smith,[1] and J. Willit[3]
[1]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545*
[2]*European Commission, JRC, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany*
[3]*Argonne National Laboratory, Argonne, Illinois 60439*
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Phonon-dispersion curves were obtained from inelastic x-ray scattering measurements on high-purity uranium single crystals at room temperature. Modes displacing atoms along $[00\zeta]$ and propagating in all three high-symmetry directions were measured. Whereas the acoustic modes agree with the neutron measurements, the longitudinal-optic branch is about 10% higher in energy, but consistent with higher cutoff energies observed in phonon density-of-states measurements on polycrystals. The application of this x-ray technique, which requires only very small samples, opens possibilities in actinide science.

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Although phonons were studied by measuring diffuse x-ray scattering patterns, most notably in Al by Walker,[1] the triple-axis neutron technique used by Brockhouse and Stewart[2,3] rapidly became the technique of choice for the measurement of phonon-dispersion curves, and has remained so for 40 years. However, despite the general interest in *f*-electron elements[4–6] details about phonon-dispersion relationships exist only for uranium.[7] This is because many isotopes have large neutron absorption cross sections and even in cases where a suitable isotope exists, crystals large enough for neutron scattering (at least 0.1 cm^3) are unavailable. Work on uranium, for example, is limited by the fact that only one large crystal has ever been produced, to our best knowledge.[6]

The development of synchrotron-based inelastic x-ray scattering (IXS) instruments[8–12] offers new hope since no special isotope requirements are required and crystals can be much smaller. In this report of a test experiment we demonstrate the potential of this technique for actinides by measuring the phonon-dispersion curves in uranium from a scattering volume of only $\sim 2\times 10^{-3}$ mm^3, or an effective mass of 40 μg.

Phonon-dispersion curve measurements performed on the uranium crystal after the first room-temperature experiments[7] were largely motivated by the discovery of several charge-density wave transitions at low temperatures.[6,13,14] More recent measurements of the phonon density of states on polycrystalline samples revealed a large harmonic softening over the entire α-phase temperature range.[15] The lack of anharmonicity implies that the interatomic potential landscape of uranium is continuously altered by electronic excitations as the temperature is raised.[15] Evidence extracted from neutron-diffraction data suggests[16] that this unusual phonon softening may occur in many of the light actinides. Moreover, the elastic constants measured on single crystals of δ-stabilized ^{239}Pu show most unusual properties, with an elastic anisotropy higher than for any other fcc material.[17] Understanding such phenomena requires measurements of the phonon-dispersion curves.

Uranium crystals were grown in the Chemical Technology Division of Argonne National Laboratory by electrotransport through a molten salt bath of a LiCl-KCl eutectic containing approximately 3 wt. % UCl_3.[18] Uranium grew on a stainless-steel cathode as dendrites shaped as parallelogram-edged platelets. The platelets were high-purity α-U (*Cmcm*) single crystals with the *c* axis of the orthorhombic structure perpendicular to the platelet faces. The orientation of the crystals was determined by Laue x-ray patterns. The residual resistivity ratio (RRR) of 115 was about three times higher than any RRR reported previously.[6] Because the uranium was deposited below the α-β transformation temperature, the single crystals were free of strain. However, they did contain a small amount of salt solution intercalated between platelet layers.

Crystals were oriented and mounted in a small vacuum chamber with two horizontally opposed Kapton-film windows for the incident and scattered beams. All measurements were made at room temperature on SRI-CAT at the Advanced Photon Source at the Argonne National Laboratory.[11,12] The spectrometer was operated with an incident energy of 21.657 keV ($\lambda = 0.57$ Å). This energy was chosen to give the maximum flux with a resolution of ~ 2 meV,[12] but has the unfortunate consequence that it is just 700-eV *above* the L_2 edge of uranium at 20.95 keV. The calculated low penetration depth of ~ 6 μm and accompanying large fluorescence initially suggested that the experiment would not succeed, or at least be very difficult, and indeed the calculation shown in Fig. 5 of Ref. 12 is equally pessimistic. It shows that the phonon signal for actinide ($Z > 90$) elements will be between one and two orders-of-magnitude smaller than for light ($Z < 20$) elements. The beam dimensions of 0.3×0.3 mm^2 (modified by $1/\sin\theta$, where θ is the scattering angle, for the footprint) multiplied by the penetration depth gives the effective scattering volume. Since the crystal thickness was ~ 1 mm, far larger than the penetration depth, all measurements had to be performed in reflection. In reflection the momentum-transfer vector **Q** is essentially perpendicular to the crystal surface and thus along the *c* axis. Measurements were therefore restricted to phonons that displace atoms along $[00\zeta]$. This is the most significant disadvantage of the x-ray method on heavy elements when compared to the traditional neutron method, which can operate in transmission. If the absorption is considerably less, as it is in the case of a recent study of

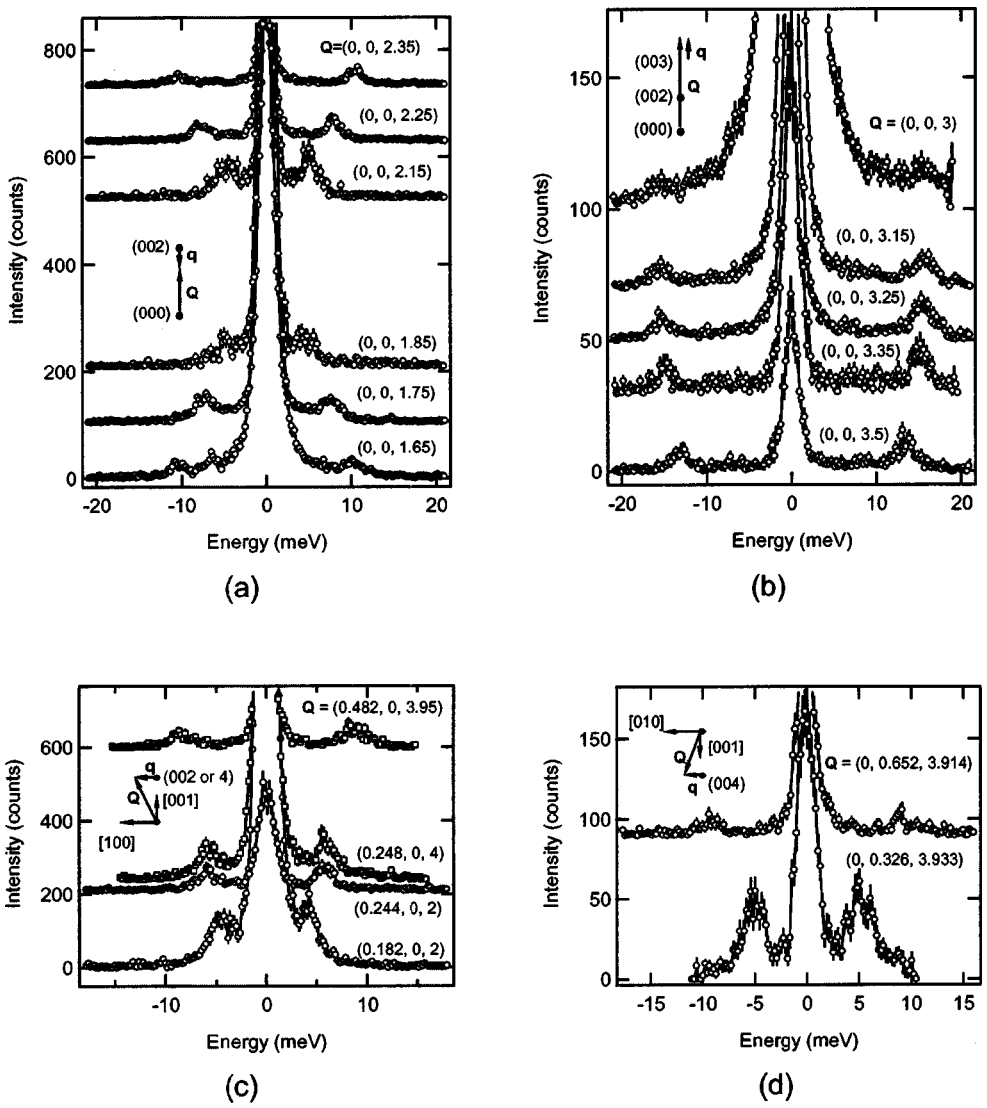

FIG. 1. Raw data counted 60 sec per point, with the data offset for clarity. Frames (a) and (b) show longitudinal modes and (c) and (d) show transverse modes. The geometry in reciprocal space is shown as an inset in each frame. The scattering vector **Q** is on the *c* axis for the longitudinal modes and is tilted slightly off axis (in either [100] or [010]) near a reciprocal-lattice point to obtain transverse modes. The phonon wave vector **q** conserves momentum according to $\mathbf{Q}=\mathbf{G}+\mathbf{q}$, where **G** is a reciprocal-lattice vector pointing to the nearest reciprocal-lattice point. The strong elastic signal in these scans most probably comes from the small amount of salt solution that remains between the crystal grains. The large signal near (003) certainly arises from multiple scattering at this (forbidden) reflection.

$CeRu_2Si_2$,[19] then a thin slice (in that case, of 100 μm) can be prepared to still allow transmission experiments. Rocking-curve measurements revealed that the (002) peak was split by about 0.5° owing to low-angle twinning visible as linear 1-mm-thick streaks across the shiny surface of the crystals.

Figure 1 shows the phonon peak intensities measured in both longitudinal and transverse geometries around (002), (003), and (004). The energy gain and loss symmetry combined with the symmetry across the (002) zone center shown in Fig. 1(a) is reassuring. Despite the small scattering volume the scattering intensities (up to 60 counts/mm) were strong and in most cases the background was negligible. Some spurious scattering can be seen near -7 meV at (0, 0, 1.65) but this appears to decrease with increasing **Q**. As expected, the phonon intensities increase with **Q**, but will do so less dramatically than in the neutron case since the scattering factor falls with **Q**. The phonon-dispersion curves as measured by the two techniques are shown in Fig. 2. The acoustic branches agree with the fit to the neutron results from Crummett *et al.*,[7] but the longitudinal-optic branch frequencies appear to be about 10% higher than those of the neutron measurements.

As far as the frequencies are concerned, the IXS and neutron techniques should give the same information. Whereas the differences in Fig. 2 between the IXS and neutron-scattering investigation are small, we believe they are significant. First, there are arguments connected with the experiments themselves. A general scaling of the IXS energies does not make the agreement better, and, as shown in Fig. 1, both energy gain and loss agree to better than 5%. Recently, a study was done of the phonons in Be on the same instrument

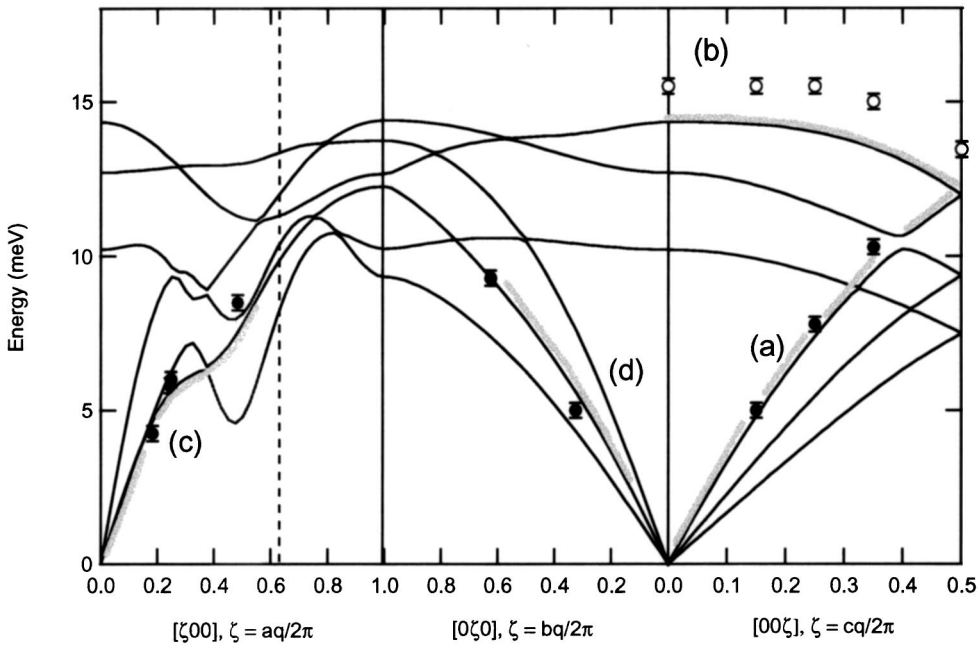

FIG. 2. The solid lines are phonon-dispersion curves as determined from a force-constant model fit of neutron data in Ref. 7, and they well reproduce the neutron data. The points are from the present IXS experiment [labels correspond to Figs. 1(a)–1(d)]. The gray lines indicate the phonon branches selected by the scattering geometries in our experiment. Unlike our data the longitudinal-optic $[00\zeta]$ modes from the neutron data (Ref. 7) fall on the line of the model.

and the agreement between neutron and IXS frequencies was ''better than 2%.'' [11,20] Given the experience of the team at Oak Ridge National Laboratory it seems unlikely the neutrons are in error, and it is significant that the highest phonon measured from the older crystal along this direction was at 12.2 meV. In fact there is only one phonon branch in this older work extending to 15 meV (at the Γ_5 position), whereas the more recent density of states[15] shows significant weight of the phonons at 15 meV and even above. These arguments suggest that the differences may be due to sample issues. The older samples are known to contain both Si and Fe impurities, and their superconducting temperature is ~0.4 K, whereas the newer samples superconduct at almost 0.8 K.[21] Without an electronic perturbation, however, this cannot explain a frequency decrease since light impurity perturbations tend to increase frequencies.[22] The presence of structural defects may also contribute, although it is not easy to attribute the whole effect to structural defects either, since it requires too high a concentration.[22] Similarly, suggestions that the small penetration depth (a few microns) of the IXS technique could result in anomalous results seem unlikely. The crystals were kept in vacuum to avoid an oxide overlayer forming and remained shiny throughout the experiment. With a clean surface we probed about 20 000 monolayers (6 μm), a bulk quantity. We were unable to fully account for this difference, but it should be born in mind that the phonon energies in uranium can shift 10% with as little as 133 K of heating.[15] This effect has been attributed to electronic effects and suggests the considerable sensitivity of the uranium phonons to electronic perturbations.

In conclusion our test experiment has been a considerable success. Phonon count rates of ~1 counts/s were obtained from an equivalent scattering mass of ~40 μg of a heavy element. This opens the way to a number of experiments such as phonons as a function of temperature (and pressure) and, twenty-five years after the elastic-constant measurements,[17] the possibility of measuring the phonons in plutonium. These are now being planned.

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[1] C. B. Walker, Phys. Rev. **103**, 547 (1956).
[2] B. N. Brockhouse and A. T. Stewart, Phys. Rev. **100**, 756 (1955).
[3] B. N. Brockhouse, in *Inelastic Neutron Scattering in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 113.
[4] *Los Alamos Science, Challenges in Plutonium Science*, edited by N. G. Cooper (Los Alamos National Laboratory, Los Alamos, NM, 2000), Number 26, Vol. I.
[5] E. Holland-Moritz and G. H. Lander, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr., L. Eyring, G. H. Lander, and G. R. Choppin (Elsevier Science, New York, 1994), Vol. 19, Chap. 130.
[6] G. H. Lander, E. S. Fisher, and S. D. Bader, Adv. Phys. **43**, 1 (1994).
[7] W. P. Crummett, H. G. Smith, R. M. Nicklow, and N. Wakabayashi, Phys. Rev. B **19**, 6028 (1979).
[8] E. Burkel, Rep. Prog. Phys. **63**, 171 (2000).
[9] F. Occelli, M. Krisch, P. Loubeyre, F. Sette, R. Le Toullec, C.

Masciovecchio, and J. P. Rueff, Phys. Rev. B **63**, 224306 (2001).
[10] M. d'Astuto, P. K. Mang, P. Giura, A. Shukla, P. Ghigna, A. Mirone, M. Braden, M. Greven, M. Krisch, and F. Sette, Phys. Rev. Lett. **88**, 167002 (2002).
[11] H. Sinn, E. E. Alp, A. Alatas, J. Barraza, G. Bortel, E. Burkel, D. Shu, W. Sturhahn, J. P. Sutter, T. S. Toellner, and J. Zhao, Nucl. Instrum. Methods Phys. Res. A **467**, 1545 (2001).
[12] H. Sinn, J. Phys.: Condens. Matter **13**, 7525 (2001).
[13] H. G. Smith, N. Wakabayashi, W. P. Crummett, R. R. Nicklow, G. H. Lander, and E. S. Fisher, Phys. Rev. Lett. **44**, 1612 (1980).
[14] J. C. Marmeggi and A. Delapalme, Physica B & C **102**, 309 (1980).
[15] M. E. Manley, B. Fultz, R. J. McQueeney, C. M. Brown, W. L. Hults, J. L. Smith, D. J. Thoma, R. Osborn, and J. L. Robertson, Phys. Rev. Lett. **86**, 3076 (2001).
[16] A. C. Lawson, B. Martinez, J. A. Roberts, B. I. Bennett, and J. W. Richardson, Jr., Philos. Mag. B **80**, 53 (2000).
[17] H. M. Ledbetter and R. L. Moment, Acta Metall. **24**, 891 (1976).
[18] C. C. McPheeters, E. C. Gay, P. J. Karell, and J. P. Ackerman, JOM **49**, 7 (1997).
[19] S. Raymond, J. P. Rueff, S. M. Shapiro, P. Wochner, F. Sette, and P. Lejay, Solid State Commun. **118**, 474 (2001).
[20] A. Alatas, Ph.D. thesis, Illinois Institute of Technology, 2002.
[21] J. C. Lashley, B. E. Lang, J. Boerio-Goates, B. F. Woodfield, G. M. Schmiedeshoff, E. C. Gay, C. C. McPheeters, D. J. Thoma, W. L. Hults, J. C. Cooley, R. J. Hanrahan, and J. L. Smith, Phys. Rev. B **63**, 224510 (2001).
[22] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation, in Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic New York, 1963), p. 129.