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Electronic, elastic and phonon properties of the rock-salt LaSb and YSb

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Abstract

The electronic structures and elastic constants of LaSb and YSb are calculated using an *ab initio* pseudopotential scheme within the generalized gradient approximation. In agreement with experimental studies, it has been found that the upper valence bands in LaSb are characterized by Sb-5p and La-5d states. Our calculated elastic constants for LaSb are compared with available experimental data. A linear-response approach to density functional theory is used to derive phonon dispersion curves and the density of states for LaSb and YSb. Our phonon results for LaSb are in good agreement with experimental data. Frequency differences between phonon modes in these materials are discussed in terms of differences involving total mass, reduced mass and the lattice constant.

1. Introduction

LaSb and YSb are currently the subject of much interest in investigations of their structural, electronic and optical properties [1–8]. Neither material has any f-electrons and both can be used as a good non-magnetic counterpart to CeSb and USb, which show anomalous physical properties such as dense Kondo behaviour and complicated magnetic states. Up to now, most experimental and theoretical studies have been concentrated on the structural, electronic and optical properties of LaSb. On the experimental side, the Fermi surface topology of this material has been investigated by several groups [9–11]. Kwon *et al* [12] measured the optical properties of LaSb. The electronic structure of LaSb has been studied using x-ray photoemission spectroscopy [13] and angle-resolved photoemission spectroscopy [14, 15]. Recently, cyclotron resonance measurements have been performed for this material [7]. In contrast, however, relatively less attention has been paid to the properties of YSb. To date, a first-order phase transition for YSb from the NaCl-type structure to a CsCl-type structure has been studied using synchrotron radiation [6]. On the theoretical side, the electronic structures of both materials have been studied by several groups. Band structure calculations using the linear muffin-tin-orbital (LMTO) method [8, 15] have been reported for LaSb, while the electronic structures of

both materials have been calculated using the full-potential augmented plane-wave (FLAPW) method and a generalized gradient approximation of the density-functional theory [1, 16]. In contrast to several theoretical works presented in recent years on the electronic properties of the LaSb and YSb [1, 5, 8, 15, 16], the elastic properties of these materials have been less studied. Very recently, the elastic properties of YSb were investigated using the full-potential augmented plane wave plus local orbital method [2]. On the experimental side, an ultrasonic measurement technique was used to determine the elastic constants of LaSb [17], while Mcwhan *et al* [18] used their experimental phonon spectrum to obtain elastic constants of LaSb. However, these compounds are of great interest to physicists in theoretical and experimental investigations of elastic constants. It is known that elastic properties relate to various fundamental solid-state phenomena, such as interatomic potentials, equations of state and phonon spectra. Moreover, they are also associated with specific heat and thermal expansion. Thus, in this work the elastic constants of LaSb and YSb are investigated using tetragonal and monoclinic strains.

Although considerable progress has been made in the theoretical description of the electronic properties of these materials, no systematic effort has been made to study phonons in these solids. Only the phonon dispersion relations of LaSb have been measured along the [100] and [110] directions [18]. To our knowledge, there have been no theoretical or experimental studies of the full phonon spectrum and density of states of either material. However, it is important to make a thorough investigation of vibrational modes, as these play a significant role in determining various material properties such as phase transition, electron-phonon interactions and transport coefficients. In this paper we report the results of calculations based on density functional theory and density functional perturbation theory. The goals of this study are: (i) to calculate the electronic structure and density of states for LaSb and YSb, (ii) to calculate the elastic constants using tetragonal and monoclinic strains, (iii) to investigate the phonon dispersion curves and density of states for both materials, (iv) to discuss the phonons of these materials in terms of the total mass, reduced mass and lattice constant differences, and (v) to compare the phonon spectra of LaSb with experimental data.

2. Method

The calculations have been performed using density-functional theory within the generalized gradient approximation [19]. The wavefunctions were expanded in a plane-wave basis set with a kinetic-energy cut-off of 60 Ryd. The electron-ion interaction was described by ultra soft pseudopotentials [20]. Brillouin-zone integrations were performed using a $24 \times 24 \times 24$ \mathbf{k} -point mesh.

The elastic constants were obtained by straining the equilibrium lattice at fixed volumes, using volume-conserving strains and then computing the free energy as a function of strain. The primitive vectors \vec{a}_i ($i = 1, 2, 3$) of crystals are transformed to new vectors under the strain by

$$\begin{pmatrix} \vec{a}'_1 \\ \vec{a}'_2 \\ \vec{a}'_3 \end{pmatrix} = \begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \\ \vec{a}_3 \end{pmatrix} \cdot (\vec{I} + \vec{\varepsilon}), \quad (1)$$

where ε is the strain tensor. This relates to the strain vector \mathbf{e} by

$$\mathbf{e} = \begin{pmatrix} e_1 & e_6/2 & e_5/2 \\ e_6/2 & e_2 & e_4/2 \\ e_5/2 & e_4/2 & e_3 \end{pmatrix}. \quad (2)$$

It is well known that a cubic crystal such as the rock-salt structure has only three independent elastic constants, namely C_{11} , C_{12} and C_{44} . Thus, a set of three equations is needed to calculate

these constants. Firstly, the bulk modulus B is determined by a linear combination of the elastic constants:

$$B = \frac{C_{11} + 2C_{12}}{3}. \quad (3)$$

To determine the bulk modulus, we calculated the total energy of the system as a function of crystal volume and then fitted it to Murnaghan's equation of state [21]. The second equation involves applying volume-conserving tetragonal strain [22]

$$\mathbf{e} = (\delta, \delta, (1 + \delta)^{-2} - 1, 0, 0, 0). \quad (4)$$

δ is the stress tensor and the corresponding strain energy is given by

$$E(\delta) = E(0) + 3(C_{11} - C_{12})V_o\delta^2 + O(\delta^3) \quad (5)$$

where $E(0)$ and V_o are the unstrained energy and the volume of the unstrained unit cell respectively. Finally C_{44} can be calculated under the volume-conserving monoclinic strain [22, 23]

$$\mathbf{e} = \left(0, 0, \frac{\delta^2}{(4 - \delta^2)}, 0, 0, \delta\right). \quad (6)$$

The corresponding strain energy is given by

$$E(\delta) = E(0) + \frac{1}{2}C_{44}V_o\delta^2 + O(\delta^4). \quad (7)$$

Using the bulk modulus and the above volume-conserving strains, C_{11} , C_{12} and C_{44} can be calculated. In addition to these strains, these elastic constants can be identified using different strains. C_{11} is calculated under simple [100] strain while $C_{11} + C_{12}$ can be calculated with both of [100] and [010] strains. Finally, C_{44} can be obtained under the simple shear strain. For these strains, the equations are given by

$$E(\delta) = E(0) + \frac{1}{2}C_{11}V_o\delta^2 \quad \mathbf{e} = (\delta, 0, 0, 0, 0, 0) \quad (8)$$

$$E(\delta) = E(0) + (C_{11} + C_{12})V_o\delta^2 \quad \mathbf{e} = (\delta, \delta, 0, 0, 0, 0) \quad (9)$$

$$E(\delta) = E(0) + \frac{1}{2}C_{44}V_o\delta^2 \quad \mathbf{e} = (0, 0, 0, 0, 0, \delta). \quad (10)$$

In this study, we have calculated 41 sets of $\frac{E(\delta) - E(0)}{V_o} - \delta$ by varying δ from -0.02 to 0.02 in steps of 0.001 . Then, we fit these results with a parabola, and the elastic constants are calculated from quadratic coefficients.

We have studied phonon properties using density-functional perturbation theory [24]. Within this scheme, second-order derivatives of the total energy were calculated to obtain the dynamical matrix. A static linear response of the valence electrons was considered in terms of the variation of the external potential corresponding to periodic displacements of the atoms in the supercell. The screening of the electronic system in response to the displacement of the atoms was taken into account in a self-consistent manner. A $(16 \times 16 \times 16)$ \mathbf{k} -point grid was used for sampling the irreducible segment of the Brillouin zone (BZ) for phonon calculations. This \mathbf{k} mesh was found to yield phonon frequencies to within 0.05 THz. We have calculated dynamical matrices at a uniform grid of 8 \mathbf{q} -points in the irreducible segment of the BZ. The dynamical matrices at arbitrary wavevectors can be evaluated by means of a Fourier deconvolution on this mesh.

3. Results

3.1. Structural and electronic properties

The equilibrium lattice constants of LaSb and YSb are calculated to be 6.52 and 6.19 Å, values which compare well with the experimental lattice constants of 6.48 and 6.16 Å [25, 26].

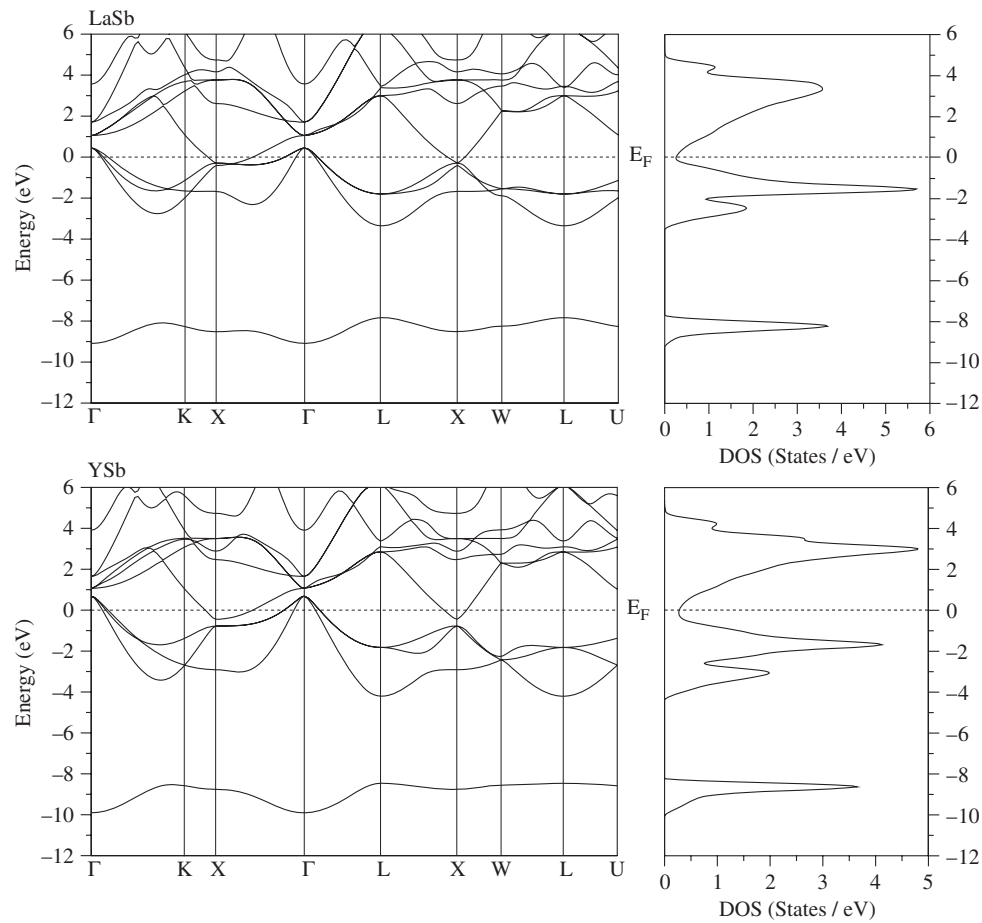


Figure 1. Calculated electronic band structure and density of states for the rock-salt LaSb and YSb. The zero of energy corresponds to the Fermi level.

The bulk modulus of LaSb and YSb are found to be 0.542 and 0.623 Mbar with the help of Murnaghan's equation of state [21]. The electronic band structures and density of states (DOS) for LaSb and YSb are displayed in figure 1. The overall band profiles are found to be similar. This figure shows the metallic nature of these materials. Occupied and unoccupied bands are well separated from each other only along the W–L and L–U symmetry directions, while at least one band crosses the Fermi level along the other symmetry directions. In the case of LaSb, the character of the lowest occupied band shown in this figure is mainly Sb-5s state hybridized with La-6p states. This band gives rise to a peak at about -8.5 eV in the electronic DOS of LaSb. In our calculations, the upper valence band width is found to be 3.5 eV which compares very well with an experimental value of 3.6 eV [13]. The DOS curves reveal two peaks at -2.5 and -1.6 eV in this energy region. The second peak arises from a band that is flat along the W–L direction. This peak can be compared with an experimental peak at -2.0 eV in the work of Baer *et al* [13]. Sb-5p and La-5d states strongly contribute to these peaks, with a small contribution from La-6p states. A similar observation has been made in the experimental studies reported in [9, 14, 15]. The peaks above the Fermi level are mainly composed of La-5d states. Peaks in the DOS of YSb have similar structures to the corresponding peaks in the DOS of LaSb, with La-5d and La-6p states replaced with Y-4d and Y-5p states, respectively.

Table 1. Calculated elastic constants (in Mbar) of LaSb and YSb using volume-conserving strains (see equations (3), (5) and (7)) and simple strains (see equations (8)–(10)), respectively. The obtained results for both materials are also compared with available theoretical and experimental results.

Material	Equations	C_{11}	C_{12}	C_{44}	$C_{11} - C_{12}$
LaSb	(3)–(5)–(7)	1.32	0.15	0.197	1.17
LaSb	(8)–(9)–(10)	1.34	0.14	0.201	1.19
Exp. [17]				0.195	0.74
Exp. from phonon spectrum [18]		1.40	0.20	0.210	1.20
YSb	(3)–(5)–(7)	1.50	0.19	0.248	1.31
YSb	(8)–(9)–(10)	1.50	0.21	0.243	1.29
Theory (GGA) [2]		1.51	0.18	0.210	1.33

3.2. Elastic and vibrational properties

Our calculated elastic constants from both methods (volume-conserving strains and simple strains) are presented in table 1 for both materials. The results from both methods are in good agreement with each other. In particular, our calculated C_{44} for LaSb is in good agreement with the experimental value of 0.195 Mbar [17]. Although our calculated $C_{11} - C_{12}$ values from both methods are similar to each other, these values for LaSb show a difference of nearly 35% from the corresponding experimental value of 0.74 Mbar. However, even different experimental values differ from each other by around 15% (see [27, 28]). While experimental results differ from each other by around 15%, it is expected that our results differ from experimental values up to 35%. In addition to experimental work of Mullen *et al* [17], McWhan *et al* [18] have used their experimental phonon spectrum to obtain elastic constants of LaSb. Their values for C_{11} , C_{44} and C_{12} are 1.4, 0.21 and 0.20 Mbar, respectively. These values compare well with both our *ab initio* results and with those evaluated from the slopes of acoustic branches. Moreover, their $C_{11} - C_{12}$ value of 1.20 Mbar is very close to our value of 1.19 Mbar in table 1. This agreement indicates that new experimental work is needed on the elastic properties of LaSb. To our knowledge, there are no experimental data available for elastic constants of YSb. However, our calculated values are in good agreement with the corresponding results from recent theoretical calculations [2].

The calculated phonon dispersion curves and density of states for LaSb are presented in figure 2(a). In this figure, filled squares indicate the experimental phonon results for LaSb from [18]. The experimental data are well reproduced by our theoretical calculations. The computed transverse and longitudinal acoustic (TA and LA) branches behave normally in the long-wave limit with steep slopes. However, the LA branch lies above the transverse optical (TO) branch along the [110] and [111] symmetry directions at large wavevectors. This picture is found to occur between $\mathbf{q} = \frac{2\pi}{a}(0.500, 0.500, 0.000)$ and $\mathbf{q} = \frac{2\pi}{a}(0.65, 0.650, 0.000)$ along the [110] direction and between $\mathbf{q} = \frac{2\pi}{a}(0.425, 0.425, 0.425)$ and $\mathbf{q} = \frac{2\pi}{a}(0.500, 0.500, 0.500)$ along the [111] direction. Interesting features have been found in the dispersion of the optic branches. Firstly, the longitudinal optic (LO) branch is quite dispersive along the main symmetry directions [100], [110] and [111]. Secondly, a striking feature in the phonon spectrum of LaSb is the inversion of the LO and TO modes in the [110] and [100] directions. Along these symmetry directions, these branches cross each other twice and thus the LO branch has a clear minimum at about $\mathbf{q} = \frac{2\pi}{a}(0.550, 0.550, 0.000)$ and $\mathbf{q} = \frac{2\pi}{a}(0.625, 0.000, 0.000)$ along the [110] and [100] symmetry directions, respectively. Figure 2(a) also shows the phonon density of states (DOS) of LaSb. We have observed an overlap of the acoustic and optical

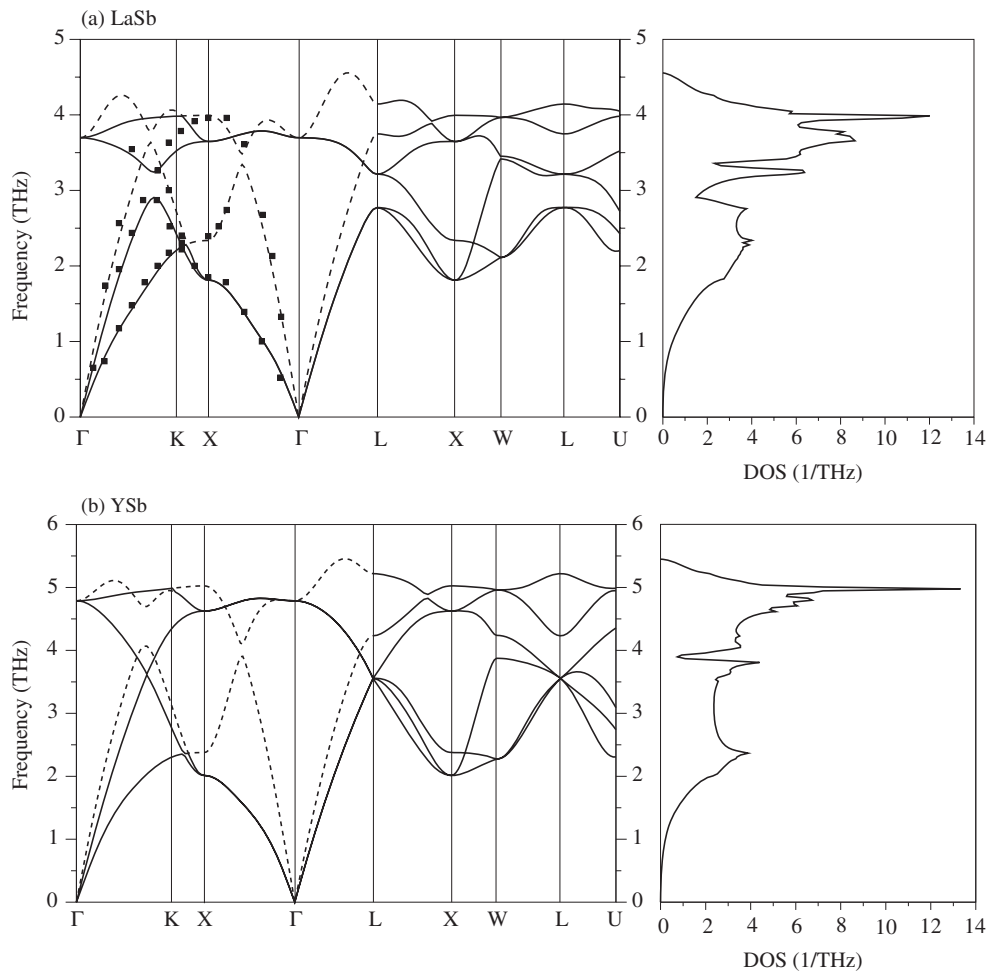


Figure 2. *Ab initio* results of phonon dispersions and density of states for LaSb and YSb in the rock-salt structure. The longitudinal branches are shown by dashed curves along the [110], [100] and [111] directions. Filled squares for LaSb are the experimental data from [18].

phonon branches so that there is no visible gap in the DOS. It can be seen from a critical assessment of this figure that there are four characteristic features in the DOS. There is a broad peak centred at 2.5 THz, and there are three sharp peaks at 3.3, 3.8 and 4 THz. A sharp peak near 3.3 THz is characterized by the lower TO and LA phonon modes due to their crossing along the [110] and [111] symmetry directions. The peaks at 3.8 and 4.0 THz result from optical phonon modes.

The phonon dispersion curves and density of states of YSb (see figure 2(b)) are very similar to those obtained for LaSb. Acoustic and optic phonon modes in both materials have similar atomic displacement patterns to each other. Thus, the frequency differences in the acoustic phonon modes in these materials can be related to the differences in their total masses (M) and lattice constants (a). Due to the nature of optical phonon modes, their frequency differences can be explained in terms of reduced mass (μ) and lattice constant differences between these materials. Thus, the acoustic ($\nu_{ac}(YSb)$) and optic ($\nu_{op}(YSb)$) phonon modes in YSb can be

calculated from the phonon frequencies ($\nu_{\text{ac}}(\text{LaSb})$ and $\nu_{\text{op}}(\text{LaSb})$) in LaSb using the following scaling relations:

$$\begin{aligned}\nu_{\text{ac}}(\text{YSb}) &= \sqrt{\frac{M^{\text{LaSb}}}{M^{\text{YSb}}}} \cdot \frac{a^{\text{LaSb}}}{a^{\text{YSb}}} \nu_{\text{ac}}(\text{LaSb}) \\ \nu_{\text{op}}(\text{YSb}) &= \sqrt{\frac{\mu^{\text{LaSb}}}{\mu^{\text{YSb}}}} \cdot \frac{a^{\text{LaSb}}}{a^{\text{YSb}}} \nu_{\text{op}}(\text{LaSb}).\end{aligned}\tag{11}$$

From the above equations, TA, LA, TO and LO phonon mode frequencies in YSb are estimated to be 2.10, 2.70, 4.50 and 4.90 THz, respectively, at the X point. These values compare very well with our calculated results of 2.01, 2.40, 4.62 and 5.02 THz. This observation indicates that the dynamical behaviour of each of these materials is very similar.

Finally, the elastic constants for LaSb can also be evaluated from the slopes of the acoustic branches in the phonon dispersion curves [29]. Along the [100] direction, we calculated the velocities $V_{\text{T}} = 2.09 \times 10^3 \text{ m s}^{-1}$ and $V_{\text{L}} = 4.71 \times 10^3 \text{ m s}^{-1}$ for the transverse and longitudinal branches, respectively. These sound velocities can be used to obtain the elastic constants of C_{11} and C_{44} . Moreover, C_{12} can be calculated using these values and the velocity of the LA phonon branch along the [110] direction ($V_{\text{LA}} = 4.09 \times 10^3 \text{ m s}^{-1}$). From our phonon spectrum, C_{11} , C_{44} and C_{12} are found to be 1.38, 0.27 and 0.16 Mbar, respectively. These values are in good agreement with our volume-conserving *ab initio* results and the experimental results of McWhan *et al* [18] in table 1.

4. Conclusions

In conclusion, we have presented *ab initio* calculations of electronic, elastic and lattice-dynamical properties of LaSb and YSb in the rock-salt structure. The electronic properties of these materials are found to be similar to each other due to their similar bonding character. In agreement with experimental studies, we have observed that the upper valence bands in LaSb are composed of Sb-5p states which hybridize with La-5d states. In order to calculate elastic constants for LaSb and YSb, we have applied tetragonal and monoclinic strains. Our calculated C_{44} for LaSb shows excellent agreement with its experimental value. In addition to the electronic and elastic properties, we have also calculated the phonon spectrum and density of states for these materials using a linear response approach. The phonon dispersion relations for LaSb fit very well with published experimental data. Finally, it was found that in order to relate the frequency locations of acoustic modes (optical modes) in LaSb to the corresponding modes in YSb, it was necessary to consider scaling of results with the lattice constant and total mass (reduced mass).

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