

Anisotropic elastic and thermal properties of the double perovskite slab–rock salt layer $\text{Ln}_2\text{SrAl}_2\text{O}_7$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$ or Dy) natural superlattice structure

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Abstract

The anisotropic elastic and thermal properties of layered compounds in the series $\text{Ln}_2\text{SrAl}_2\text{O}_7$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$ or Dy) are calculated from first principles using density functional theory combined with the Debye quasi-harmonic approximation. The polycrystalline values of the elastic constants and bulk, shear and Young's moduli are consistent with those determined experimentally. All compounds in the compositional series have weakly anisotropic elastic and thermal properties. For instance, thermal expansion in the $[001]$ direction of the tetragonal unit cell is slightly larger than along the $[100]$ or $[010]$ directions for most $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds and the calculated in-plane thermal conductivity is always larger than that along the c -axis, parallel to the layer stacking direction.

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1. Introduction

Mechanical and thermal properties, such as the elastic moduli, hardness, heat capacity, thermal expansion coefficients and thermal conductivity are all fundamental properties that must be determined before new materials can be considered for many of today's technological applications. This is especially so of materials for applications such as thermal barrier coatings and thermoelectrics, where a combination of outstanding properties are required [1,2]. For instance, new thermal barrier coatings will have to not only have a lower thermal conductivity than the currently

used 6–8 mol.% yttria-stabilized zirconia (6–8YSZ) but also higher thermal expansion (to minimize the thermal expansion mismatch with the underlying nickel-based superalloy) and superior sintering resistance [3].

In searching for materials with lower thermal conductivity there are a number of guidelines for identifying candidate compounds, for instance a large mean atomic mass, a large number of atoms per unit cell, site disorder of ions on multiple sub-lattices, weak atomic bonding and a high concentration of defects and a distorted crystal structure [4,5]. Using these guidelines a number of layered compounds have been identified and shown to have very low thermal conductivities, between 1 and 2 W m K^{-1} [6–9]. One of these compounds is an unusual layered perovskite, in essence a natural superlattice, consisting of alternating layers of a double perovskite block with a rock salt block. The compound, a rare earth strontium aluminate, forms a

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compositional series with the rare earth ions from La to Dy, and has the nominal formula $\text{Ln}_2\text{SrAl}_2\text{O}_7$ [10]. Measurements indicate that the thermal conductivity depends on the atomic number of the rare earth, as well as on the unit cell volume [8]. Single crystals of these very refractory compounds are not known and so only a number of the polycrystalline properties have been measured and there is no information about their crystalline anisotropy. In this contribution we compute the anisotropic elastic and thermal properties of these compounds, as well as their dependence on the rare earth ion. It is anticipated that this will guide selection of the appropriate rare earth member of the series for different applications and guide future experiments.

2. Methods and details

The crystal structure of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ (Ln = La, Nd, Sm, Eu, Gd or Dy) is illustrated in Fig. 1. As described else-

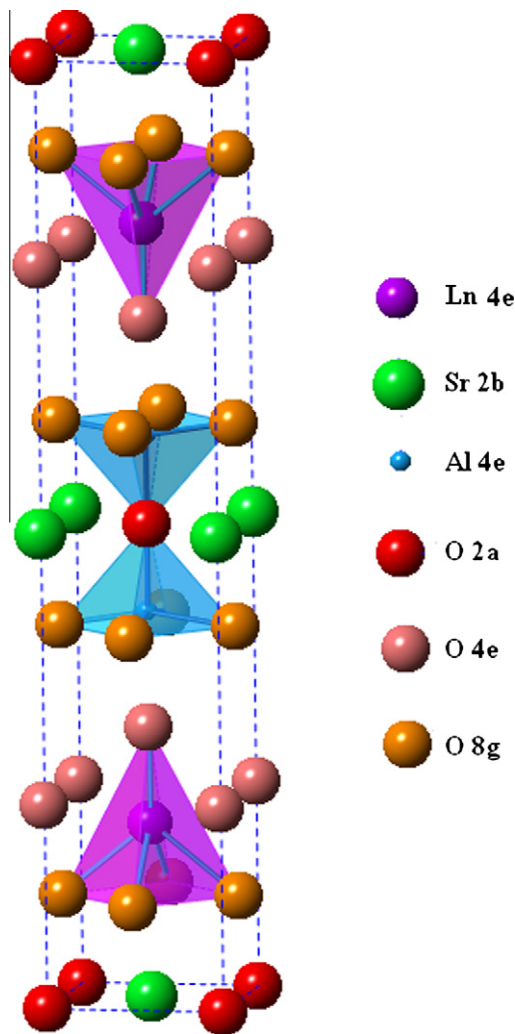


Fig. 1. The crystal structure of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ (Ln = La, Nd, Sm, Eu, Gd or Dy) indicating the layered sequence of a double perovskite and a rock salt block.

where, it is a tetragonal structure and consists of a periodic stacking of double perovskite blocks, formed from AlO_6 octahedra, and a rock salt block, based on LnO_5 polyhedra [10]. The space group is determined to be $I4/mmm$ (No. 139). The pertinent features of the structure for the computations is that the rare earth and strontium atoms occupy the 4e (0,0,0.318 ± 0.008) and 2b (0,0,0.5) Wyckoff sites, respectively. In addition, the aluminum atoms occupy the 4e (0,0,0.094 ± 0.008) sites, and the oxygen atoms are situated at the 2a (0,0,1), 8g (0,0.5,0.097 ± 0.008), and 4e (0,0,0.199 ± 0.008) sites.

The calculations in this work were implemented using the first principles, density functional perturbation theory (DFPT) method [11]. This method combines density functional theory [12] with the electron density linear response method, which have been successfully applied to calculate the thermal properties of many materials with simple crystal structures. The calculations were supplemented using the quasi-harmonic approximation (QHA) [13] in order to compute the thermal expansion and Grüneisen anisotropies. In implementing the density functional calculations the spin polarized local density approximation (LSDA) was employed to approximate the exchange correlation energy [14]. The ultrasoft pseudo-potentials in the CASTEP [15] database were used for Ln, Sr, Al, and O atoms. For different atomic species the valence shells and electronic configurations for pseudo-atoms are O $2s^2 2p^4$, Al $3s^2 3p^1$, Sr $4s^2 4p^6 5s^2$, La $5s^2 5p^6 5d^1 6s^2$, Nd $4f^4 5s^2 5p^6 6s^2$, Sm $4f^6 5s^2 5p^6 6s^2$, Eu $4f^7 5s^2 5p^6 6s^2$, Gd $4f^7 5s^2 5p^6 5d^1 6s^2$ and Dy $4f^{10} 5s^2 5p^6 6s^2$. The change in total energy was reduced to 1.0×10^{-6} eV per atom. The Monkhorst–Pack scheme was used for k point sampling ($10 \times 10 \times 10$) in the first irreducible Brillouin zone (BZ). The kinetic energy cut-off was set to 500.0 eV [16].

In order to investigate the anisotropic mechanical properties we calculated the elastic stiffness and other mechanical properties (including second order elastic constants, bulk modulus (B), shear modulus (G) and Young's modulus (E)). The second order elastic constants were determined by means of linear fitting of the stress–strain curves obtained from first principles calculations [17,18]. To illustrate the procedure in Fig. 2 we show the deformed unit cell of a $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compound after applying one of the monoclinic strain modes. The deformed lattice vectors are

$$a_{ix} = a_{ix}^0 + \eta \sum_{\beta} T_{\alpha\beta} a_{i\beta}^0 \quad (1)$$

where a_{ix} and a_{ix}^0 are the initial and deformed lattice vectors, respectively and $T_{\alpha\beta}$ is a matrix which characterizes the symmetry of the strain mode. For the distorted crystal structures the lattice constants and the shape of the cell are fixed and so only the atomic positions were optimized before calculating the total energy and Cauchy stress tensor. Once the elastic constants had been computed the other mechanical properties were evaluated by standard procedures [19,20].

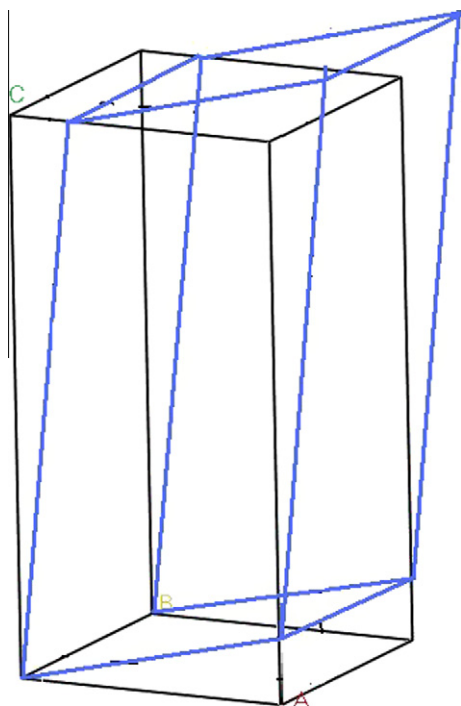


Fig. 2. The unit cell of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ deformed by monoclinic mode strain. The second order elastic constants are determined by means of linear fitting of the stress–strain curves obtained from first principles calculations. One usually applies several different strain patterns to the optimized crystal structure and, by varying the strain amplitude for a specific strain pattern, the Cauchy stress tensor can be evaluated as a function of strain.

3. Results

3.1. Elastic constants and polycrystalline moduli

The calculated elastic constants of the $\text{Ln}_2\text{SrAl}_2\text{O}_7$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$ or Dy) series of compounds are listed in Table 1, and the elastic compliance matrices calculated directly from them are listed in Table 2. For tetragonal crystals such as the rare earth strontium alumi-

nates $C_{11} = C_{22} \neq C_{33}$, and the difference between them is a measure of the anisotropic properties of mechanical moduli in the stacking plane and in the perpendicular $[001]$ direction. Examination of the results in Table 1 indicates that these compounds have relatively weak anisotropic elastic properties with only a weak directional dependence of the moduli, a point we will return to later. Notably, though, the values of C_{11} and C_{66} are slightly larger than those of C_{33} and C_{44} , respectively, implying that the intra-layer chemical bonds are stronger than those between the layers. Also shown in Table 1 are the elastic constants of Al_2O_3 and SrO for comparison. As expected, the elastic constants are intermediate between those of Al_2O_3 and SrO [21,22].

From the values of the elastic constants the intrinsic mechanical stability of the structure can be checked, since the condition for mechanical stability of tetragonal crystals is usually characterized by the conditions [23].

$$\begin{aligned} C_{11} > 0, C_{33} > 0, C_{44} > 0, C_{66} > 0, \\ (C_{11} - C_{12}) > 0, (C_{11} + C_{33} - 2C_{13}) > 0, \\ [2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0 \end{aligned} \quad (2)$$

As indicated in Table 1, the calculated elastic constants of all the $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds do satisfy these criteria, indicating that they are intrinsically stable. This is consistent with the results of the energy calculations, for instance the formation enthalpy and cohesive energy [24].

As mentioned in the Introduction, no single crystals of these compounds are known to exist and so for comparison with the available polycrystalline data the polycrystalline moduli have been calculated from the single crystal elastic constants. The Voigt–Reuss–Hill approximation, an arithmetic average of the Voigt and Reuss moduli [19,20], has been used.

$$B_{\text{VRH}} = \frac{1}{2}(B_V + B_R) \quad (3)$$

$$G_{\text{VRH}} = \frac{1}{2}(G_V + G_R) \quad (4)$$

Table 1

The calculated independent elastic constants of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$ or Dy) using the strain–stress method (the same methods have been used to calculate the elastic coefficients of $\alpha\text{-Al}_2\text{O}_3$ and SrO).

	Method	C_{ij}					
		C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}
$\text{La}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	252.7	272.4	117.7	137.6	130.1	141.6
$\text{Nd}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	292	276.5	120.2	131.2	113.4	131.9
$\text{Sm}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	283.7	275.1	123.2	123.8	102.8	129
$\text{Eu}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	288.4	273	118.9	124.4	103.9	121.3
$\text{Gd}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	298.3	285.3	122.1	120.2	109.4	126.6
$\text{Dy}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	286.4	261.8	120.1	132.3	102.6	134.8
$\alpha\text{-Al}_2\text{O}_3$	Calculated ^a	489.7	491	138.05		142.6	126.6
	Experimental ^b	497	501	147		163	116
SrO	Calculated ^a	170.7		56.9		44.1	
	Experimental ^c	160.1		59		43.5	

^a Calculated in this work.

^b From Kittel [22].

^c From Grimvall [21].

Table 2

The elastic compliance matrix of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ (Ln = La, Nd, Sm, Eu, Gd or Dy) calculated from the elastic coefficients using the strain–stress method.

	S_{ij}					
	S_{11}	S_{33}	S_{44}	S_{66}	S_{12}	S_{13}
$\text{La}_2\text{SrAl}_2\text{O}_7$	0.006200	0.005965	0.008496	0.007267	−0.00196	−0.00221
$\text{Nd}_2\text{SrAl}_2\text{O}_7$	0.004588	0.005245	0.008319	0.007622	−0.00101	−0.00171
$\text{Sm}_2\text{SrAl}_2\text{O}_7$	0.004647	0.005291	0.008117	0.008078	−0.00088	−0.00177
$\text{Eu}_2\text{SrAl}_2\text{O}_7$	0.004467	0.005051	0.00841	0.008039	−0.00095	−0.00156
$\text{Gd}_2\text{SrAl}_2\text{O}_7$	0.004334	0.004838	0.008190	0.008319	−0.00095	−0.00156
$\text{Dy}_2\text{SrAl}_2\text{O}_7$	0.004719	0.005939	0.008326	0.007559	−0.00072	−0.00206

$$E = 9B_{\text{VRH}}G_{\text{VRH}}/(3B_{\text{VRH}} + G_{\text{VRH}}) \quad (5)$$

In the above equations B , G and E are the bulk modulus, shear modulus and Young's modulus, respectively and VRH refers to the Voigt–Reuss–Hill approximation. Calculation of the Voigt and Reuss moduli are straightforward using the obtained elastic constants, the formula for which is

$$\begin{cases} B_V = \frac{1}{9}[2(C_{11} + C_{12}) + C_{33} + 4C_{13}] \\ G_V = \frac{1}{30}(M + 3C_{11} - 3C_{12} + 12C_{44} + 6C_{66}) \\ B_R = C^2/M, G_R = \frac{15}{\{(18B_V/C^2) + [6/(C_{11} - C_{12})] + (6/C_{44}) + (3/C_{66})\}} \\ M = C_{11} + C_{12} + 2C_{33} - 4C_{13}, C^2 = (C_{11} + C_{12})C_{33} - 2C_{13}^2 \end{cases} \quad (6)$$

These are listed in Table 3. Comparison of the tabulated results indicates only a weak dependence of the mechanical properties of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds on the radius of the Ln^{3+} ion. Furthermore, the numerical values are very similar. In contrast, the experimental values of B and E increase slightly with decreasing ionic radius of the Ln^{3+}

ion, especially for the Young's modulus. Since the Young's modulus characterizes the resistance to uniaxial deformation it is closely related to the values of C_{11} and C_{33} and, interestingly, the calculated C_{11} and C_{33} also increase from $\text{La}_2\text{SrAl}_2\text{O}_7$ to $\text{Gd}_2\text{SrAl}_2\text{O}_7$. On the other hand, the shear modulus does not change significantly with the radius of the Ln^{3+} ion, because C_{44} is almost a constant for all the compounds in the series. The calculated bulk moduli for all of the $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds are less than 200 GPa, with the largest being that of $\text{Gd}_2\text{SrAl}_2\text{O}_7$, at 188 GPa, and the smallest being that of $\text{Eu}_2\text{SrAl}_2\text{O}_7$, at 172 GPa. Similar results were found for the shear moduli.

In Table 3 we also show the Young's modulus in different crystallographic directions. Interestingly, the modulus in the [001] direction, perpendicular to the layer planes, is smaller than that in the basal plane (in the [100] and [010] directions) for all the compounds in the rare earth series. The experimental results for polycrystalline samples are also listed in Table 3. The theoretical results are qualitatively in agreement with the experimental results [8]. The experimental values are sensitive to porosity.

Table 3

The bulk modulus (GPa), shear modulus (GPa), Young's modulus (GPa), Poisson ratio (ν) of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ (Ln = La, Nd, Sm, Eu, Gd or Dy) calculated using the elastic constants, with the Voigt–Reuss–Hill approximations applied for the evaluation of mechanical moduli.

	Method	B			G			$B_V/G_V (B/G)$	E		ν		
		B_V	B_R	B_H	G_V	G_R	G_H		$E_x = E_y$	E_z	ν_{xy}	ν_{xz}	ν_{zx}
$\text{La}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	178.3	177.7	178	98.9	87.3	93.1	1.803	161.2	167.6	0.215	0.356	0.37
	Experimental ^b	137			100			1.37	166.4		0.203		
$\text{Nd}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	179.4	179.4	179.4	106.5	101.2	103.9	1.685	218	190.7	0.22	0.372	0.325
	Experimental ^b	140			104			1.346	186		0.199		
$\text{Sm}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	173.8	173.6	173.7	106.1	100.7	103.4	1.638	251.2	188.9	0.19	0.38	0.334
	Experimental ^b	159.8			109.1			1.465	252.3		0.223		
$\text{Eu}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	171.4	171.4	171.4	106	102.2	104.1	1.617	223.8	197.9	0.213	0.35	0.309
	Experimental ^b	160			102			1.569	240		0.237		
$\text{Gd}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	188.6	188	188.3	109.5	108.3	108.9	1.722	264.8	205.9	0.211	0.346	0.325
	Experimental ^b	174.5			108.9			1.602	257.9		0.243		
$\text{Dy}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	184.3	178.9	181.6	108.7	106.3	107.5	1.695	245.9	198.6	0.179	0.306	0.356
	Experimental ^b	188			109			1.725	230.4		0.257		
$\alpha\text{-Al}_2\text{O}_3$	Calculated ^a	251.3	251.3	251.3	161.6	159.1	160.3	1.555	430.6	440.2	0.241	0.196	0.2
	Experimental ^c										0.23		
SrO	Calculated ^d	86.1	86.1	86.1	59.3	59.3	59.3	1.452	151.8	151.8	0.206	0.206	0.206
	Experimental ^d	82.37	82.37	82.37	58.72	58.72	58.72	1.403			0.21		

^a Calculated in this work.^b From Wan et al. [8].^c From Kittel [22].^d From Grimvall [21].

3.2. Anisotropy of acoustic velocities

We have calculated the phase velocities of pure transverse and longitudinal modes of the $\text{Ln}_2\text{SrAl}_2\text{O}_7$ series from the single crystal elastic constants following the procedure of Brugger [25]. The tetragonal symmetry of the compounds dictates that pure transverse and longitudinal modes can only exist for the symmetry directions of type [001] (or [010]), [001] and [110]. In all other directions the propagating waves are either quasi-transverse or quasi-longitudinal. In the principal directions the acoustic velocities can be simply written as:

$$\begin{aligned} \text{for } [100] = [010] v_l &= \sqrt{C_{11}/\rho}; & [001] v_{l1} \\ &= \sqrt{C_{44}/\rho}; & [010] v_{l2} = \sqrt{C_{66}/\rho}; & \text{for } [001] v_l \\ &= \sqrt{C_{33}/\rho}; & [100] v_{l1} = [010] v_{l2} = \sqrt{C_{66}/\rho} \end{aligned}$$

$$\begin{aligned} \text{for } [110] v_l &= \sqrt{(C_{11} + C_{12} + 2C_{66})/2\rho}; & [001] v_{l1} \\ &= \sqrt{C_{44}/\rho}; & [1\bar{1}0] v_{l2} = \sqrt{(C_{11} - C_{12})/2\rho} \end{aligned}$$

The correlations between the calculated longitudinal, transverse and average sound velocities (v_m) of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ (Ln = La, Nd, Sm, Eu, Gd or Dy) compounds and the radii of the rare earth atoms are shown in Figs. 3 and 4. In the same figures we also compare the experimental values for the sound velocities with the theoretical calculations.

With the computed transverse and longitudinal acoustic velocities it is straightforward to calculate the Debye temperature Θ_D using the equation [22]:

$$\Theta_D = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{1/3} v_m \quad (7)$$

where h and k_B are the Planck and Boltzmann constants, respectively, N_A is Avogadro's number, n is the total

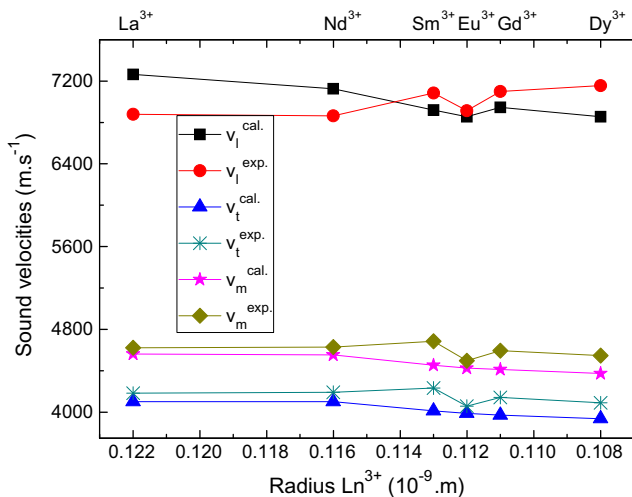


Fig. 3. The correlation between the longitudinal, transverse and average sound velocities (v_m) of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ (Ln = La, Nd, Sm, Eu, Gd or Dy) compounds and the radius of rare earth atoms.

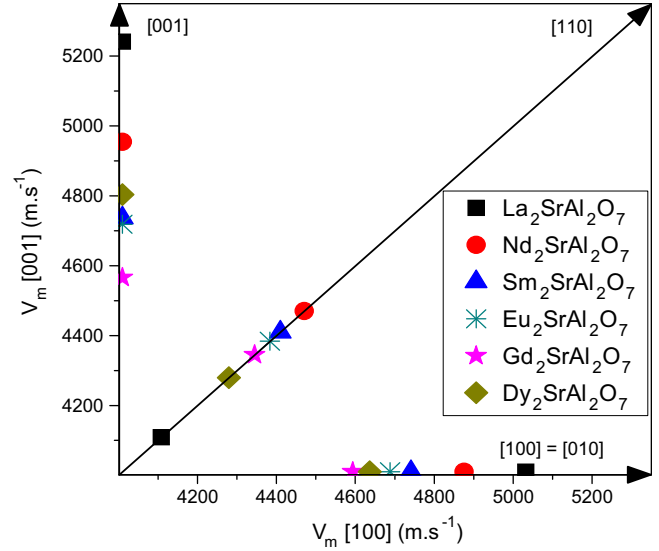


Fig. 4. The average sound velocities (v_m) in the [100], [001] and [110] directions of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ (Ln = La, Nd, Sm, Eu, Gd or Dy) compounds calculated by first principles. For most of the compounds the average sound velocities (v_m) along the [110] direction are smaller than those in the [100] and [001] directions.

number of atoms in the formula unit, M is the mean molecular weight, and ρ is the density. The average sound velocity v_m is given by [17]

$$v_m = \left[\frac{1}{3} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \right]^{-1/3} \quad (8)$$

$$\begin{cases} v_l = \sqrt{(B + \frac{4}{3}G)/\rho} \\ v_t = \sqrt{G/\rho} \end{cases} \quad (9)$$

where B and G are isothermal bulk and shear moduli, v_l is the longitudinal sound velocity and v_t the transverse sound velocity. These are tabulated, together with the calculated Debye temperature, in Table 4. Since the elastic moduli do not vary much with the atomic number of the rare earth element, the small variation in average acoustic velocity and Debye temperature is not unexpected.

3.3. Angular variation in elastic moduli

Although the calculations suggest that the elastic properties of the series of rare earth strontium aluminates are rather weakly anisotropic, the complexity of the structure suggests that it is still useful to characterize the elastic anisotropy. A number of metrics, including the universal anisotropic index (A^U) [26], percent anisotropy and shear anisotropic factors have been proposed. Their definitions are given in Appendix A and the numerical values listed in Table 5 for the different rare earth members of the series. In many respects, however, the most straightforward way to illustrate the mechanical anisotropic properties is as a plot the mechanical moduli in three dimensions as a function of crystallographic orientation. The procedure is

Table 4
Sound velocities along different directions and the average velocities for $\text{Ln}_2\text{SrAl}_2\text{O}_7$ (Ln = La, Nd, Sm, Eu, Gd or Dy) calculated by first principles and measured experimentally.

	Method	ρ	[100] v_l	[001] v_l	[010] v_l	[001] v_t	[100] v_t	[010] v_t	[110] v_l	[001] v_t	[1-110] v_t	v_l	v_t	v_m	θ_D
$\text{La}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	5.879	6.556	4.474	4.838	6.807	4.838	4.838	7.481	4.474	3.229	7.735	4.102	4.584	586
	Experimental ^b	5.711										4.898	4.185	4.376	554
$\text{Nd}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	6.331	6.791	4.357	4.552	6.609	4.552	4.552	7.262	4.357	3.756	7.226	4.101	4.560	594
	Experimental ^b	5.914										4.865	4.193	4.376	557
$\text{Sm}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	6.583	6.565	4.326	4.337	6.464	4.337	4.337	6.940	4.326	3.707	6.871	4.015	4.452	583
	Experimental ^b	6.082										5.126	4.235	4.463	569
$\text{Eu}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	6.655	6.583	4.227	4.324	6.405	4.324	4.324	6.940	4.227	3.723	6.824	3.991	4.426	581
	Experimental ^b	6.193										5.083	4.058	4.307	552
$\text{Gd}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	6.936	6.558	4.196	4.163	6.414	4.163	4.163	6.835	4.196	3.690	6.944	3.973	4.415	584
	Experimental ^b	6.343										5.245	4.143	4.407	566
$\text{Dy}_2\text{SrAl}_2\text{O}_7$	Calculated ^a	7.006	6.394	4.140	4.346	7.186	4.346	4.346	6.830	4.140	3.622	6.770	3.939	4.370	576
	Experimental ^b	6.508										5.375	4.093	4.383	564

The unit of velocity is km s^{-1} , of density is g cm^{-3} and the Debye temperature is in K.

^a Calculated in this work.

^b From Wan et al. [8].

Table 5

The calculated universal anisotropic index (A^U), percent anisotropy (A_G and A_B) and shear anisotropic factors (A_1 and A_2) of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ (Ln = La, Nd, Sm, Eu, Gd or Dy).

Species	A^U	A_B	A_G	A_1	A_2
$\text{La}_2\text{SrAl}_2\text{O}_7$	0.667	0.002	0.062	1.946	2.078
$\text{Nd}_2\text{SrAl}_2\text{O}_7$	0.262	0	0.025	1.578	1.535
$\text{Sm}_2\text{SrAl}_2\text{O}_7$	0.269	0.001	0.026	1.638	1.402
$\text{Eu}_2\text{SrAl}_2\text{O}_7$	0.186	0	0.018	1.492	1.407
$\text{Gd}_2\text{SrAl}_2\text{O}_7$	0.059	0.002	0.006	1.478	1.318
$\text{Dy}_2\text{SrAl}_2\text{O}_7$	0.143	0.015	0.011	1.724	1.543

described in Appendix B and the results are shown in Figs. 5 and 6 for the bulk and Young's moduli, respectively.

3.4. Thermal expansion anisotropy

The thermal expansion coefficients and their temperature dependence are of importance in estimating the thermal expansion mismatch with potential substrate materials. Rather than compute them from first principles at different temperatures we have computed them from the specific heats and elastic constants using the approach described below [27]. This then enables us to estimate the anisotropic Grüneisen parameters and thermal conductivity anisotropy at very high temperatures in the next subsection.

The starting point is that the temperature dependence of thermal expansion is related to the isothermal bulk modulus and the difference between the specific heats at constant pressure and constant volume, C_P and C_V , respectively, as [21]

$$C_P - C_V = \beta^2 V(T) T B_0 \quad (10)$$

where β is the volume expansion coefficient and $V(T)$ represents the cell volume at temperature T , calculated as $V(T) = (1 + \beta T) V_0$, and B_0 is the isothermal bulk modulus at the equilibrium cell volume (V_0). The difference between the two specific heats also enables direct calculation of the isotropic Grüneisen parameter γ_G [21]:

$$C_P - C_V = \beta \gamma_G C_V T \quad (11)$$

The specific heat at constant pressure C_P was calculated using the CASTEP code, which determines it automatically by analyzing the phonon frequencies of the crystal structure. The specific heat at constant volume C_V cannot be calculated directly from the same code and so, instead, was calculated from using the Debye QHA [22]:

$$c_V(T) = 9nN_A k_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (12)$$

In this equation n is the total number of atoms in the unit cell and the other parameters and constants have their usual meaning. Using the Debye temperatures already calculated the difference in specific heat for each compound in the series is shown in Fig. 7 and the calculated volumetric thermal expansion coefficients are shown in Fig. 8. The vol-

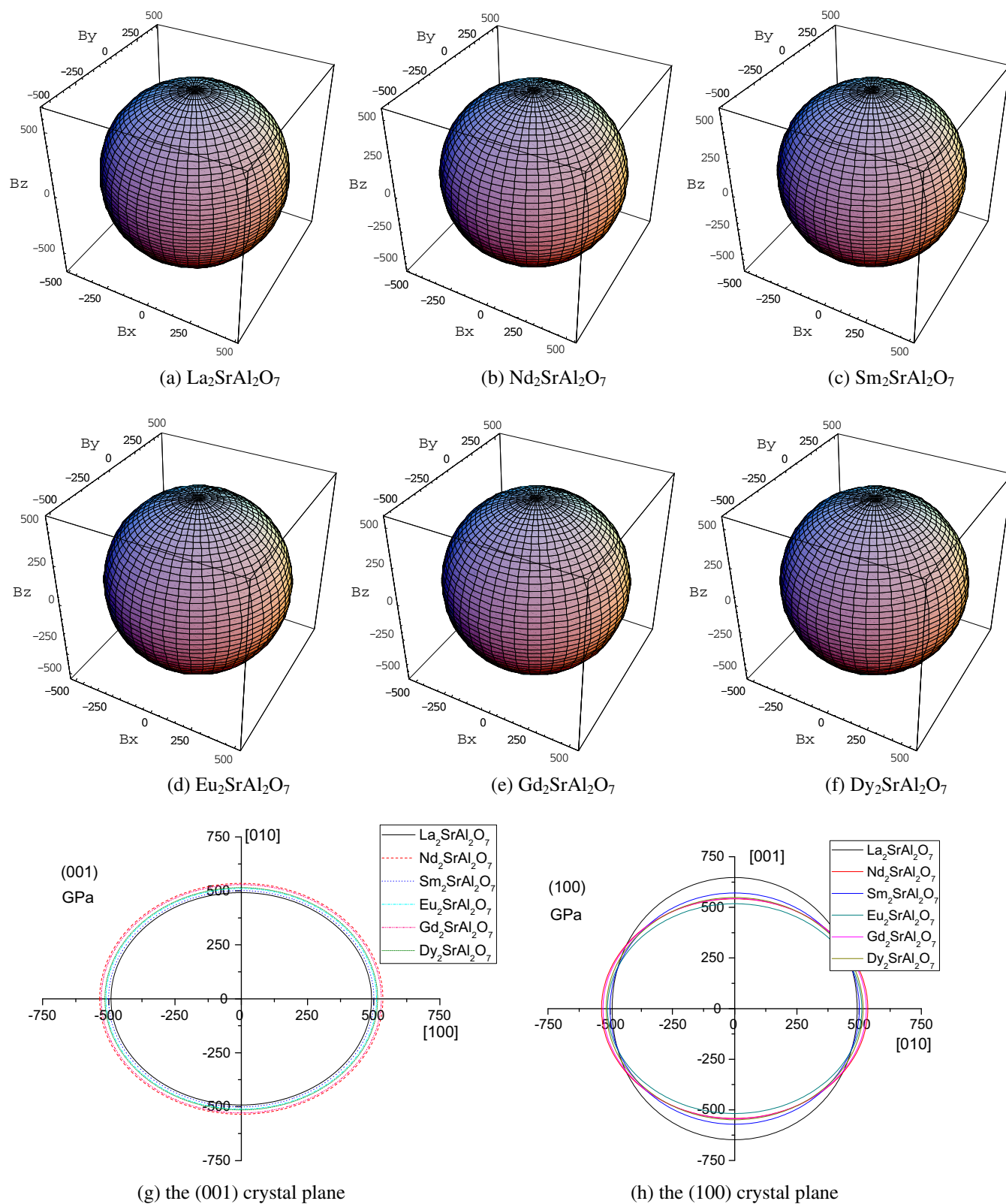


Fig. 5. (a–f) The surface construction of the bulk modulus of Ln₂SrAl₂O₇ compounds. The anisotropy of the bulk modulus of Ln₂SrAl₂O₇ compounds is weak. (g and h) The (001) and (100) planar projections, respectively, of the bulk modulus for the Ln₂SrAl₂O₇ compounds.

umetric expansion coefficients vary between 2.3×10^{-5} and $3.6 \times 10^{-5} \text{ K}^{-1}$, with La₂SrAl₂O₇ having the smallest coefficients and Sm₂SrAl₂O₇ having the largest values. The

results shown in Fig. 8 seem to indicate that the volumetric coefficients of different structures are not correlated with the radius of the Ln³⁺ ion.

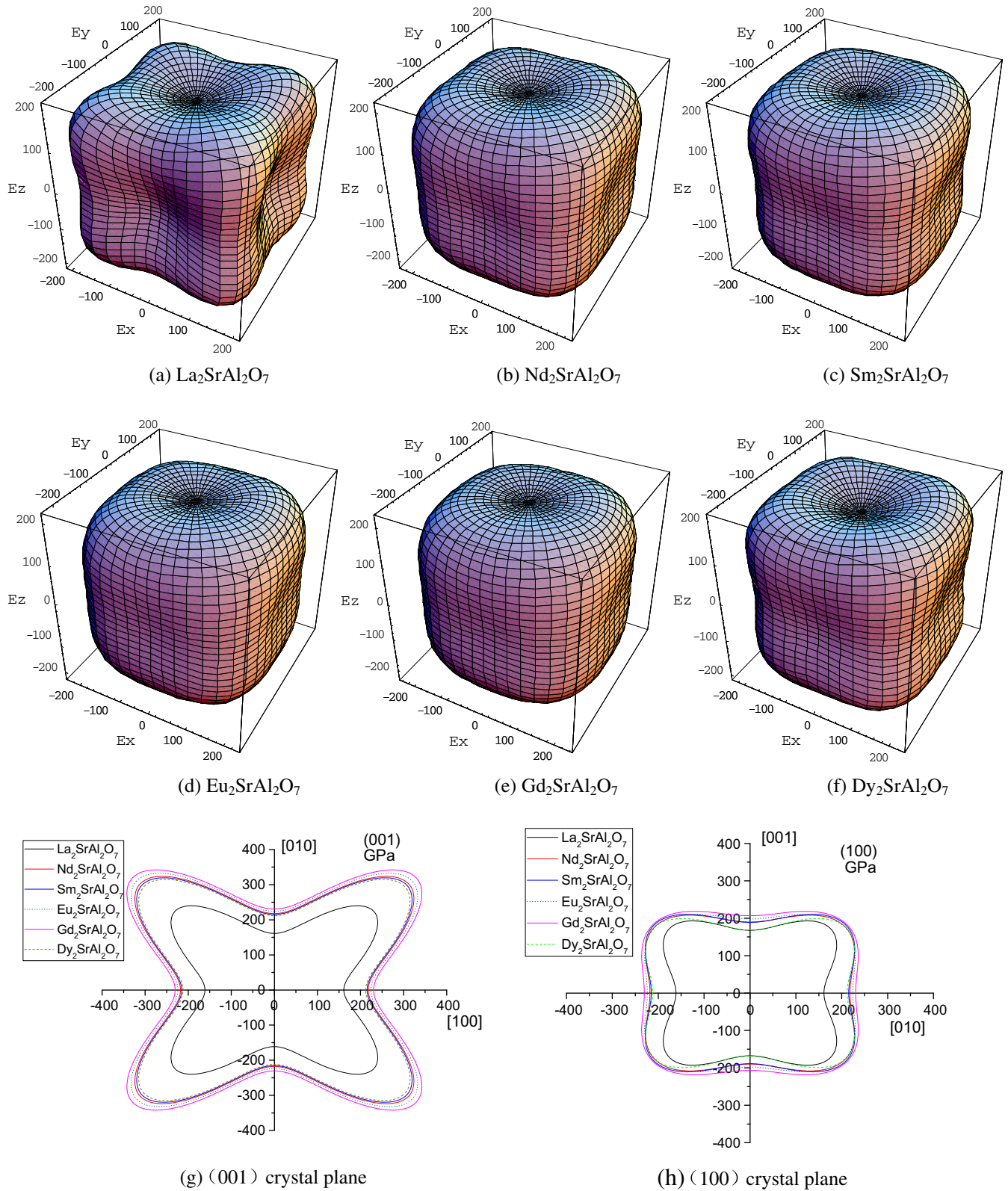


Fig. 6. (a–f) The directional dependence of the Young's modulus of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ structures (from La to Dy). (g and h) The (001) and (100) planar projections, respectively, of the Young's modulus for the $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds.

Having determined the volumetric thermal expansion, the thermal expansion along different directions can be calculated from the linear compressibilities. By definition, the

volumetric thermal expansion is the trace of the thermal expansion tensor. For a tetragonal crystal only the diagonal elements are non-zero and, moreover, due to symmetry

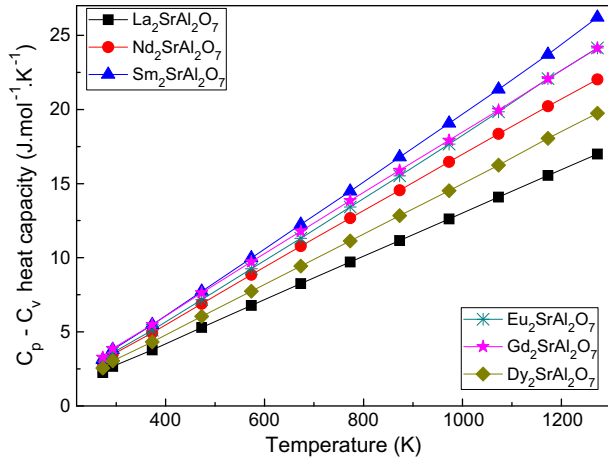


Fig. 7. The calculated difference in specific heat as a function of temperature for each $\text{Ln}_2\text{SrAl}_2\text{O}_7$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$ or Dy) compound. The large difference between C_P and C_V leads to large thermal expansion coefficients.

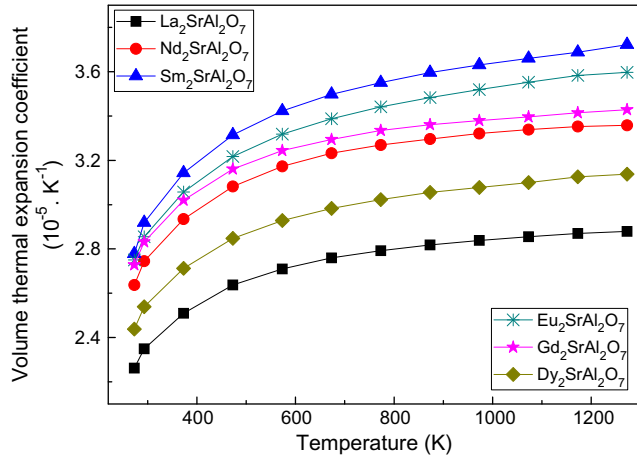


Fig. 8. The volumetric thermal expansion coefficient as a function of temperature for each $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compound.

$\alpha_{aa} = \alpha_{bb} \neq \alpha_{cc}$. Consequently, the relationship between the volumetric coefficient β and α_{ij} is given by [21]

$$\beta = 2\alpha_a + \alpha_c \quad (13)$$

In order to determine the individual linear expansion coefficients an additional relationship between them is required. This is given by the ratio of the linear compressibilities in the a - and c -directions [21,22].

$$\frac{\sigma_a}{\sigma_c} = \frac{\alpha_a}{\alpha_c} \quad (14)$$

The linear compressibilities, $\sigma_a = -d\ln a/dP$ and $\sigma_c = -d\ln c/dP$, are related to α_a and α_c along the [100] and [001] directions and can be calculated from the elastic constants [28,29].

$$\sigma_a = \frac{C_{33} - C_{13}}{(C_{11} + C_{12})C_{33} - 2C_{13}^2} \quad (15)$$

$$\sigma_c = \frac{C_{11} + C_{12} - 2C_{13}}{(C_{11} + C_{12})C_{33} - 2C_{13}^2} \quad (16)$$

The anisotropic thermal expansion coefficients shown in Fig. 9 were calculated by substituting in the values for the elastic constants in Table 1.

Knowledge of the thermal expansion anisotropy, in turn, enables an estimate to be made of the anisotropic Grüneisen parameters $\gamma_{G,i}$ using as a generalization Eq. (17), using the Voigt's notation for the thermal expansion coefficient α_j [21],

$$\gamma_{G,i} = \frac{V}{C_P} \sum_{j=1}^6 (c_{ij}) \alpha_j \quad (17)$$

For tetragonal crystal structures symmetry dictates that there are only two independent Grüneisen parameters, in-plane and out of plane, $(\gamma_G)_a$ and $(\gamma_G)_c$, respectively, given by:

$$(\gamma_G)_a = (V/C_P)[(C_{11} + C_{12}) \cdot \alpha_a + C_{13} \cdot \alpha_c] \quad (18)$$

$$(\gamma_G)_c = (V/C_P)(2C_{13} \cdot \alpha_a + C_{33} \cdot \alpha_c) \quad (19)$$

The calculated values are shown in Fig. 10 for each member of the series. For each composition $(\gamma_G)_c$ is larger than $(\gamma_G)_a$, indicating that there is greater anharmonicity along the [001] direction than in the stacking plane. This is consistent with our previous calculations of the electronic structures and bond populations of the $\text{Ln}_2\text{SrAl}_2\text{O}_7$ structure, where it was found that the chemical bonds are different in the rock salt and double perovskite layers, leading to a natural anisotropy of bonding [24].

3.5. Minimum thermal conductivity and anisotropy

The calculation from first principles of the thermal conductivity and its anisotropy for large unit cells is presently computationally prohibitive, since the full phonon spectrum needs to be determined as an essential part of the calculation. However, for high temperature applications it is the value of the minimum conductivity that is of practical importance, since the conductivity decreases with increasing temperature to a limiting value known as the minimum thermal conductivity [4,6,7,9]. In this section we calculate the minimum thermal conductivity and its value parallel and perpendicular to the stacking plane.

According to Cahill, the minimum thermal conductivity can be computed from the transverse and longitudinal sound velocities and the number of atoms per mole of the compound [30]:

$$\kappa_{\min} = \frac{k_B}{2.48} n^{2/3} (v_l + v_{t1} + v_{t2}) \quad (20)$$

Using the acoustic velocities listed in Table 4, the minimum thermal conductivities parallel and perpendicular to the block layers can be evaluated. These are listed in Table 6 and compared with the high temperature values extrapolated from the measured, polycrystalline values [8]. Clearly, Cahill's model underestimates the thermal conductivity by nearly 1 W mK^{-1} . In Fig. 11 the directional dependence of minimum thermal conductivity is plotted for a bulk

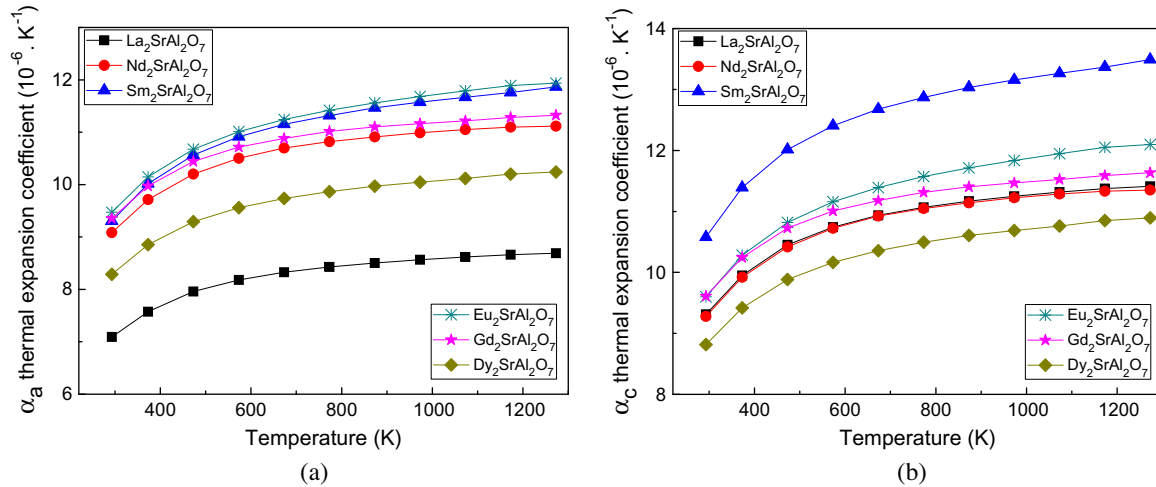


Fig. 9. The calculated linear thermal expansion coefficients α_a and α_c along the [100] and [001] directions for $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds as a function of temperature. (a) α_a along the [100] direction; (b) α_c along the [001] direction. Obviously, thermal expansion in the [001] direction is slightly larger than that in the [100] or [010] direction for most $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds.

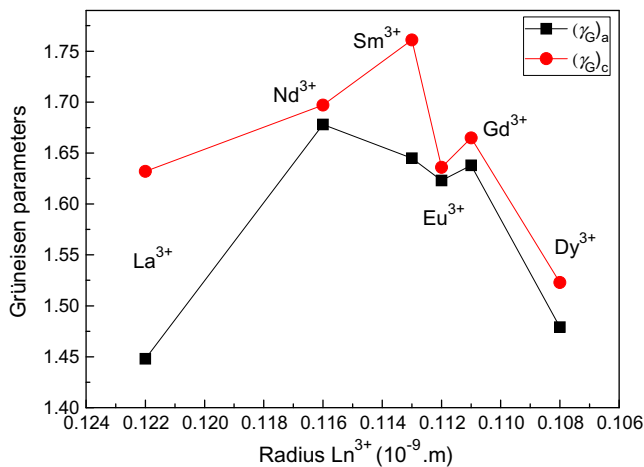


Fig. 10. Dependence of the Grüneisen parameters on the radii of rare earth ions in $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds. Obviously γ_c is larger than γ_a , indicating that the anharmonicity along the [001] direction is stronger than the basal plane and the bonds are relatively weak along the c -axis for most $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds.

polycrystalline material without any texture, along with the minimum thermal conductivities in the [001], [110] and [001] directions, given in Table 6.

Table 6

The minimum thermal conductivity of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ (Ln = La, Nd, Sm, Eu, Gd or Dy) evaluated by Cahill's method.

Species	n (10^{28})	[100] $k_{\text{calc}}^{\text{Min}}$ (W mK $^{-1}$)	[001] $k_{\text{calc}}^{\text{Min}}$ (W mK $^{-1}$)	[110] $k_{\text{calc}}^{\text{Min}}$ (W mK $^{-1}$)	$k_{\text{calc}}^{\text{Min}}$ (W mK $^{-1}$)	$k_{\text{exp}}^{\text{Min}}$ (W mK $^{-1}$)	$k_{1273\text{K}}^{\text{Exp}}$ (W mK $^{-1}$)
$\text{La}_2\text{SrAl}_2\text{O}_7$	7.33	1.55	1.61	1.48	1.51	1.49	3.1
$\text{Nd}_2\text{SrAl}_2\text{O}_7$	7.74	1.59	1.5	1.55	1.55	1.54	2.5
$\text{Sm}_2\text{SrAl}_2\text{O}_7$	7.87	1.56	1.55	1.53	1.53	1.59	2.6
$\text{Eu}_2\text{SrAl}_2\text{O}_7$	7.91	1.55	1.54	1.53	1.52	1.54	2.4
$\text{Gd}_2\text{SrAl}_2\text{O}_7$	8.09	1.55	1.54	1.53	1.55	1.60	2.3
$\text{Dy}_2\text{SrAl}_2\text{O}_7$	8.02	1.54	1.64	1.51	1.53	1.59	2.3

^a From Wan et al. [8].

4. Discussion and conclusions

The results of the calculations clearly indicate that the elastic and thermal properties of the rare earth strontium aluminate $\text{Ln}_2\text{SrAl}_2\text{O}_7$ series of compounds are crystallographically anisotropic, but weakly so. Reflecting the crystal structure of the unit cell, which consists of a periodic stacking of a double perovskite block and a rock salt block, the properties perpendicular to the stacking plane are different from those in the stacking plane. The anisotropies are found to be relatively insensitive to the particular rare earth ion in the compound, despite systematic variations in the lattice parameter and unit cell volume [10]. The elastic constants and elastic moduli are typical of many oxides, such as zirconia, but the thermal expansion coefficients are larger. The bonding anisotropy, reflected in the elastic constant anisotropy, leads to anisotropy of the thermal expansion coefficients and, in turn, leads to anisotropy in the Grüneisen parameter and to anisotropy in the high temperature limit of thermal conductivity.

The high temperature stability of the rare earth strontium aluminates suggests a comparison between their calculated properties with those of yttria-stabilized zirconia (8YSZ), the current material of choice for thermal barrier

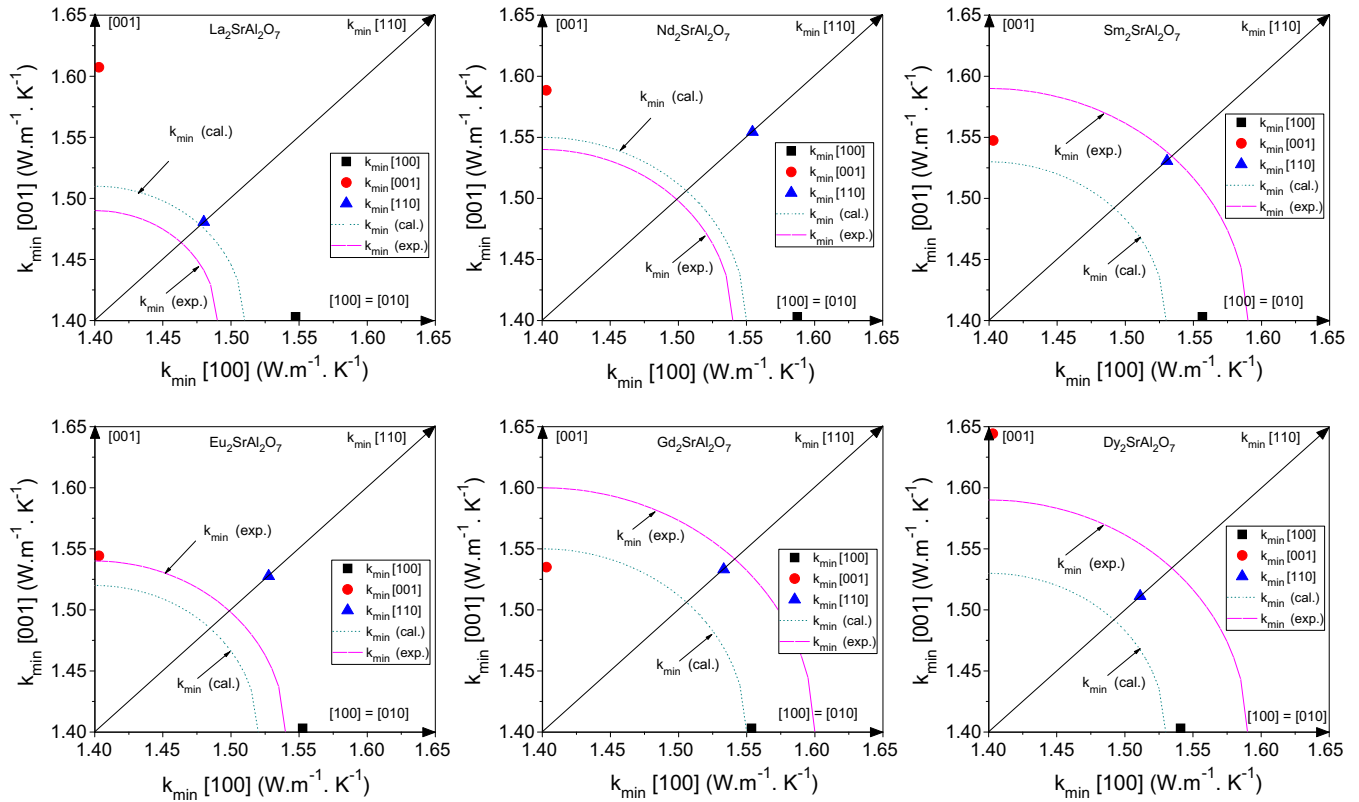


Fig. 11. The minimum thermal conductivities along different principle directions of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$ or Dy) evaluated using Cahill's equation are compared with the experimental results measured using an ultrasonic instrument (ultrasonic pulser/receiver model 5900 PR, Panametrics, Waltham, MA).

coatings. The calculated and measured thermal conductivities of all the members of the rare earth strontium aluminate series are comparable with that of fully dense 8YSZ, which is approximately 2.3 W m K^{-1} [4,31]. On the other hand, the volumetric thermal expansion coefficients are all larger than that of 8YSZ, which averages $1.06 \times 10^{-5} \text{ K}^{-1}$ between room temperature and 1073 K. This is a significant difference, since the thermal expansion mismatch between 8YSZ and single crystal nickel-based superalloys is a major factor limiting the life of thermal barrier coatings. The thermal expansion coefficients of second generation superalloys increases from $1.2 \times 10^{-5} \text{ K}^{-1}$ at room temperature up to $1.8 \times 10^{-5} \text{ K}^{-1}$ at 1400 K, so the larger thermal expansion of the $\text{Sm}_2\text{SrAl}_2\text{O}_7$ compound makes it particularly attractive, especially as it is amongst the least anisotropic.

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Appendix A. Anisotropy parameters

The universal anisotropic index (A^U) and percent anisotropies (A_B and A_G) can be written as

$$A^U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6 \geq 0 \quad (\text{A.1})$$

$$\begin{cases} A_B = \frac{B_V - B_R}{B_V + B_R} \\ A_G = \frac{G_V - G_R}{G_V + G_R} \end{cases} \quad (\text{A.2})$$

For isotropic structures the Voigt and Reuss approximations should give the same values for B and G, respectively. Thus all of the indices in Eqs. (A.1) and (A.2) are zero. Deviations from zero indicate anisotropy. In Xiao et al. [23], the shear anisotropic factors A_1 and A_2 are defined as

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \quad (\text{A.3})$$

$$A_2 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}} \quad (\text{A.4})$$

The results are shown in Table 5. It is found that $\text{Gd}_2\text{SrAl}_2\text{O}_7$ has the smallest A^U value among $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds. The elastic moduli of this compound are not strongly dependent on different orientations, and the calculated A_G , A_1 and A_2 values support this conclusion. The calculated A_G for $\text{Nd}_2\text{SrAl}_2\text{O}_7$ and $\text{Eu}_2\text{SrAl}_2\text{O}_7$ are zero,

as expected, because the Voigt and Reuss approximations predict the same values for the shear modulus. For the other $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds A_G has a very small value, indicating that these compounds do not show strong anisotropy in shear modulus. It seems that the elastic anisotropy parameters of $\text{La}_2\text{SrAl}_2\text{O}_7$ are slightly different from those of other $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds; this behavior is possibly related to the empty $4f$ orbitals of La. Although A_G , A_1 and A_2 all determine the anisotropy of the shear modulus, the values of A_1 and A_2 are quite different from A_G . The calculated A_1 and A_2 values seem to support the hypothesis that the shear modulus of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds has a strong directional dependence. The universal anisotropic index (A^U) is a better indicator than other indices, which can provide unique and consistent results for the mechanical anisotropic properties of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds. This can be clearly seen in Table 5. When A^U is large the other calculated anisotropic indices are also large, and vice versa.

Appendix B. Graphical representation of the crystallographic dependence of the elastic moduli

For tetragonal crystals [25] the elastic moduli are related to the direction cosines, l_i ,

$$\frac{1}{B} = (S_{11} + S_{12} + S_{13})(l_1^2 + l_2^2) + (2S_{13} + S_{33})l_3^2 \quad (\text{B.1})$$

$$\frac{1}{E} = S_{11}(l_1^4 + l_2^4) + (2S_{13} + S_{44})(l_1^2 l_3^2 + l_2^2 l_3^2) + S_{33}l_3^4 + (2S_{12} + S_{66})l_1^2 l_2^2 \quad (\text{B.2})$$

Substituting the relationships of the direction cosines in spherical coordinates with respect to θ and φ into Eqs. (B.1) and (B.2) we obtain the equations used to plot the anisotropic mechanical properties in three dimensions.

$$\frac{1}{B} = (S_{11} + S_{12} + S_{13})\sin^2 \theta + (2S_{13} + S_{33})\cos^2 \theta \quad (\text{B.3})$$

$$\begin{aligned} \frac{1}{E} = & S_{11}[\sin^4 \theta (\cos^4 \varphi + \sin^4 \varphi)] + (2S_{13} + S_{44}) \\ & \times \sin^2 \theta \cos^2 \theta + S_{33} \cos^4 \theta + (2S_{12} + S_{66}) \\ & \times \sin^4 \theta \cos^2 \varphi \sin^2 \varphi \end{aligned} \quad (\text{B.4})$$

Two planar projections on the (100) and (001) crystal planes are illustrated for the Young's and bulk moduli of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds, respectively. The analytical solutions of the projections of B and E for each compound can be derived from Eqs. (B.3) and (B.4). Some results are shown below.

B.1. The (001) plane

$$\begin{cases} B_{[010]} = \frac{\sin \varphi}{(S_{11} + S_{12} + S_{13})} \\ B_{[100]} = \frac{\cos \varphi}{(S_{11} + S_{12} + S_{13})} \end{cases} \quad (\text{B.5})$$

The contour is a circle and $B_{[010]}$ and $B_{[100]}$ satisfy $(B_{[010]})^2 + (B_{[100]})^2 = B^2$, consistent with the bulk moduli being isotropic in the stacking plane. Similarly, for the Young's modulus the results are

$$\begin{cases} E_{[100]} = \frac{\cos \varphi}{S_{11}(\cos^4 \varphi + \sin^4 \varphi) + (2S_{12} + S_{66})\cos^2 \varphi \sin^2 \varphi} \\ E_{[010]} = \frac{\sin \varphi}{S_{11}(\cos^4 \varphi + \sin^4 \varphi) + (2S_{12} + S_{66})\cos^2 \varphi \sin^2 \varphi} \end{cases} \quad (\text{B.6})$$

B.2. The (100) plane

$$\begin{cases} B_{[010]} = \frac{\sin \theta}{(S_{11} + S_{12} + S_{13})\sin^2 \theta + (2S_{13} + S_{33})\cos^2 \theta} \\ B_{[001]} = \frac{\cos \theta}{(S_{11} + S_{12} + S_{13})\sin^2 \theta + (2S_{13} + S_{33})\cos^2 \theta} \end{cases} \quad (\text{B.7})$$

$$\begin{cases} E_{[010]} = \frac{\sin \theta}{S_{11}\sin^4 \theta + (2S_{13} + S_{44})\sin^2 \theta \cos^2 \theta + S_{33}\cos^4 \theta} \\ E_{[001]} = \frac{\cos \theta}{S_{11}\sin^4 \theta + (2S_{13} + S_{44})\sin^2 \theta \cos^2 \theta + S_{33}\cos^4 \theta} \end{cases} \quad (\text{B.8})$$

From Fig. 5 we can see that the bulk moduli of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds show weak anisotropy. Other than $\text{Dy}_2\text{SrAl}_2\text{O}_7$, the surface constructions of the $\text{Ln}_2\text{SrAl}_2\text{O}_7$ compounds are close to a sphere. The projections on the (001) and (100) planes show more details about the anisotropic properties of the bulk modulus. On the basal plane (the (001) plane for tetragonal crystals) the bulk modulus of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ is isotropic, due to the symmetry of tetragonal crystals. On the other hand, on the (001) plane the bulk modulus of $\text{Ln}_2\text{SrAl}_2\text{O}_7$ in the $[110]$ direction is smaller than those in the $[010]$ and $[100]$ directions. Other than for $\text{La}_2\text{SrAl}_2\text{O}_7$, the bulk moduli in the $[100]$ and $[010]$ directions on the (001) crystal plane are comparable with each other. This is consistent with the calculated elastic constants; for example, the difference between C_{11} and C_{33} is found to be small for these compounds. For $\text{La}_2\text{SrAl}_2\text{O}_7$ we find $B_{[001]} > B_{[010]}$, because C_{33} is larger than C_{11} in this case. Projections of the Young's modulus on the (100) and (001) planes show more anisotropic features than the bulk modulus. One can clearly see some butterfly shaped curves for the Young's modulus projected on the (001) plane. Therefore, the Young's modulus has a strong directional dependence on this plane, and the value along the $[100]$ or $[010]$ direction is significantly smaller than that along the $[110]$ direction (Fig. 6). The difference between the two directions for the Young's modulus is estimated to be 100 GPa for $\text{Ln}_2\text{SrAl}_2\text{O}_7$. The longitudinal modulus of the tetragonal crystal class in the $[110]$ direction is calculated as $L_{[110]} = C_{11} + C_{12} + 2C_{66}$, and the Young's modulus $E_{[110]}$ can be related to the longitudinal modulus using $E = \frac{(1+\nu)(1-2\nu)}{(1-\nu)}L$, where ν is the Poisson ratio and L represents the longitudinal modulus along a specific direction. For $\text{Ln}_2\text{SrAl}_2\text{O}_7$ the calculated ν is close to 0.3. The Young's moduli in different directions are simply proportional to L , because $L_{[110]} > L_{[100]} = L_{[010]}$, thus $E_{[110]} > E_{[100]} = E_{[010]}$ is obvious on the (001) plane. A similar analysis can be used to explain the results on the (100) plane.

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