

**Measurement of the phonon density of states of PuO<sub>2</sub>(+2% Ga): A critical test of theory**M. E. Manley,<sup>1</sup> J. R. Jeffries,<sup>1</sup> A. H. Said,<sup>2</sup> C. A. Marianetti,<sup>3</sup> H. Cynn,<sup>1</sup> B. M. Leu,<sup>2</sup> and M. A. Wall<sup>1</sup><sup>1</sup>*Lawrence Livermore National Laboratory, Livermore, California 94550, USA*<sup>2</sup>*Argonne National Laboratory, Argonne, Illinois 60439, USA*<sup>3</sup>*Department of Applied Physics, Columbia University, New York, New York 10027, USA*

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Using inelastic x-ray scattering, we determine the phonon density of states of PuO<sub>2</sub> (+2% Ga) and compare results with recent predictions made using density functional theory (DFT), DFT plus the Hubbard U (DFT + U), and dynamical mean-field theory. The DFT prediction underestimates the measured energies of most features. The DFT + U prediction accurately reflects the low-energy features but incorrectly splits off an isolated high-energy oxygen mode. Ramifications for predictions of thermodynamic and transport properties of this nuclear fuel material are discussed.

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Plutonium dioxide (PuO<sub>2</sub>) has been a subject of intense interest in recent years owing to its use in mixed-oxide nuclear fuels and for the theoretical challenges posed by its *5f* electrons, which inhibit development of predictive capabilities for its use and storage. Because of difficulties in preparing and handling PuO<sub>2</sub>, much of the theoretical work has proceeded without rigorous experimental testing. In particular, the lattice vibrations, which are critical for understanding phase stability<sup>1</sup> and thermal transport,<sup>2</sup> are known only through predictions made using various theoretical approaches including density functional theory (DFT),<sup>3</sup> DFT plus the Hubbard U (DFT + U),<sup>4</sup> and dynamical mean-field theory (DMFT).<sup>5</sup> However, DFT is known to incorrectly describe PuO<sub>2</sub> as a ferromagnetic conductor<sup>6</sup> when it is actually an insulator,<sup>7</sup> and DFT + U obtains an insulator but incorrectly obtains an antiferromagnetic ground state.<sup>8–11</sup> Furthermore, neither the DFT nor the DFT + U calculations include spin-orbit coupling, which has been shown to be a strong perturbation on the electronic structure,<sup>12</sup> although it is unclear how relevant this is to the phonons. The DMFT calculation by Yin and Savrasov<sup>5</sup> includes spin-orbit coupling but is performed with the Hubbard-I approach, which should be well suited to PuO<sub>2</sub> but is still an approximation. Here, we use high-resolution inelastic x-ray scattering (IXS) at a synchrotron source to measure the phonon density of states (DOS) of PuO<sub>2</sub> (+2% Ga). We find that the limitations of these predictions also manifest as differences between theoretical and experimental phonons. Ramifications of these errors on predictions made of the thermal conductivity and phase stability are also discussed.

Measuring the phonons of plutonium-bearing materials is challenging because neutron scattering, the standard approach, requires large quantities of special isotopes with low neutron-absorption cross sections. Here, we avoid this constraint by using high-resolution IXS with the HERIX instrument at the Advanced Photon Source at Argonne National Laboratory;<sup>13–15</sup> this IXS technique has proven effective for measuring phonon dispersions in actinides<sup>16,17</sup> and the phonon DOS of plutonium.<sup>18</sup> To obtain an accurate representation of the phonon DOS from IXS on a powder sample, it is necessary to measure over a large range of momentum transfers (*Q*) so as to cover several Brillouin zones. Partial averages using a

limited number of *Q* points<sup>19</sup> have been shown with neutron scattering to lead to errors in the evaluation of thermodynamic quantities.<sup>20</sup> Using a 23.8-keV x-ray beam with nine equally spaced analyzers positioned at a series of overlapping angles, a complete *Q* range from 2 to 7 Å<sup>-1</sup> was measured. Since, for PuO<sub>2</sub> (+2% Ga), a reciprocal unit length is  $a^* = 1.16 \text{ \AA}^{-1}$ , the measured range provides a good reciprocal space average. The detector signals were each normalized by the detector efficiency, corrected for the x-ray form factors  $f^2(Q)$  (for this part, the Pu and O modes were treated as separable in the spectrum, which is justified according to partial phonon DOS calculations<sup>4</sup>) and the  $(\cos 2\theta)^2$  term, and then the spectra were summed over *Q*. A phonon DOS was extracted from the reduced spectra by subtracting the elastic peak and the incoherent multiphonon scattering, which was determined iteratively<sup>21–23</sup> and dividing out the thermal occupation and Debye-Waller factors. X-ray diffraction patterns collected *in situ* revealed that 10% unreacted metallic  $\delta$ -Pu was contained within the scattering volume. Since the phonon DOS of  $\delta$ -Pu resides at lower energies than PuO<sub>2</sub>, the presence is also evident in the inelastic spectra, which is corrected using spectra measured on the metal with the same Ga concentration ( $\delta$ -Pu + 2% Ga) using the same instrument.<sup>18</sup> The size of the correction needed in the phonon DOS independently confirmed that the unreacted material in the beam occupied a 10% volume fraction. However, the need for the correction introduces uncertainty in the low-energy sloping part of the oxide phonon DOS, which retained artifacts (slight wiggles) not expected at these low energies [see Fig. 1(a) at energies below ~10 meV].

Figure 1 compares the measured phonon DOS, Fig. 1(a), with several theoretical phonon DOS, Fig. 1(b), and theoretical phonon dispersion curves, Fig. 1(c). At low energies, the transverse acoustic (TA) peak in the DOS, measured at 13.8 meV, is fairly well matched by all three predictions. However, the longitudinal acoustic (LA) peak, measured at 22.8 meV, is significantly higher in energy than the 19.5-meV prediction by Minamoto *et al.* using DFT.<sup>3</sup> The inclusion of the Hubbard U (DFT + U) by Zhang *et al.*<sup>4</sup> appears to correct for this shortcoming, increasing the energy of the LA mode putting it in good agreement with measurement, Figs. 1(a) and 1(b). The DMFT prediction by Yin *et al.*<sup>5</sup> also correctly stiffens

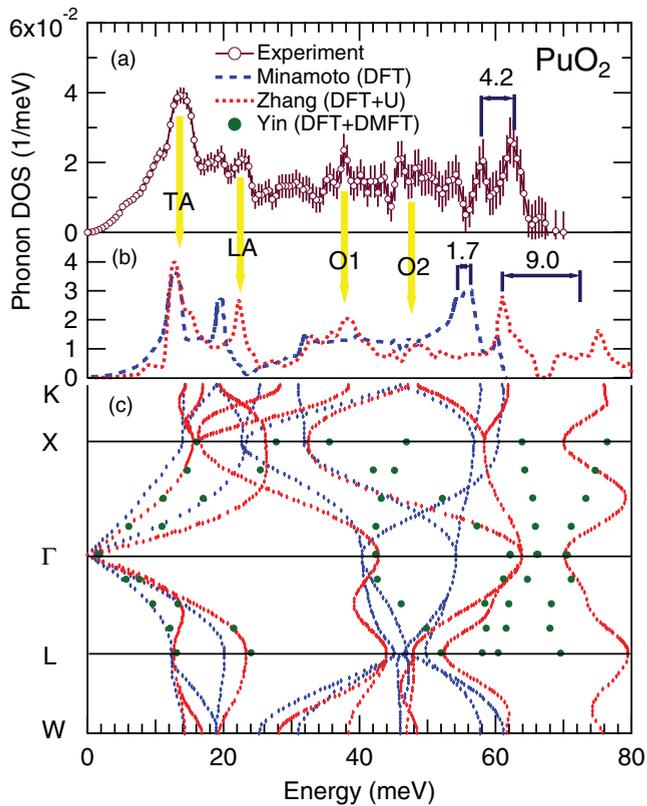


FIG. 1. (Color online) Comparison of experimental and theoretical phonons: (a) experimental phonon DOS determined by inelastic x-ray scattering in this Brief Report; (b) theoretical phonon DOS determined using DFT by Minamoto *et al.*<sup>3</sup> (blue dashed line) and DFT + U by Zhang *et al.*<sup>4</sup> (red dotted line); and (c) theoretical phonon dispersion curves associated with the DFT (blue) and DFT + U (red) phonon DOS above plus partial phonon dispersion curves calculated using DMFT by Yin *et al.*<sup>5</sup> (green symbols).

the LA modes to about the same level as the Zhang calculation as shown in the dispersion curves in Fig. 1(c). On the other hand, the DFT + U calculation misplaces the small feature between the TA and the LA peaks, placing it closer to the TA while the measurement shows this feature about halfway in between these peaks as does the DFT calculation. Judging from the overlap in the DMFT and DFT + U calculated dispersions in the acoustic region, Fig. 1(c), it appears that DMFT also probably misplaces the feature between the main TA and the LA peaks. It is difficult, however, to uniquely identify the origin of this feature since, in the DFT + U prediction, an optic mode drops down to this energy at the X high-symmetry point, yet for the DFT and DMFT predictions, only the split in the TA branch accounts for this feature. At midrange energies, the DFT calculation continues to underestimate the energies of the features by about 6 meV, while the DFT + U manages to accurately capture the two most significant optic features, labeled O1 and O2 in Fig. 1. The dispersion data in the DMFT prediction by Yin *et al.*<sup>5</sup> are too limited to pinpoint optic features of the phonon DOS in this range, although they are clearly different than the DFT + U result. At the highest energies (>50 meV), there is little correspondence that can be found between any of the measured and predicted

features. The measured phonon DOS shows two significant peaks separated by 4.2 meV located at 58 and 62.2 meV. The DFT and the DFT + U appear dramatically different, with the DFT showing essentially no split while the DFT + U shows a very large ~9-meV split with a gap actually opening up. The gap in the Zhang *et al.*<sup>4</sup> DFT + U calculation is attributed to a lifting of the mode degeneracy in the dispersion curves by spin and orbital orderings. A similar but smaller splitting is also apparent in the DMFT calculations;<sup>5</sup> in this case, there is only orbital order splitting. These splits/gaps can be seen in the calculated dispersion curves shown in Fig. 1(c). Comparing all results, it appears that measurement is revealing some splitting as might be expected for orbital ordering in the insulating state, but that the calculations are overestimating the amount of splitting.

In the analysis of thermal conductivity using the DMFT calculated phonons, Yin *et al.*<sup>5</sup> find that the LA mode dominates the thermal conductivity owing to its large group velocity and small anharmonicity implied by its Grüneisen constant.<sup>5</sup> Unlike the TA mode, however, which all three calculations and the experiment agree on (Fig. 1), the LA mode is not handled consistently by the calculations. The DFT calculation underestimates the experimental upper bound of the LA mode [Figs. 1(a) and 1(b)], and both DMFT and DFT predict a maximum slope (group velocity) along X that is about 1.6 times less than the DFT + U calculation [Fig. 1(c)]. A lower LA mode group velocity in the DMFT calculations might partially explain why Yin *et al.*<sup>5</sup> predict a thermal conductivity at 1000 K [ $1.74 \text{ W m}^{-1} \text{ K}^{-1}$  (Ref. 5)] that is about a factor of 2 lower than the experimental value [ $3.8 \text{ W m}^{-1} \text{ K}^{-1}$  (Ref. 24)]. However, they also underestimate the thermal conductivity in UO<sub>2</sub> by a factor of 2 (Ref. 5), even though that calculation matches the previously measured UO<sub>2</sub> phonon dispersion curves.<sup>25</sup> Furthermore, uncertainty in the phonon energies prediction suggests uncertainty in the predicted mode Grüneisen constant and its use to estimate the phonon mean-free-path (phonon-phonon scattering rate) contribution to the thermal conductivity.<sup>2</sup> Finally, although Minamoto *et al.*<sup>3</sup> and Zhang *et al.*<sup>4</sup> obtain reasonably accurate predictions of the experimental heat-capacity curve using quite different phonon DOS curves, such success does not translate to phase stability predictions where even small shifts in the phonon DOS produce vibrational entropy changes that can dramatically reshape phase diagram predictions.<sup>1</sup> Hence, there is a practical need to improve calculations of the lattice vibrations to enhance the predictive capabilities regarding phase stability and thermal transport in extreme environments not easily accessible by experiment.

High-resolution inelastic x-ray scattering measurements of the phonon DOS of PuO<sub>2</sub> (+ 2% Ga) provide critical guidance for improving theoretical predictions. Comparing our results with a series of theoretical predictions shows how adding new physics to the calculation (e.g., DFT to DFT + U or DMFT) improves on the predictive capability of electronic structure theory when applied to the lattice vibrations, but that further work is needed. Future calculations incorporating these advances will surely provide more reliable predictions of thermodynamic and transport properties of this important nuclear fuel material.

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