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Wave-propagation properties of alpha and beta Lanthanum studied by ab-initio calculations

第一原理計算を用いたアルファおよびベータ La の超音波伝播特性

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1. Introduction

Lanthanum (La) is the first metal of the lanthanoid, which includes Ce, Pr, Nd, Yb, and so on. La exhibits the double hexagonal closed packed (dhcp) structure (α-La) below 600 K, the face centered cubic (fcc) structure (β-La) between 600 and 1140 K, and the body centered cubic (bcc) structure (γ-La), as shown in **Fig. 1**. Since the energy of α-La and β-La is close, β-La can exist below 600 K as a meta-stable phase.[1, 2] The dhcp structure consists of ABAC… layers the along [0001] direction, whereas the fcc structure consists of ABC… layers along the [111] direction. Stassis *et al*. measured the elastic constants of monocrystalline β-La by the neutron scattering method.[3] However, those of α-La have never been measured. Thus, acoustic properties of α-La remain unclear although Lanthanum composites are widely used in many applications such as $LaNi_5$ for hydrogen automobiles, LaB_6 for electronic microscopes, La_2O_3 for optics for infrared absorbing glass.

Electronic structures of La largely affect its physical properties. La has two 6*s* electrons, one 5*d* electron, and no *f* electrons. It also has a high density of state at the Fermi level. These feathers lead to unusual physical properties such as relatively high superconductive transition temperature of 5–6 K at ambient pressure,[4] which reaches 13 K at 20 GPa. [5] The pressure dependence of sound velocities also shows anomalies,[6] where the contribution of the electronic structure is of interest due to a strong electron-phonon coupling and *s*-*d* band transition. For example, elastic constants of Pd and Pt show unusual temperature dependence due to 4*d* electrons.[7, 8]

In this study, we calculate the elastic constants and sound velocities of α-La and β-La based on the density functional theory, and discuss wave-propagation properties, anisotropy, and their pressure dependence.

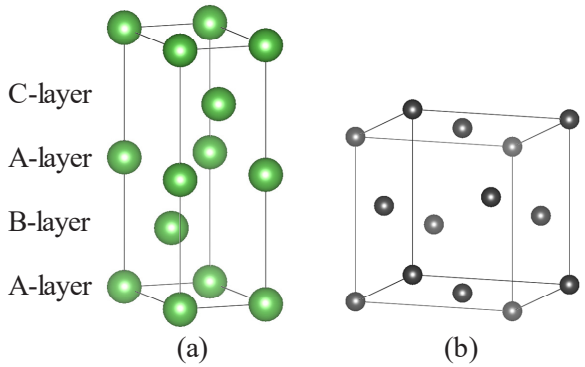


Fig. 1 The structures of (a) dhcp α-La and (b) fcc β-La.

2. Calculation

We used the Vienna *ab-initio* simulation package (VASP), using several types of generalized gradient approximation (GGA-PBE)[9, 10] potentials and local density approximation (LDA)[11] potentials. The cutoff energy of plane wave function is 1300 eV. We applied the Methfessel-Paxton scheme with the width of 1μ–1 eV for the partial occupation of electrons, and the *k*-point mesh is from 8×8×8 to 40×40×40 made by the Monkhorst pack.

First, we calculate the total energy and volume for each calculation condition, and determine the lattice constants. The elastic constants are calculated through the strain-energy relationships by applying ±1% strains for several deformation modes. We also change the volume to calculate the pressure dependence of the elastic constants.

3. Result

First, we calculated the lattice constants *a* and

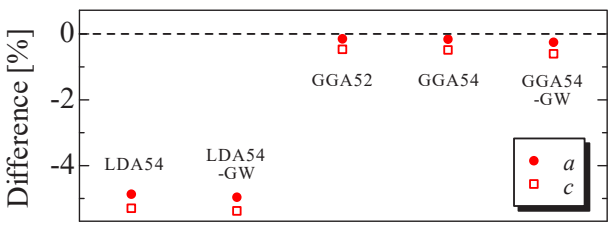


Fig. 2 The difference between the reported and calculated lattice constants *a* and *c* of α-La using several potentials.

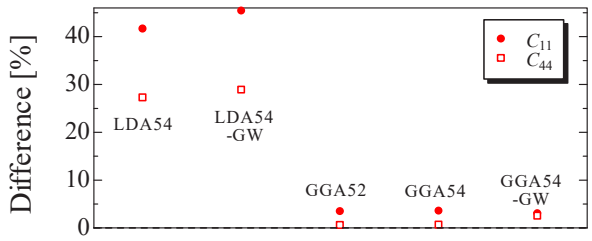


Fig. 3 The difference between the reported and calculated elastic constants of α-La using several potentials.

c of α-La using GGA and LDA potentials with a 10 × 10 × 10 *k*-point mesh and 0.1-eV width smearing. All of the GGA potentials provide good agreement with measurement values[12] whereas LDA potentials underestimate them by ~5% as shown in **Fig. 2**. Elastic constants calculated by GGA also agree with measurement values[13] within 5% as shown in **Fig. 3**. On the other hand, LDA fail to provide proper results.

Second, we calculate the elastic constants of α-La using a GGA, and evaluate the anisotropy. Ranganathan and Starzewski defined the universal elastic anisotropy index $A^U = 5G_V/G_R + B_V/B_R - 6$ (>0), where *G* and *B* are the shear and bulk moduli, and subscribes of V and R mean Voigt and Reuss approximations, respectively.[14] We plot A^U of several hexagonal materials for the *c*/*a* ratio in **Fig. 4**. Here, La, Nd, and Pr are plotted for *c*/2*a* since they show the dhcp structure. We find that α-La exhibits relatively large anisotropy among hexagonal materials. (Note that, Cd, Zn, and Tl has much larger A^U of 1–2.)

The large anisotropy of α-La is also represented by a polar velocity curve. We calculate the phase velocities in the *x*-*z* plane of α-La (A^U =0.16) and Mg (A^U =0.04) as shown in **Fig. 5**. The two shear velocities propagating [101] direction of Mg show 8.4% difference, whereas those of α-La show 17% difference. The difference between the fastest and slowest longitudinal velocities in the *x*-*z* plane of Mg and α-La are 4.7 and 11%, respectively.

4. Conclusion

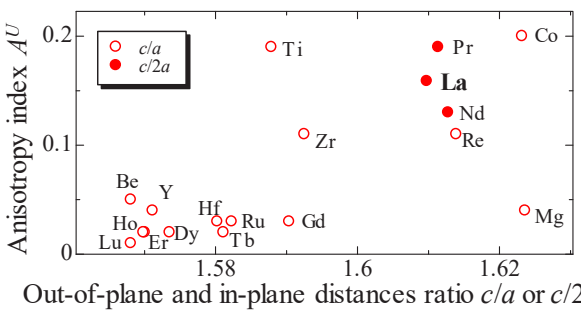
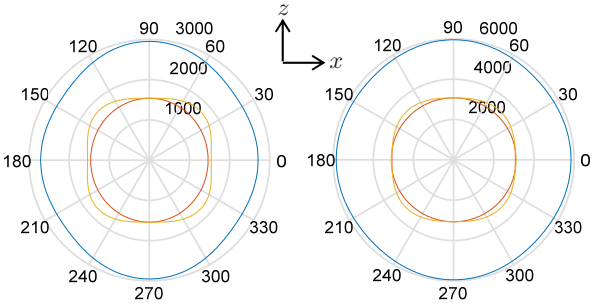


Fig. 4 The universal anisotropy index A^U of hexagonal materials.



(a) α-La (b) Mg

Fig. 5 Polar velocity curves in the *x*-*z* plane of (a) α-La and (b) Mg.

We calculated the lattice constants and elastic constants of α-La by the *ab-initio* method, and found that GGA provides proper values. Our calculation results indicate that α-La exhibits relatively large velocity anisotropy among hexagonal materials. We will discuss its pressure dependence in further calculations.

References

1. D. K. Finnzmore, D. L. Johnson, J. E. Ostenson, F. H. Spedding, and B. J. Seaudry: Phys. Rev. **137** (1965) A550.
2. L. W. Nixon, D. A. Papaconstantopoulos, and M. J. Mehl: Phys. Rev. B **78** (2008) 214510.
3. C. Stassis, G. S. Smith, B. N. Harmon, K. M. Ho, and Y. Chen: Phys. Rev. B **31** (1985) 6298.
4. D. L. Johnson and D. K. Finnemore: Phys. Rev. **158** (1967) 376.
5. H. Balster and J. Wittig: J. Low Temp. Phys. **21** (1975) 377.
6. V. A. Goncharova and G. G. Ilina: J. Exp. Theor. Phys. **59** (1985) 995.
7. J. A. Rayne: Phys. Rev. **118** (1960) 1545.
8. S. M. Collard and R. B. McLellan: Acta Metall. Mate. **40** (1992) 699.
9. J. P. Perdew, K. Burke, and M. Ernzerhof: Phys. Rev. Lett. **77** (1996) 3865.
10. J. P. Perdew, K. Burke, and M. Ernzerhof: Phys. Rev. Lett. **78** (1997) 1396.
11. J. P. Perdew and A. Zunger: Phys. Rev. B **23** (1981) 5048.
12. B. J. Beaudry and P. E. Palmer: J. Less-Common Met. **34** (1974) 225.
13. V. A. Goncharova and G. G. Ilina: J. Exp. Theor. Phys. **59** (1985) 995.
14. S. I. Ranganathan and M. O. Starzewski: Phys. Rev. Lett. **101** (2008) 055504.