PHYSICAL REVIEW B **78**, 180301(R) (2008)

Lattice dynamics of Eu from nuclear inelastic scattering and first-principles calculations

Svetoslav Stankov,[1,*] Przemysław Piekarz,[2] Andrzej M. Oleś,[2] Krzysztof Parlinski,[2] and Rudolf Rüffer[1]
[1]*European Synchrotron Radiation Facility, BP220, F-38043 Grenoble, France*
[2]*Institute of Nuclear Physics, Polish Academy of Sciences, Radzikowskiego 152, PL-31342 Kraków, Poland*
(Received 22 September 2008; published 5 November 2008)

We report on combined determination of the density of phonon states of an epitaxial Eu metallic single crystal by *in situ* ^{151}Eu nuclear inelastic scattering and by first-principles phonon calculations. Thermodynamic (specific heat and vibrational entropy) and elastic (mean atomic displacement, mean force constant, and sound velocity) properties of Eu were obtained. The very good agreement between the experiment and theory indicates that in general, the lattice dynamics of the 4*f* metals can be reliably investigated by the *ab initio* approach applying the direct method.

DOI: 10.1103/PhysRevB.78.180301 PACS number(s): 63.20.−e, 71.20.Eh, 76.80.+y

Determination of the lattice dynamics of pure rare-earth metals has been a great challenge for both experimentalists and theoreticians. Until now, reliable information on the lattice dynamics of the rare-earth metals could only be scarcely found in the literature. The phonon density of states (DOS) has been experimentally obtained for La (Ref. 1) and Dy (Ref. 2), while for Ce,[3] Tb,[4] and Ho (Ref. 5) only few dispersion curves have been measured. In the theory the phonon DOS has been calculated for Gd,[6] Dy,[7] and Er (Ref. 8) from the extrapolated force constants of the neighboring Tb and Ho. A comparison with the experimental data for Dy showed that this semiempirical approach leads to unacceptably large errors.[2] An attempt for analytical study of the lattice dynamics of the hcp rare-earth metals has also been made,[9] which, however, resulted only in a poor agreement with the limited experimental data. Therefore, in order to obtain reliable and complete information on the lattice dynamics of the 4*f* elements, one either has to perform an experiment, which is always a rather demanding task, or to study the lattice dynamics by *ab initio* methods.

Ab initio electronic structure methods have already been introduced to systematically investigate the valency and the lattice parameters of the lanthanides.[10,11] On one hand, the first-principles phonon calculations using the direct method,[12] which gives the *exact* phonon frequencies at high-symmetry points, were (in the last few years) employed to study the lattice dynamics of various materials with strongly correlated electrons, including the 5*f* actinide compounds $PuCoGa_5$,[13] $UCoGa_5$,[14] and transition metals.[15] Recently it also served to resolve[16] the puzzle of the Verwey transition in Fe_3O_4. On the other hand, recent progress in nuclear inelastic scattering made it possible to verify the predictions made by the theory for complex systems. For example, a systematic experimental and theoretical investigation of the phonon DOS for iron monolayers[17] and for the Fe(110) surface[18] led to significant insights into the lattice dynamics in layered systems. Such combined experimental and theoretical studies on the 4*f* metals, however, have not been performed until now.

Europium is perhaps the most reactive element among the rare earths, which makes the experimental work with pure metal a real challenge, and requires a dedicated sample environment. Here we report on determination of the lattice dynamics of metallic Eu by nuclear inelastic scattering and by first-principles phonon calculations. The remarkable agreement between the experiment and the theory demonstrates that the *ab initio* approach based on the direct method is a reliable and powerful tool for investigation of the lattice dynamics of the 4*f* metals. This suggests that the 4*f* electrons, despite their strong local correlations and (to a large extent) localized character, may be treated by the density-functional theory (DFT) in a reliable way.

We studied a 200-nm-thick epitaxial bcc (110) Eu film prepared, maintained, and investigated *in situ*, i.e., at ultrahigh vacuum (UHV) conditions.[19] A vacuum-outgassed europium with a natural abundance (48%) in the resonant ^{151}Eu isotope was deposited on a (110) Nb buffered $(11\bar{2}0)$ Al_2O_3 substrate following an elaborated procedure.[20] The high single-crystalline quality of the film was confirmed by a wide-angle x-ray diffraction (XRD) scan [Fig. 1(a)] performed *ex situ* after covering the sample with a 10-nm-thick Nb layer to protect the highly reactive europium from oxidation. The derived lattice constant, 4.582(1) Å, is fully consistent with that of the bulk Eu (4.581 Å, see Ref. 21). In addition to the XRD the quality of the Eu film was controlled by the time spectra of coherent grazing incidence nuclear forward scattering [Fig. 1(b)] (open circles) measured *in situ* at 100 K. As expected, at this temperature the film is nonmagnetic (Eu is an antiferromagnet with Néel temperature of T_N=91 K, see Ref. 22), which is confirmed also by the theoretical simulation[23] shown in Fig. 1(b) with the solid (red) line, thus proving the high purity of Eu.

The experiment[24] was performed at the nuclear resonance end station ID22N of the European Synchrotron Radiation Facility. The synchrotron beam was monochromatized with a previously developed high-resolution optics[25] for the resonant transition in the nuclei of the ^{151}Eu with energy 21.541 keV. The Eu film was deposited in a recently constructed UHV system[26] and transferred to the ID22N station in a portable UHV chamber dedicated to nuclear resonance-scattering experiments where it was studied *in situ*. The measurements were performed at 100 K in order to reduce the multiphonon excitations which, similarly to the case of Dy,[2] form a major part of the measured signal at room temperature.

The energy dependence of nuclear inelastic x-ray absorption[27,28] is shown in Fig. 2.[29] It gives the probability of

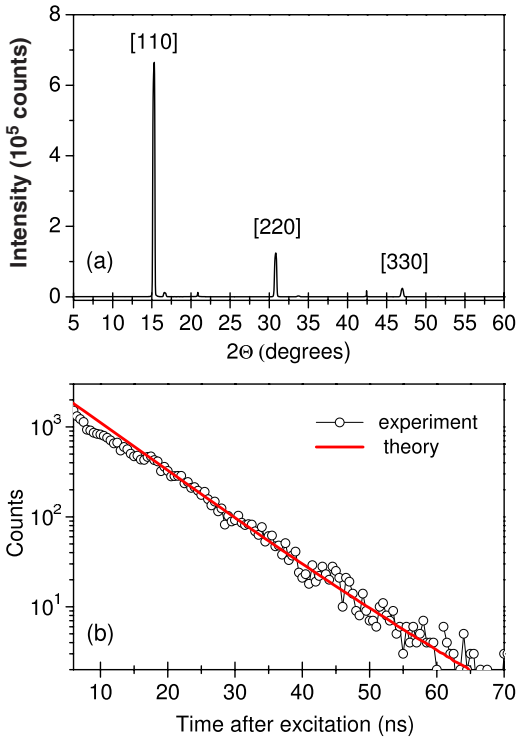

FIG. 1. (Color online) (a) X-ray diffraction scan ($\lambda=0.86$ Å) with the assigned Eu reflections. Peaks arising from the substrate are also visible. (b) Time spectrum (open circles) of the coherent nuclear forward scattering recorded at 100 K and at an incidence angle of 0.1°, which corresponds to the critical angle. The solid (red) line is a simulation according to the theory.

nuclear inelastic absorption as a function of the energy transfer due to phonon annihilation ($E<0$) and phonon creation ($E>0$) in the crystal lattice. The inset shows the instrumental function (solid circles) of the spectrometer measured in parallel and used in the data analysis. The solid (red) line represents a Gaussian distribution with the full width at half maximum of 1.45(2) meV.

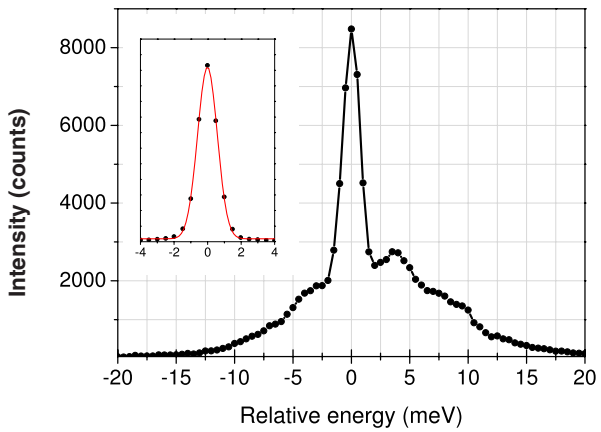

FIG. 2. (Color online) Energy dependence of nuclear inelastic x-ray absorption in the 200-nm-thick bcc (110) Eu metallic film measured at 100 K. The inset shows a fit of the instrumental function (solid circles) with a Gaussian distribution (solid/red line) with a full width at half maximum of 1.45(2) meV.

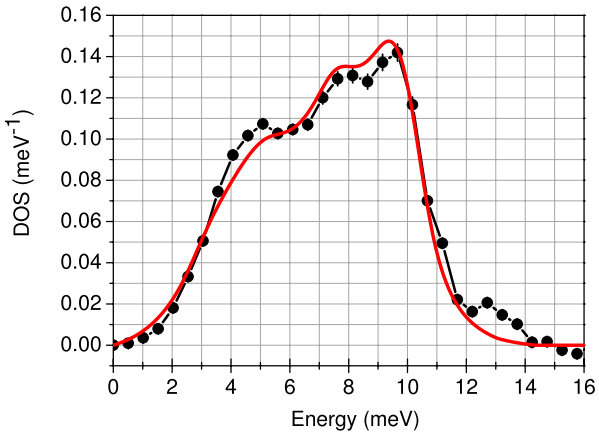

FIG. 3. (Color online) Phonon DOS for bcc europium. The closed circles and the thin solid (black) line mark the DOS derived from the energy dependence of the nuclear inelastic absorption measured at 100 K. The solid (red) line represents the calculated DOS from Fig. 4(b) convoluted with a Gaussian function accounting for the instrumental broadening.

The phonon DOS was derived[30] from the measured energy dependence of nuclear inelastic absorption at 100 K (see Fig. 3). One clearly observes phonon peaks at 5, 8, and 9.5 meV, and the high-energy cutoff at about 12 meV. A peak onset at 13 meV could also be identified (see below).

In order to test the applicability of the first-principles theory to determine the lattice dynamics of the $4f$ elements and to get further insights into the thermodynamic and elastic properties of Eu, we performed *ab initio* calculations using the DFT implemented in the VASP program.[31] The program uses a highly accurate full-potential projector augmented-wave method[32] with the generalized gradient approximation (GGA). All calculations were performed in the $2\times2\times2$ supercell with 16 atoms and the periodic boundary conditions. The valence basis consists of 17 electrons per atom in the configuration $5s^25p^64f^76s^2$. The energy cutoff for the plane-wave expansion was set at 520 eV since the contribution of states with higher energies is negligible.

The magnetic ground state in Eu is an incommensurate spin spiral state,[22] with the period $3.6a$ (with a being the lattice constant) below 91 K. Such a complex state cannot be modeled precisely using the standard DFT approach, so we assumed here a ferromagnetic ground state which has lower energy than the simple antiferromagnetic one.[33] It gives the total magnetic moment $7.1\mu_B$ for the Wigner-Seitz radius $r=2$ Å. In the half-filled f shell the orbital degrees of freedom are suppressed due to Hund's exchange (orbital moment is less than 0.1); therefore, in the phonon calculations we have not included the spin-orbit coupling. The obtained lattice constant $a=4.432$ Å is smaller by 2.7% than the experimental value of $a=4.555$ Å at 100 K; see Ref. 22. Such a difference could result from over binding of the $4f$ orbitals and has also been found in the previous DFT studies.[33] Including the Hubbard-type local interaction U in the local-density approximation (LDA+U) shifts the $4f$ valence states to lower energies[34] and increases the lattice constant. We remark that the effective value of U is rather small as it is strongly screened by s-p electrons in a metal,[15] so we did not have to include it in the GGA calculations.

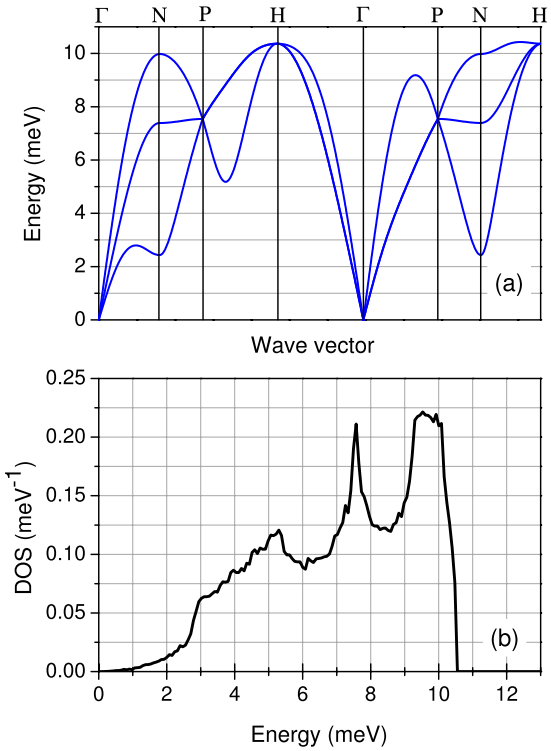

FIG. 4. (Color online) Results of the calculations with PHONON code (Ref. 36) for bulk bcc europium: (a) phonon-dispersion relations within the first Brillouin zone and (b) phonon DOS. The high-symmetry points in units of $2\pi/a$ are $\Gamma=(0,0,0)$, $N=(\frac{1}{2},\frac{1}{2},0)$, $P=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and $H=(0,0,1)$.

Phonon frequencies were calculated using the direct method[12,35] implemented in the PHONON code.[36] The combination of atomic displacements and Hellmann-Feynman forces allows one to obtain the force constants, and next the dynamical matrix is constructed and diagonalized. The calculated dispersion relations for bulk bcc metallic Eu obtained for the theoretical lattice constant are plotted in Fig. 4(a), while Fig. 4(b) shows the resulted phonon DOS. The phonon peaks at 5, 7.5, and 9.5 meV, as well as the high-energy cutoff at 10.5 meV, are consistent with the experimental observations (Fig. 3).

A comparison with the available data for other rare-earth metals reveals that the Eu phonon DOS is shifted to lower energies, suggesting that it probably exhibits the softest crystal lattice among the lanthanides. The mean force constant, for example, is smaller by 36% compared to Dy (Ref. 37) and by 33% compared to the neighboring Sm. Most likely, the reason is in the bcc lattice structure of europium. All other lanthanides at room temperature and ambient pressure crystallize in hexagonal-based lattices, which are stiffer compared to the bcc one, due to the higher packing efficiency (74% for hcp vs 68% for bcc).

The calculated phonon DOS (solid/red line in Fig. 3) shows remarkable agreement with the experiment. The small but detectable misfits between 3 and 6 meV, and 8 and 10 meV, as well as the peak onset at about 13 meV, are not accounted for by the calculated phonon DOS. All these features seen in experiment most likely arise due to the adsorption of adatoms from the residual gases at the very reactive Eu surface, which cannot be avoided during the prolonged experiment (lasting about 20 h) even at UHV conditions.[38]

TABLE I. Thermodynamic (specific heat and vibrational entropy) and elastic (mean atomic displacement, mean force constant, and sound velocity) properties of europium at 100 K obtained from the experimental and theoretical phonon DOS.

Physical quantity	Experiment	Theory
Specific heat (k_B/atom)	2.8(1)	2.8
Vibrational entropy (k_B/atom)	3.8(1)	3.8
Mean atomic displacement (Å)	0.094(2)	0.091
Mean force constant (N/m)	33(2)[a]	32.42
Sound velocity (m/s)	1658(30)	1639

[a]The value was obtained from the second moment of the phonon DOS in the energy range 0–12 meV.

The knowledge of the phonon DOS allows one to compute a number of thermodynamic and elastic properties of the solid. Table I summarizes the values obtained in this way (called experiment) for the specific heat, vibrational entropy, mean atomic displacement, mean force constant, and sound velocity of Eu at 100 K and compares them with those obtained from the theory (called theory). The consistency between the reported values is remarkable.

In summary, we have obtained the phonon DOS of Eu, which is the most reactive among the rare-earth elements, by *in situ* nuclear inelastic scattering. The dispersion relations were obtained from the first-principles theory allowing for complete determination of the lattice dynamics of Eu. From the measured and calculated phonon DOS several thermodynamic and elastic properties of this metal were derived. Although Eu is not a typical rare-earth metal, a satisfactory agreement between the experiment and theory reported here strongly suggests that the *ab initio* approach based on the direct method provides reliable results for the lattice dynamics of the $4f$ elements. The reported results represent a demanding test of the first-principles theory, thus, allowing for further systematic and comparative investigation of the vibrational properties of the rare earths, which have been a largely unexplored area for a long time.

We thank I. Sergueev for his help during the experiment and A. I. Chumakov for fruitful discussions. This work was partly supported by the European Community under the Specific Targeted Research Project No. NMP4-CT-2003-001516 (DYNASYNC) and by the Polish Ministry of Science and Education under Project No. 44/N-COST/2007/0. A.M.O. acknowledges support by the Foundation for Polish Science (FNP).

*Present address: Institute for Synchrotron Radiation, Forschungszentrum Karlsruhe; stankov@iss.fzk.de

[1] N. Nücker, *Lattice Dynamics* (Flammarion, Paris, 1978).
[2] A. I. Chumakov, R. Rüffer, O. Leupold, A. Barla, H. Thiess, J. M. Gil, H. V. Alberto, R. C. Vilao, N. Ayres de Campos, V. G. Kohn, M. Gerken, and M. Lucht, Phys. Rev. B **63**, 172301 (2001).
[3] C. Stassis, T. Gould, O. D. McMasters, K. A. Gschneidner, and R. M. Nicklow, Phys. Rev. B **19**, 5746 (1979).
[4] J. C. Glyden Houmann and R. M. Nicklow, Phys. Rev. B **1**, 3943 (1970).
[5] R. M. Nicklow, N. Wakabayashi, and P. R. Vijayaraghavan, Phys. Rev. B **3**, 1229 (1971).
[6] R. R. Rao and C. S. Menon, J. Phys. Chem. Solids **35**, 425 (1974).
[7] R. Ramji Rao and C. S. Menon, J. Phys. Chem. Solids **34**, 1879 (1973).
[8] R. R. Rao and A. Ramanand, Acta Crystallogr. **33**, 146 (1977).
[9] J. C. Upadhyaya and A. O. E. Animalu, Phys. Rev. B **15**, 1867 (1977).
[10] J. Forstreuter, L. Steinbeck, M. Richter, and H. Eschrig, Phys. Rev. B **55**, 9415 (1997).
[11] P. Strange, A. Svane, W. M. Temmerman, Z. Szotek, and H. Winter, Nature (London) **399**, 756 (1999).
[12] K. Parlinski, Z-.Q. Li, and Y. Kawazoe, Phys. Rev. Lett. **78**, 4063 (1997).
[13] P. Piekarz, K. Parlinski, P. T. Jochym, A. M. Oleś, J. P. Sanchez, and J. Rebizant, Phys. Rev. B **72**, 014521 (2005); P. Piekarz, A. M. Oleś, and K. Parlinski, Physica C **460-462**, 655 (2007).
[14] M. Metoki, K. Kaneko, S. Raymond, J. P. Sanchez, P. Piekarz, K. Parlinski, A. M. Oleś, S. Ikeda, T. D. Matsuda, Y. Haga, Y. Onuki, and G. H. Lander, Physica B **378-380**, 1003 (2006).
[15] J. Łażewski, P. Piekarz, A. M. Oleś, and K. Parlinski, Phys. Rev. B **74**, 174304 (2006).
[16] P. Piekarz, K. Parlinski, and A. M. Oleś, Phys. Rev. Lett. **97**, 156402 (2006); Phys. Rev. B **76**, 165124 (2007).
[17] S. Stankov, R. Röhlsberger, T. Ślęzak, M. Sladecek, B. Sepiol, G. Vogl, A. I. Chumakov, R. Rüffer, N. Spiridis, J. Łażewski, K. Parlinski, and J. Korecki, Phys. Rev. Lett. **99**, 185501 (2007).
[18] T. Ślęzak, J. Łażewski, S. Stankov, K. Parlinski, R. Reitinger, M. Rennhofer, R. Rüffer, B. Sepiol, M. Ślęzak, N. Spiridis, M. Zając, A. I. Chumakov, and J. Korecki, Phys. Rev. Lett. **99**, 066103 (2007).
[19] The base pressure of the UHV system and the transfer chamber was 3×10^{-10} mbar, while during the deposition it was 4×10^{-9} mbar.
[20] S. Soriano, K. Dumesnil, C. Dufour, and D. Pierre, J. Cryst. Growth **265**, 582 (2004).
[21] I. R. Harris and G. V. Raynor, J. Less-Common Met. **17**, 336 (1969).
[22] N. G. Nereson, C. E. Olsen, and G. P. Arnold, Phys. Rev. **135**, A176 (1964); R. L. Cohen, S. Hüfner, and K. W. West, *ibid.* **184**, 263 (1969).
[23] The coherent nuclear forward scattering spectrum was calculated using the software REFTIM, http://www.esrf.fr/computing/scientific/REFTIM/MAIN.htm
[24] http://www.esrf.fr/UsersAndScience/Experiments/HRRS/NRG/
[25] O. Leupold, J. Pollmann, E. Gerdau, H. D. Rüter, G. Faigel, M. Tegze, G. Bortel, R. Rüffer, A. I. Chumakov, and A. Q. R. Baron, Europhys. Lett. **35**, 671 (1996).
[26] S. Stankov, R. Rüffer, M. Sladecek, M. Rennhofer, B. Sepiol, G. Vogl, T. Ślęzak, and J. Korecki, Rev. Sci. Instrum. **79**, 045108 (2008).
[27] M. Seto, Y. Yoda, S. Kikuta, X. W. Zhang, and M. Ando, Phys. Rev. Lett. **74**, 3828 (1995).
[28] W. Sturhahn, T. S. Toellner, E. E. Alp, X. Zhang, M. Ando, Y. Yoda, S. Kikuta, M. Seto, C. W. Kimball, and B. Dabrowski, Phys. Rev. Lett. **74**, 3832 (1995).
[29] In order to enhance the bulk sensitivity the energy scans were performed at an incidence angle of 0.2°, which is twice as big as the critical angle.
[30] V. G. Kohn and A. I. Chumakov, Hyperfine Interact. **125**, 205 (2000).
[31] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[32] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994); G. Kresse and D. Joubert, *ibid.* **59**, 1758 (1999).
[33] I. Turek, J. Kudrnovský, M. Diviš, P. Franek, G. Bihlmayer, and S. Blügel, Phys. Rev. B **68**, 224431 (2003).
[34] J. Kuneš and R. Laskowski, Phys. Rev. B **70**, 174415 (2004).
[35] R. M. Pick, M. H. Cohen, and R. M. Martin, Phys. Rev. B **1**, 910 (1970); F. Detraux, P. Ghosez, and X. Gonze, Phys. Rev. Lett. **81**, 3297 (1998).
[36] K. Parlinski, Software PHONON, Cracow, 2008.
[37] A. I. Chumakov (private communication).
[38] E. Partyka-Jankowska, B. Sepiol, M. Sladecek, D. Kmiec, J. Korecki, T. Ślęzak, M. Zając, S. Stankov, R. Rüffer, and G. Vogl, Surf. Sci. **602**, 1453 (2008).