

## Influence of pressure and transition metal ( $T=\text{Fe,Co}$ ) on the lanthanum bare frequency in $\text{LaT}_4\text{Sb}_{12}$

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In this paper we explore, by means of first-principles calculations, the influence of pressure and transition-metal ( $T=\text{Fe,Co}$ ) on the structure and lanthanum bare frequency in  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$ . The guest ion bare frequency decreases almost linearly with the La-Sb distance. Substitution of Fe for Co in the framework structure promotes a reduction in the La bare frequency from around 98 to 76  $\text{cm}^{-1}$  at 0 GPa. Accordingly, the influence of the transition metal on the La bare frequency is thus an indirect effect of the former on the equilibrium La-Sb distance. A pressure increase to 1 GPa changes the guest bare frequency by 3.1  $\text{cm}^{-1}$  and 2.2  $\text{cm}^{-1}$  for  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$ , respectively. The measurable effect of pressure on the La bare frequency and, consequently, on La atomic displacement parameter, points to the possibility of using even moderate pressures to tune the guest rattling mode amplitude and controllably explore the resulting effect on the lattice thermal conductivity of ternary skutterudites and other similar open framework thermoelectric materials.

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### I. INTRODUCTION

In recent years a continued research effort has been focused on skutterudite compounds. These compounds have attracted so much attention due to a variety of electrical and magnetic properties, including superconductivity, metal-insulator transition, and ferromagnetism.<sup>1-3</sup> However, by far most of the interest in these compounds is due to their excellent thermoelectric properties. In fact, some skutterudite compounds have high thermoelectric figures of merit and are pursued as strong candidates for applications in thermoelectric devices.<sup>4-6</sup>

Skutterudites are body-centered-cubic compounds, space group  $Im\bar{3}$ , with a general formula  $\square TX_3$ , where  $T$  is a transition-metal (site  $8c$ :  $1/4,1/4,1/4$ ),  $X$  are pnictide atoms (site  $24g$ :  $0,y,x$ ) and  $\square$  corresponds to a site at the center of a cage formed by the  $TX_3$  framework (site  $2a$ :  $0,0,0$ ), which may be empty (as in the binary skutterudites) or totally/partially filled by rare-earth ions (in ternary or quaternary skutterudites). Figure 1 illustrates the local structure of a ternary skutterudite around the rare-earth ion site. In ternary (or quaternary) skutterudites the rare-earth ion inside the oversized cage rattles around the equilibrium position with large amplitudes. These rattling modes reduce significantly the lattice thermal conductivity of the filled skutterudites, thus improving their thermoelectric efficiency.<sup>4,6-12</sup>

In this work we will focus on two totally filled ternary skutterudites, namely,  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$ . While  $\text{LaFe}_4\text{Sb}_{12}$  can be prepared from the elements, the cobalt antimonide can be obtained only up to a limiting stoichiometry corresponding to  $\text{La}_{0.23}\text{Co}_4\text{Sb}_{12}$ .<sup>8</sup> Besides the end members, the mixed iron and cobalt antimonide  $\text{LaFe}_3\text{CoSb}_{12}$  has been also the subject of previous studies.<sup>9,13,14</sup> Accordingly,  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$  constitute good choices to study the effect on the La bare frequency of substituting iron for cobalt in the skutterudite framework. By bare frequency we refer to the frequency obtained from the variation in total energy as a function of the displacement of the La sublattice

relative to the  $T_4\text{Sb}_{12}$  framework ( $T=\text{Fe,Co}$ ), whose atoms are kept fixed at their equilibrium positions.<sup>15,16</sup> Previous studies have dealt with the bare frequencies of different guest ions in the same framework structure.<sup>15,16</sup> By keeping the same guest ion (i.e., La) while changing only a portion of the atoms in the framework (i.e., substituting Fe for Co) we hope to be able to explore more subtle effects of the guest-host interaction in filled ternary skutterudites.

This paper will proceed as follows: in the next section we present some computational details relevant to the calculations performed with  $\text{LaT}_4\text{Sb}_{12}$ . In Sec. III we present the main results obtained from the density-functional theory (DFT) calculations on  $\text{LaT}_4\text{Sb}_{12}$  concerning the structure, bulk modulus, and La bare frequencies. The paper ends with a discussion on the effect of moderate pressures over the La atomic displacement parameter in  $\text{LaT}_4\text{Sb}_{12}$  and how this could be relevant to explore the relationship between the guest ion rattling mode amplitude and the lattice thermal conductivity in totally and partially filled ternary skutterudites.

### II. COMPUTATIONAL DETAILS

All the calculations were performed in the athermal limit, with the CRYSTAL06 computer code.<sup>17</sup> The crystalline orbitals were each expressed as a sum of atomic-centered Gaussian functions over all equivalent sites in the periodic system. Total energies were evaluated according to density-functional theory with the B3LYP gradient-corrected hybrid exchange-correlation density functional.<sup>18</sup> All-electron basis sets were employed for both lanthanum,<sup>19</sup> cobalt,<sup>20</sup> iron,<sup>21</sup> and antimony.<sup>22</sup> The outermost Gaussian exponents and coefficients for La, Sb, and Co valence basis sets were optimized by minimizing the total energy for  $\text{LaCo}_4\text{Sb}_{12}$ . Exponents and coefficients for the Fe outermost orbitals were optimized by minimizing the total energy for  $\text{LaFe}_4\text{Sb}_{12}$ .<sup>23</sup>

The calculations were performed with the following tolerances (in atomic units) for the evaluation of the infinite

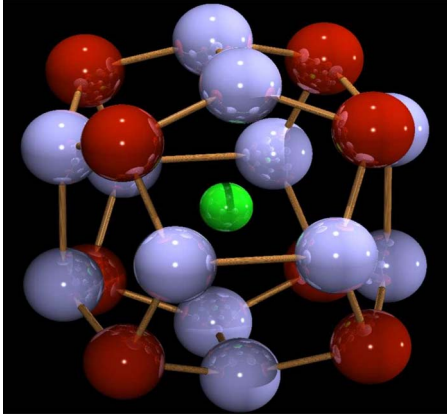


FIG. 1. (Color online) Representation of the  $\text{LaT}_4\text{Sb}_{12}$  local crystal structure around the lanthanum ion (small green sphere), showing the oversized cage formed by the transition-metal ( $T=\text{Fe}, \text{Co}$ —red spheres) and Sb (blue spheres) atoms.

Coulomb and exchange series:  $10^{-12}$  for the exchange overlap, Coulomb overlap, Coulomb penetration, and the first exchange pseudo-overlap; and  $10^{-24}$  for the second exchange pseudo-overlap tolerance.<sup>17</sup> Such tight tolerances were needed in order to reduce the numerical noise in the calculation of the variation in total energy for small displacements of La from its equilibrium position. The Fock matrix has been diagonalized at 45  $k$  points within the irreducible Brillouin zone, corresponding to a shrinkage factor of 6 in the Monkhorst net.<sup>24</sup> The number of  $k$  points in the Gilat net was set to 249, corresponding to a shrinkage factor of 12.<sup>25</sup> To improve convergence, the Anderson's method<sup>26</sup> was employed and the Fock matrix was updated with a mixing of 85% with the previous Fock matrix at each iteration of the self-consistent field procedure.

Full geometry optimization (cell constant and atomic positions) was performed using analytical gradients combined with a quasi-Newton optimization scheme.<sup>17</sup> Convergence was achieved when the maximum gradient, the root-mean-square (rms) gradient, the maximum atomic displacement and the rms atomic displacement on all atoms become less than 0.000009 a.u., 0.000006 a.u., 0.000018 a.u., and 0.000012 a.u., respectively. To reduce the influence of numerical noise, all the calculations were performed keeping the same set of indexed bielectronic integrals selected from a reference geometry. The tolerance for energy convergence was set to  $10^{-7}E_h$ .

Bulk moduli ( $B_0$ ) and their pressure first derivative ( $B'_0$ ) for  $\text{LaCo}_4\text{Sb}_{12}$  and  $\text{LaFe}_4\text{Sb}_{12}$  were obtained from the fitting of the Murnaghan equation of state (EOS) to total energy versus unit-cell volume curves.<sup>27</sup> The deformations used to generate the strained lattices were limited to  $\pm 8\%$  of the optimized lattice parameters. Atomic positions were fully relaxed after each deformation of the unit cell. The bulk modulus of the cage around the La ion in  $\text{LaT}_4\text{Sb}_{12}$  was calculated by fitting a Murnaghan EOS to the cage volume versus pressure data. The cage volume was calculated from the optimized atomic positions for each lattice parameter using the program IVTON.<sup>28</sup> The same procedure was applied for the calculation of the bulk moduli of  $\text{FeSb}_6$  and  $\text{CoSb}_6$  first-coordination polyhedra.

TABLE I. Lattice parameter and Sb atomic position free parameters (site  $24g=0,y,z$ ) for some filled skutterudite antimonides. The figures in parenthesis are the uncertainties in the last significant digit.

Compound	$a_0$ (Å)	$y$	$z$
$\text{LaFe}_4\text{Sb}_{12}$ (This work)	9.2433	0.3380	0.1616
$\text{LaCo}_4\text{Sb}_{12}$ (This work)	9.2654	0.3335	0.1569
$\text{LaFe}_3\text{CoSb}_{12}$ <sup>a</sup> [Exp. (Ref. 9)]	9.0971(6)	0.33678(9)	0.16021(8)
$\text{LaFe}_4\text{Sb}_{12}$ <sup>b</sup> [Exp. (Ref. 29)]	9.1395(2)	0.33696(6)	0.16042(5)
$\text{LaFe}_4\text{Sb}_{12}$ <sup>b</sup> [Exp. (Ref. 30)]	9.1957(8)	0.3335(9)	0.1572(5)

<sup>a</sup>Actual composition:  $\text{La}_{0.743}\text{Fe}_{2.74}\text{Co}_{1.26}\text{Sb}_{12}$ . Lattice parameter at 296 K.

<sup>b</sup>Lattice parameter at 296 K.

The harmonic bare frequencies of La in  $\text{LaT}_4\text{Sb}_{12}$  at 0 and 1 GPa were obtained from the variation in total energy for small displacements of the La ion along the unit-cell trigonal axis. La displacements were constrained to be within  $\pm 0.4$  Å of the origin. In these calculations the framework atoms were kept fixed at their equilibrium positions, both at 0 and at 1 GPa.

### III. RESULTS AND DISCUSSION

Full optimization of the  $\text{LaT}_4\text{Sb}_{12}$  crystal structure was obtained by minimizing the total energy in the athermal limit, at zero pressure, as a function of three parameters, namely, the lattice parameter and  $y$  and  $z$  Sb atomic position free parameters. Table I shows the optimized parameters along with a comparison with some experimental results for similar skutterudites. The slight overestimation of the lattice parameter is expected according to the general trend observed with DFT calculations.<sup>31</sup>

After performing full optimization of the  $\text{LaT}_4\text{Sb}_{12}$  crystal structures at zero pressure, the Sb atomic position was optimized for a series of fixed lattice parameters. Figure 2 shows the variation in total energy versus primitive cell volume for  $\text{LaCo}_4\text{Sb}_{12}$  and  $\text{LaFe}_4\text{Sb}_{12}$ . The fitting of a Murnaghan equation of state to the data in Fig. 2 yielded the bulk modulus and its pressure derivative, at zero pressure, for  $\text{LaCo}_4\text{Sb}_{12}$  and  $\text{LaFe}_4\text{Sb}_{12}$ , as given in Table II. The values for  $B_0$  and  $B'_0$  obtained from density-functional theory calculations with the B3LYP hybrid functional are well within the range of recent experimental and theoretical results for similar filled skutterudite antimonides. Figure 3 shows the dependence with pressure of Sb atomic position  $y$  and  $z$  free parameters for  $\text{LaT}_4\text{Sb}_{12}$ .

The crystal structure of skutterudites such as  $\text{LaT}_4\text{Sb}_{12}$  has been represented in the literature either as a simple cubic transition-metal unit cell with four-membered Sb rings along the [100], [010], and [001] crystallographic directions or, alternatively, as a framework structure consisting of corner-sharing  $\text{TSb}_6$  octahedra, with La occupying the interstitial site  $2a$ . It has been pointed out, however, that at least for  $\text{CoSb}_3$ , the shorter Sb-Sb bonds in the four-membered rings

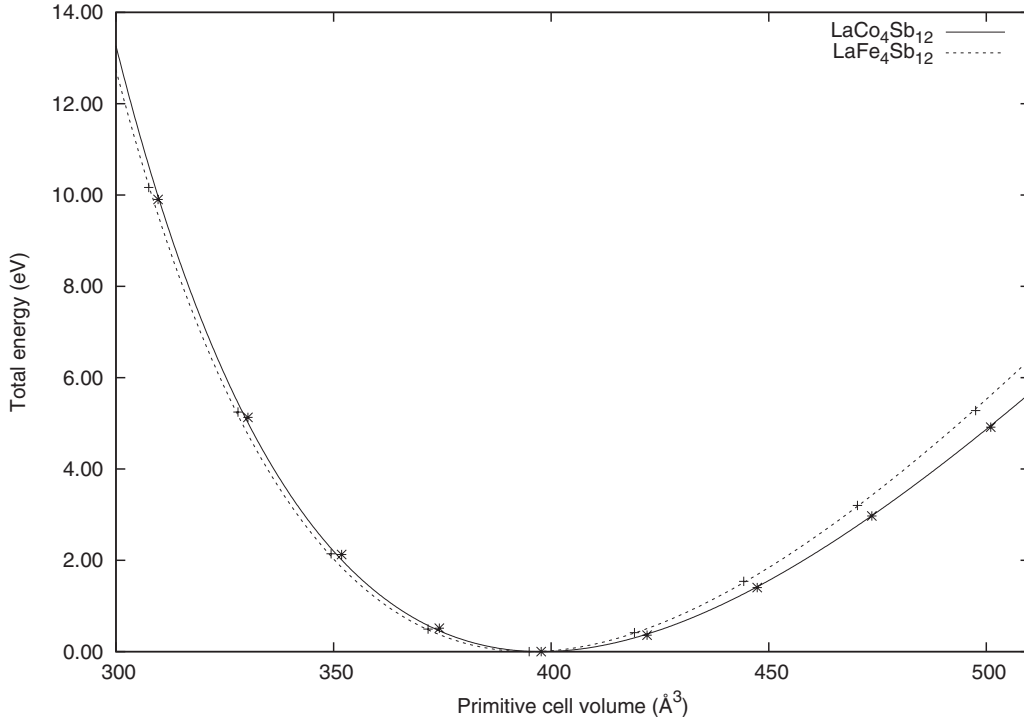


FIG. 2. Variation in total energy with primitive cell volume for  $\text{LaT}_4\text{Sb}_{12}$ . Dotted and full lines represent the Murnaghan EOS fitted to energy vs volume data for  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$ , respectively.

and the Co-Sb bonds in the  $\text{CoSb}_6$  octahedra are qualitatively similar and, thus, neither of the above mentioned representations of the skutterudite structure could be regarded as fully compatible with recent theoretical and experimental results concerning the electronic charge distribution in  $\text{CoSb}_3$ .<sup>34,35</sup> This issue will be further explored here by observing the evolution of  $\text{LaT}_4\text{Sb}_{12}$  crystal structures under isotropic stress.

In Table III we compare the bulk moduli for the unit cell, the cage around La, and the  $\text{TSb}_6$  polyhedra in  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$ . The volume of the cage formed by Fe, Co and Sb atoms around La in the skutterudite structure and the  $\text{TSb}_6$  polyhedral volume were calculated from the parameters of the optimized structures (at each pressure) using IVTON.<sup>28</sup> To allow a better comparison with the bulk moduli previ-

TABLE II. Bulk modulus ( $B_0$ ) and its pressure derivative ( $B'_0$ ), at zero pressure, for some filled skutterudite antimonides. The figures in parenthesis are the uncertainties in the last significant digit.

Compound	$B_0$ (GPa)	$B'_0$
$\text{LaFe}_4\text{Sb}_{12}$ (This work)	99.0	5.0
$\text{LaCo}_4\text{Sb}_{12}$ (This work)	93.3	5.3
$\text{LaFe}_4\text{Sb}_{12}$ [ <i>Ab initio</i> (Ref. 32)]	101.4	
$\text{LaFe}_3\text{CoSb}_{12}$ [Exp. (Ref. 12)]	89(2)	3.5(5)
$\text{CeFe}_4\text{Sb}_{12}$ [Exp. (Ref. 33)]	88(4)	4(1)
$\text{CeRu}_4\text{Sb}_{12}$ [Exp. (Ref. 33)]	97(5)	8(1)
$\text{LaRu}_4\text{Sb}_{12}$ [Exp. (Ref. 33)]	98(4)	8(1)
$\text{PrRu}_4\text{Sb}_{12}$ [Exp. (Ref. 33)]	111(5)	5(1)

ously calculated for the unit cell of the iron and cobalt skutterudites, the fittings of the Murnaghan EOS to the pressure-volume data for the skutterudite cages and  $\text{TSb}_6$  polyhedra were performed keeping the bulk modulus pressure derivative  $B'_0$  fixed at the values given in Table II for the unit-cell EOS. If  $B'_0$  is allowed to vary in the fitting of the cage's EOS,  $B_0$  converges to 103.0 GPa and 103.1 GPa for  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$ , respectively, while  $B'_0$  converges to 5.1 for both compounds. It is noteworthy that the cage around La is slightly less compressible than the whole framework structure for both  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$ . This observation leads to the conclusion that compression of the transition-metal first-coordination polyhedra is also involved in the mechanism responsible for reducing the skutterudite unit-cell volume upon pressure increase. In fact, the greater compressibility of the  $\text{LaCo}_4\text{Sb}_{12}$  unit cell can be ascribed to the greater compressibility of the  $\text{CoSb}_6$  octahedra, which is approximately 10% more compressible than  $\text{FeSb}_6$ . The polyhedral bulk modulus for  $\text{FeSb}_6$  remains greater than that for  $\text{CoSb}_6$  even if  $B'_0$  is allowed to vary (101.7 GPa and 94.7 GPa, respectively, with  $B'_0$  converging to 5.4 for both iron and cobalt first-coordination polyhedra).

The reason why  $\text{FeSb}_6$  octahedra are more stiff than  $\text{CoSb}_6$  in the ternary  $\text{LaT}_4\text{Sb}_{12}$  skutterudites can be figured out by analyzing how bond lengths and bond angles vary with pressure. Table IV gives the equilibrium bond distances and intrapolyhedral and interpolyhedral bond angles and their pressure derivatives at zero pressure. There are two distinct intrapolyhedral Sb-T-Sb ( $T=\text{Fe, Co}$ ) angles which are related by symmetry as  $90^\circ \pm \Delta$ , and just one of them is presented in Table IV. It is noteworthy that, while the Fe,Co-Sb bond compressibility is almost the same, the in-

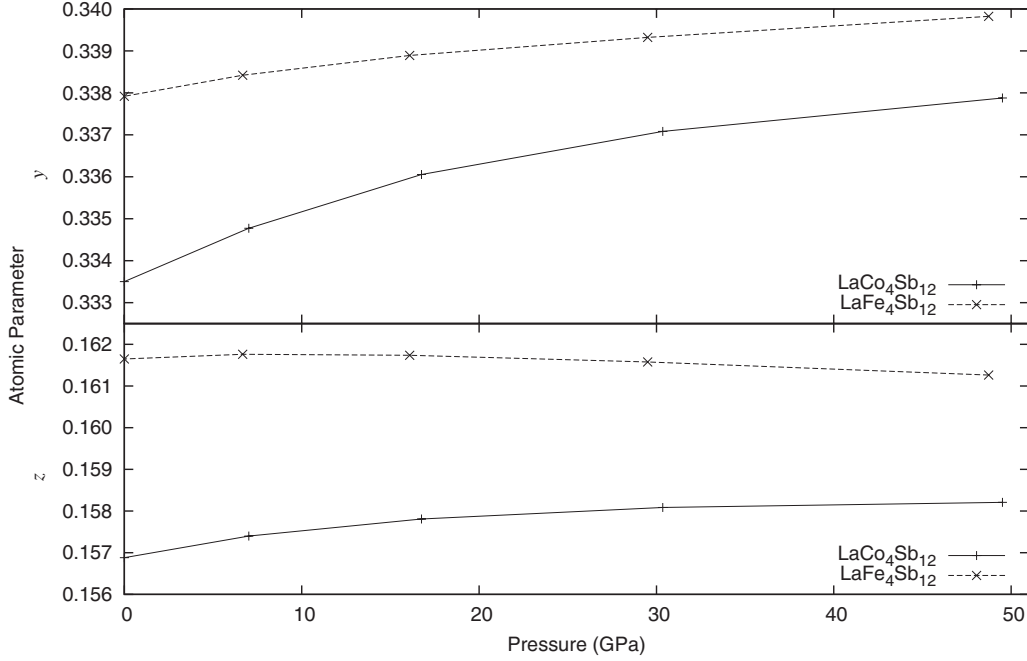


FIG. 3. Pressure dependence of Sb  $y$  and  $z$  atomic position free parameters for  $\text{LaT}_4\text{Sb}_{12}$ .

trapolyhedral Sb-Co-Sb angle derivative with respect to pressure is almost three times greater than that for Sb-Fe-Sb, contributing to make the  $\text{CoSb}_6$  octahedra more compressible than  $\text{FeSb}_6$  and, thus,  $\text{LaCo}_4\text{Sb}_{12}$  more compressible than  $\text{LaFe}_4\text{Sb}_{12}$ .

Interestingly, bond compressibilities for  $T$ -Sb are always intermediate between those of the two distinct Sb-Sb bonds. In other words, the transition-metal bond to Sb is stiffer (weaker) than the longer (shorter) Sb-Sb bond, in accordance with the conclusions drawn from previous theoretical and experimental studies on the electronic charge distribution in  $\text{CoSb}_3$ .<sup>34,35</sup>

Crystal symmetry imposes some constraints on the pressure dependence of the skutterudite lattice parameter and bond lengths. In fact, in terms of the lattice parameter  $a$  and the two Sb atomic position free parameters  $y$  and  $z$ , the two distinct Sb-Sb distances in the skutterudite structure are given by  $r_1 = 2az$  and  $r_2 = a(1 - 2y)$ , while the  $T$ -Sb distance is given by  $r_3 = \frac{a}{4}[1 + (1 - 4y)^2 + (1 - 4z)^2]^{1/2}$ . For both  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$ ,  $r_2 > r_1$ . Using this notation, the skutterudite lattice parameter first derivative with respect to the pressure can be written as

$$a' = [(a - 2r_1)r_1' + (a - 2r_2)r_2' + 8r_3r_3'] \left( \frac{3}{2}a - r_1 - r_2 \right)^{-1}, \quad (1)$$

where the prime stands for pressure derivative. Bond lengths and bond compressibilities given in Table IV satisfy the above relationship within 1%.

We now turn our attention to the main point of this paper, i.e., the effect of pressure and the transition metal on the La bare frequency in the ternary skutterudites  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$ . The variation in total energy as a function of La displacement from its equilibrium position in  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$  is shown in Fig. 4. The calculations were performed for  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$  crystal structures optimized for lattice parameters corresponding to 0 and 1 GPa. Deviation from harmonic behavior is more apparent in the skutterudite with iron, both at 0 and at 1 GPa. Figure 4 also shows a comparison of the variation in total energy as a function of La displacement for  $\text{LaCo}_4\text{Sb}_{12}$  and  $\text{LaFe}_4\text{Sb}_{12}$  both at 0 GPa and at 1 GPa. Table III gives the La harmonic bare frequencies calculated from the fitting of fourth-order

TABLE III. Comparison between the bulk moduli at zero pressure for the unit cell, the transition-metal ( $T=\text{Fe, Co}$ ) first coordination polyhedra and the cage around La for  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$ . In the fitting of pressure-volume data, the bulk modulus pressure derivative at zero pressure ( $B'_0$ ) was kept fixed at the values found for the unit cell, i.e., 5.0 and 5.3 for  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$ , respectively. Also presented in this table are the La bare frequencies calculated for  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$  at 0 and 1 GPa.

Compound	Bulk modulus (GPa)			La bare frequency ( $\text{cm}^{-1}$ )	
	Unit cell	$T\text{Sb}_6$	Cage	0 GPa	1 GPa
$\text{LaFe}_4\text{Sb}_{12}$	99.0	105.7	103.5	75.6	78.7
$\text{LaCo}_4\text{Sb}_{12}$	93.3	95.7	104.9	97.9	100.1

TABLE IV. Bond lengths (Sb-Sb and  $T$ -Sb,  $T=Fe, Co$ , in angstrom) and angles (intrapolyhedral Sb- $T$ -Sb,  $T=Fe, Co$ , and interpolyhedral Sb-Sb-Sb, in degrees) at zero pressure for  $LaFe_4Sb_{12}$  and  $LaCo_4Sb_{12}$ . The figures in parenthesis are bond compressibilities ( $-d \ln r/dP$ , in units of  $10^{-3} \text{ GPa}^{-1}$ ) and derivatives of the angles with respect to pressure (in units of  $10^{-4} \text{ degrees GPa}^{-1}$ ), at zero pressure.

Compound	Sb-Sb	$T$ -Sb	Sb- $T$ -Sb	Sb-Sb-Sb
$LaFe_4Sb_{12}$	2.989(3.2)	2.582(3.3)	84.4(-240)	46.0(-35)
	2.997(3.9)			51.2(-210)
				109.42(<1)
$LaCo_4Sb_{12}$	2.907(2.9)	2.590(3.5)	86.1(-710)	45.1(5)
	3.085(5.0)			51.8(-470)
				109.37(<1)

polynomial to the *ab initio* data shown in Fig. 4. All data exhibited in Fig. 4 for  $LaT_4Sb_{12}$  could be well fitted by fourth-order polynomial (within 1.5 meV) both at 0 and at 1 GPa. Despite the calculations were performed in different approximations [generalized gradient approximation versus local-density approximation (LDA)], it is worth noting that the La bare frequency calculated for  $LaFe_4Sb_{12}$  at zero pressure is in very good agreement with the LDA calculations by Feldman *et al.*<sup>15</sup> The fitting uncertainties for the bare frequencies quoted in Table III were always less than  $1 \text{ cm}^{-1}$ .

The lattice parameter, Sb atomic position free parameters and bulk modulus do not change appreciably with the substitution of Fe for Co in  $LaT_4Sb_{12}$ . Indeed, the lattice parameter and Sb atomic position free parameters vary by less than 1% and, at most, 3%, respectively, while the bulk modulus varies by 6%. On the other hand, when Fe substitutes for Co in  $LaT_4Sb_{12}$  the La bare frequency diminishes by approximately 23%. Thus, despite the substitution of atoms in the cage does not significantly alters the crystal structure and bulk modulus, it has a very pronounced effect on La bare frequency.

In order to verify whether the La bare frequency depends on the particular La- $T$  ( $T=Fe, Co$ ) interaction or it is purely a result of the local structure of the confinement cage around La, calculations were performed using the optimized lattice parameter and Sb atomic position for  $LaFe_4Sb_{12}$  and substituting Co for Fe. In this way we were able to check the influence of the transition metal while keeping the same structure-related parameters. The bare frequency for  $LaCo_4Sb_{12}$  with the lattice parameter and Sb atomic position optimized for  $LaFe_4Sb_{12}$ ,  $77.2 \text{ cm}^{-1}$ , result very close to the value obtained for  $LaFe_4Sb_{12}$ . Furthermore, the analysis of the results quoted in Table III reveals that the guest ion bare frequency in  $LaT_4Sb_{12}$  does not varies monotonically either with the cage volume or the La-Co distance. Instead, it does decreases almost linearly with the La-Sb distance (which is shorter than the La-Co distance for both  $LaT_4Sb_{12}$ ). The influence of the transition metal on the La bare frequency is, therefore, indirect: the metal (in our case, Co or Fe) influences the skutterudite equilibrium lattice parameter and Sb atomic position, so determining the La-Sb distance and, thus, the La bare frequency. The influence of the Sb atoms from

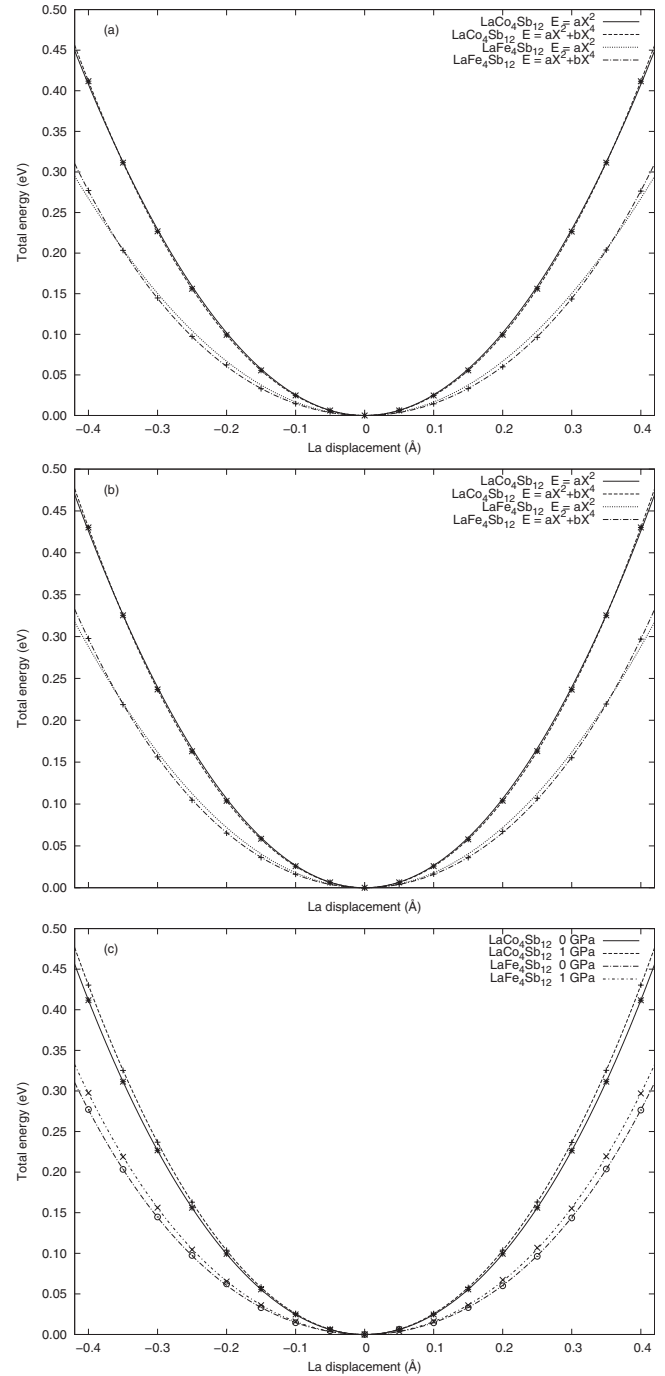


FIG. 4. Variation in total energy vs lanthanum displacement for  $LaT_4Sb_{12}$  (a) at 0 GPa and (b) at 1 GPa. The lines represent second- and fourth-order polynomial fitting curves. Observe the greater anharmonicity of the potential in the iron skutterudite at both pressures. In (c), variation in total energy vs lanthanum displacement in  $LaT_4Sb_{12}$  at 0 and 1 GPa. Lines represent fourth-order polynomial fitting curves.

the cage on the La bare frequency, pointed out by the frozen-phonon calculations described in this work, is consistent with recent dynamical studies which have pointed out strong evidence of a coupling between cage vibrational modes and the rattler ion in  $LaFe_4Sb_{12}$ .<sup>36</sup>

Besides the transition metal, pressure also has a marked effect on the La bare frequency. This is indeed the case, as the results quoted in Table III show that even a moderate pressure increase of 1 GPa has a measurable effect on the La bare frequency, which changes by  $3.1 \text{ cm}^{-1}$  and  $2.2 \text{ cm}^{-1}$  for  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$ , respectively. Moreover, the increase in guest bare frequency with pressure is about 40% greater for the iron skutterudite. This is consistent with the above observation relating the La bare frequency to the La-Sb distance. In fact, at zero pressure, the modulus of the La-Sb distance pressure derivative is about 20% greater for  $\text{LaFe}_4\text{Sb}_{12}$ , leading to a greater variation in the rattler bare frequency with pressure in the iron skutterudite.

The effect of pressure on the rattling of La inside the  $\text{LaT}_4\text{Sb}_{12}$  cages may also affect the lanthanum's isotropic atomic displacement parameter (ADP). From the La bare frequencies, the isotropic ADP for lanthanum can be estimated as<sup>37,38</sup>

$$U_{iso} = \langle u^2 \rangle = \frac{h}{8\pi^2 \mu \nu} \coth\left(\frac{h\nu}{2kT}\right) \quad (2)$$

or, for  $h\nu \gg 2kT$ ,

$$U_{iso} = \langle u^2 \rangle = \frac{h}{8\pi^2 \mu \nu}, \quad (3)$$

where  $\nu$  can be taken as the La bare frequency. The above expression yields  $\langle u^2 \rangle = 0.00162 \text{ \AA}^2$  and  $0.00124 \text{ \AA}^2$  for  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$ , respectively, at zero pressure. Our estimate agrees well with Chakoumakos *et al.*, who estimated  $0.0022(2) \text{ \AA}^2$  as an upper limit for the thermal contribution to La atomic displacement parameter at 0 K, from the analysis of the temperature dependence of lanthanum isotropic displacement parameter in  $\text{LaFe}_3\text{CoSb}_{12}$ .<sup>9</sup> Calculations of La displacement parameter in  $\text{LaT}_4\text{Sb}_{12}$  for the equilibrium structures at 1 GPa yields  $0.00154 \text{ \AA}^2$  and  $0.00121 \text{ \AA}^2$  for  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$ , respectively. This represents a variation of almost 5% for the lanthanum's ADP in the iron skutterudite over a pressure increase of only 1 GPa, relatively easy to access experimentally.

The sensibility of lanthanum's ADP on the external pressure suggests an interesting experimental approach to investigate how the amplitude of the guest rattling modes influ-

ences the lattice thermal conductivity of ternary skutterudites. In fact, measurements of the heat conductivity of filled skutterudites under a moderate pressure of 1 GPa or even of a few gigapascals seems feasible and could be performed along with x-ray and/or neutron diffraction to allow the simultaneous determination of the guest ion ADP. Our results suggest that pressure should be a very efficient way to controllably tune the amplitude of guest ion rattling modes, thus enabling the exploration of the resulting effect on the ternary skutterudite lattice thermal conductivity.

#### IV. CONCLUSIONS

In this work we have reported on first-principles calculations of the crystal structure, bulk modulus, and La bare frequencies in the antimonides skutterudites  $\text{LaFe}_4\text{Sb}_{12}$  and  $\text{LaCo}_4\text{Sb}_{12}$ . The lattice parameter and Sb atomic position free parameters optimized at zero pressure are in good agreement with the available experimental data and the bulk moduli are consistent with the values available in the literature for similar antimonides skutterudites. The substitution of iron for cobalt in the cage framework has only a minor effect on lattice parameter, Sb atomic position and bulk modulus. However, the substitution of the transition metal changes considerably the La bare frequency, which was shown to decrease almost linearly with the La-Sb distance. Pressure also has a marked effect on the guest ion bare frequency, particularly for  $\text{LaFe}_4\text{Sb}_{12}$ , which exhibits an increase of almost 5% in the La bare frequency upon a pressure increase of only 1 GPa. The marked effect of pressure on the filler bare frequency (and, consequently, on its atomic displacement parameter) suggests a very effective way to explore the effect of the guest ion rattling amplitude on the lattice thermal conductivity of ternary skutterudites.

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