

Electronic structure and high pressure phase transition in LaSb and CeSb

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Abstract. The electronic structure and high pressure structural phase transition in lanthanum and cerium antimonides have been investigated using the tight binding LMTO method. Calculation of the total energy reveals that the simple tetragonal structure is stable at high pressure for both the compounds. In LaSb, the calculated values of the equilibrium cell volume and the cell volume at which phase transition occurs agree with the experimental results. However, in CeSb, the agreement is not so good. We have also predicted the most favoured c/a value in the simple tetragonal phase for these compounds. Further, we present the calculated results on the electronic structure of these systems at the equilibrium as well the reduced cell volumes.

Keywords. Electronic structure; high pressure phase transition; lanthanum antimonide; cerium antimonide.

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1. Introduction

The high pressure structural phase transitions in the rare earth (RE) compounds have been an interesting field of research in the last two decades, ever since the discovery of metallization of SmS at high pressure [1]. Most of these RE compounds undergo a structural phase transition, associated with electronic and valence transitions. Several experimental work exists on the RE systems depicting a variety of phenomena at high pressure [1–5]. However the theoretical understanding of such diverse phenomena has been incomplete, particularly in RE-pnictides, which show different behaviour at high pressure, as compared to the RE-chalcogenides.

In this paper we report the results of our investigation on the structural and electronic properties of lanthanum and cerium antimonides (LaSb and CeSb) at high pressures. We have calculated their electronic structures and total energy at different values of the lattice parameter assuming different structures and the results were used in understanding the structural and electronic transitions in these systems. For calculating the electronic structure, we have made use of the tight binding LMTO method, which is convenient for systems having many atoms per unit cell. Especially, in the present work where we calculate the electronic structure at different lattice parameters, this method is most convenient. The details of this method may be found elsewhere [6–8]. In the following sections, we describe the results of our calculations alongwith a brief survey of the earlier work on these systems.

2. Survey of earlier work and outline of the present study

Both these systems, namely LaSb and CeSb crystallize in the NaCl structure at ambient conditions and the values of the lattice parameters are 6.49 Å and 6.42 Å for LaSb and CeSb respectively. Both these systems exhibit a structural phase transition around 11 GPa and transform to simple tetragonal (ST) phase [4,5]. A volume discontinuity is associated with this phase transition. So far as their electrical properties are concerned, LaSb has a metallic character with a very low density of states at the Fermi energy ($N(E_F)$) and the metallicity in this compound is caused by the slight overlap of the Sb 5p bands with the La 5d bands. On the other hand CeSb is known to have semi-metallic character with unusual magnetic properties [5].

In the present work we explain the observed structural transition in these systems from the calculation of the total energy as a function of cell volume. In addition, we have obtained the variation of $N(E_F)$ and the integrated density of states with the change in cell volume. We present the calculated band structure and density of states at the normal pressure.

3. The electronic structure

The electronic structures of both these systems were calculated at different cell volumes ranging from 110% to 70% of the equilibrium cell volume, in two different structures, viz. NaCl and simple tetragonal phases. In our calculations, the eigenvalues were calculated at 64 k-points uniformly distributed in the irreducible wedge of the Brillouin zone. The sphere radii of the atoms were so chosen that there is a maximum overlap between the spheres and the charge transfers in proper direction. The sphere radii of the atoms used in the calculation at the equilibrium cell volume are 3.704 a.u. for La and 3.899 a.u. for Sb in LaSb and 3.664 a.u. for Ce and 3.857 a.u. for Sb in CeSb. For calculating the electronic structure at different cell volumes, the sphere radii were correspondingly changed keeping the radii ratio same.

The band structure and density of states corresponding to the equilibrium cell volume in NaCl phase for LaSb and CeSb are shown in figures 1 to 4. The low-lying band in both cases is due to the 5s orbital of Sb. The conduction bands are formed

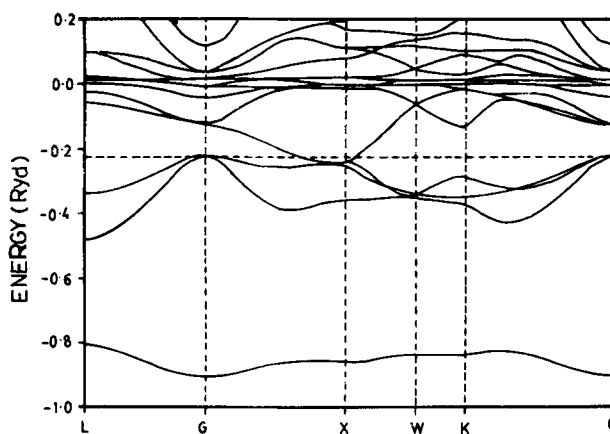


Figure 1. Band structure of LaSb in NaCl phase.

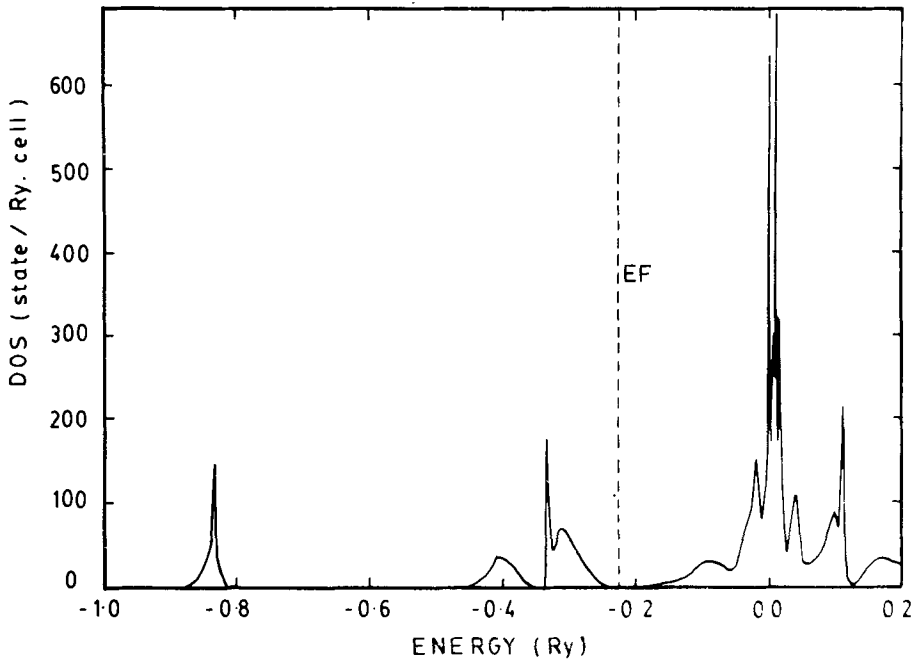


Figure 2. Density of states of LaSb in NaCl phase.

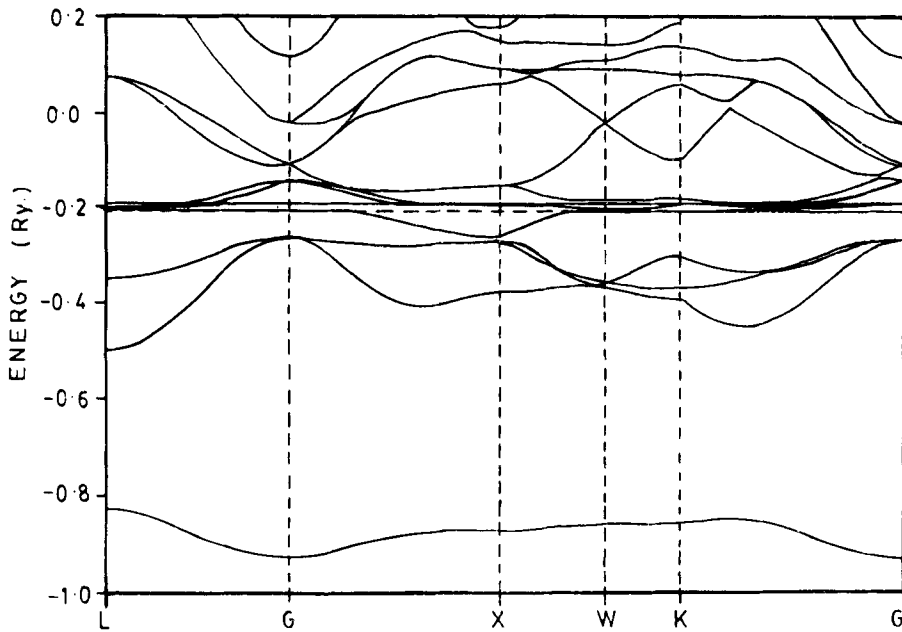


Figure 3. Band structure of CeSb in NaCl phase.

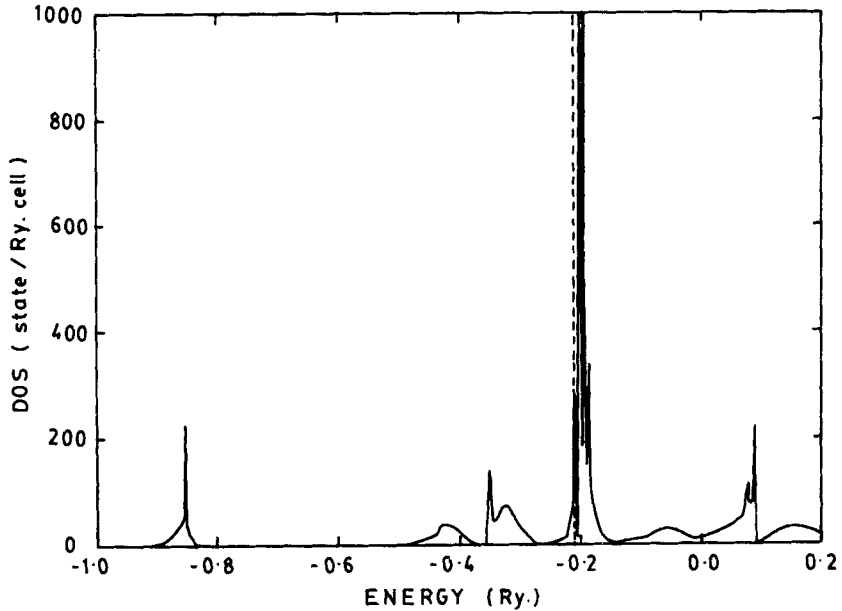


Figure 4. Density of states of CeSb in NaCl phase.

Table 1. $N(E_F)$ and integrated density of states of LaSb and CeSb at two different cell volumes.

LaSb

Cell volume (NaCl) (a.u)³: 444.6935

$N(E_F)$: 0.339 states/Ryd-Cell

Cell volume (ST) (a.u)³: 378.9983

$N(E_F)$: 7.372 States/Ryd-cell

CeSb

Cell volume (NaCl) (a.u)³: 401.6416

$N(E_F)$: 264.508 states/Ryd-cell

Cell volume (ST) (a.u)³: 357.132

NaCl phase

Number of states (electrons/cell)

	La	Sb	Ce	Sb
<i>s</i>	0.3040	1.7451	0.3121	1.738
<i>p</i>	0.5062	3.8713	0.4884	3.7471
<i>d</i>	1.2089	0.1479	1.3793	0.240
<i>f</i>	0.2161	—	1.095	—

Simple tetragonal phase

Number of states (electrons/cell)

	La	Sb	Ce	Sb
<i>s</i>	0.2610	1.7481	0.2681	1.685
<i>p</i>	0.3711	3.6103	0.3931	3.4461
<i>d</i>	1.4229	0.3329	1.6819	0.405
<i>f</i>	0.2531	—	1.121	—

by the Sb 5*p* and La (or Ce) 5*d* orbitals. It may be seen from figure 1 that in LaSb the hybridization branch of La is substantially above the Fermi level. These factors have resulted in very low density of states at the Fermi level for LaSb. However, in CeSb, the Fermi level lies at the bottom of the narrow Ce 4*f* band and hence leads to a large value of the density of states at the Fermi level. The density of states at the Fermi level corresponding to the equilibrium cell volumes are 0.339 states/Ryd-cell for LaSb and 264.508 states/Ryd-cell for CeSb. In table 1 we have given the integrated density of states at two different cell volumes corresponding to NaCl and ST phases. It can be noted from table 1 that at high pressures the density of states at the Fermi level is increased in LaSb whereas it is decreased in CeSb. The increase in Sb5*p* and La5*d* hybridization in LaSb and the broadening of the Ce4*f* bands at high pressure are the major causes of decrease in density of states at E_F in CeSb.

As the high pressure phase of both the systems is simple tetragonal (ST), it is desirable to have the band structure and density of states in this phase. Therefore we have calculated the band structures and density of states corresponding to the ST phase and reported them elsewhere [9].

4. Total energy and structural stability

As mentioned earlier, the total energy of these two systems were evaluated at various lattice parameters in two different structures and calculated values of the total energy for LaSb and CeSb are plotted in figures 5 and 6. In these figures the total energies are plotted with respect to the corresponding equilibrium cell volumes. For calculating of the total energy in the ST phase, we have used the *c/a* value of 0.8158 for LaSb and 0.8161 for CeSb, which are the experimental values [4]. It may be seen from

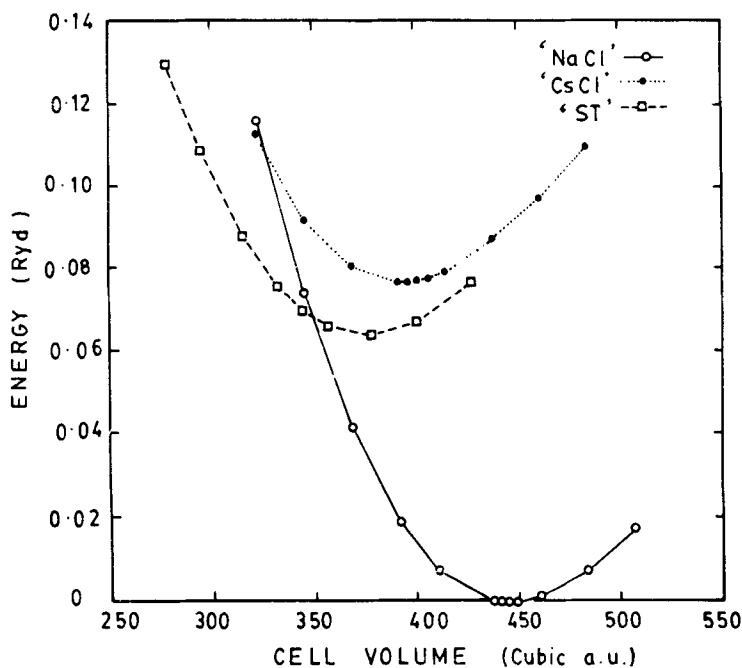


Figure 5. Total energy as a function of cell volume for LaSb.

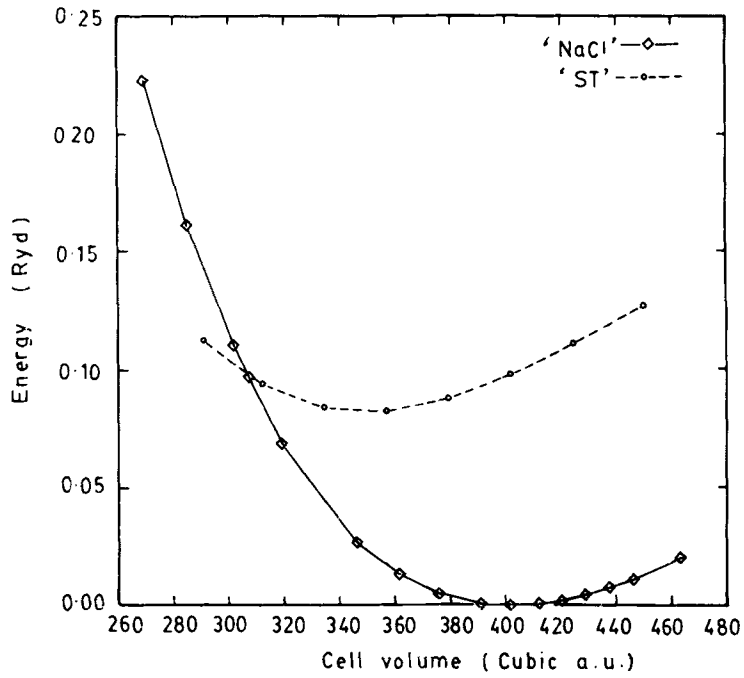


Figure 6. Total energy as a function of cell volume for CeSb.

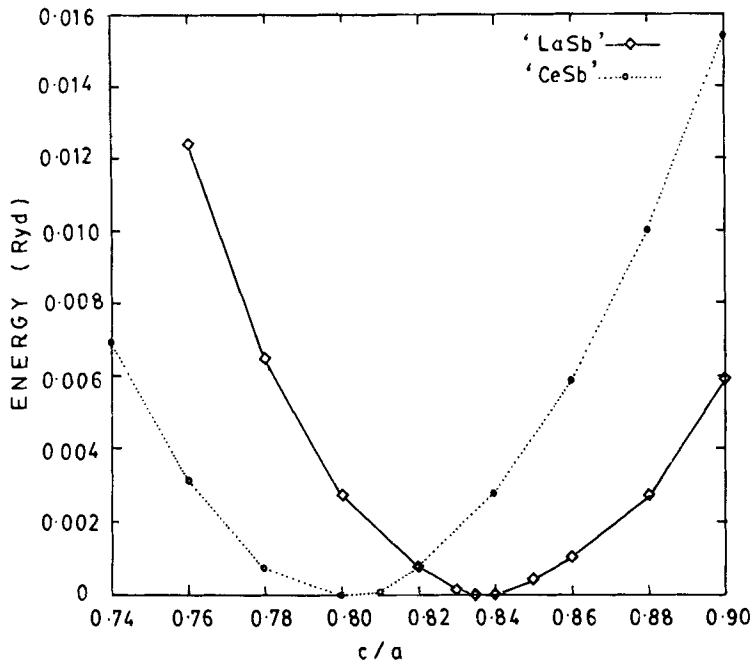


Figure 7. Total energy as a function c/a ratio for LaSb and CeSb.

figures 5 and 6 that the equilibrium cell volumes for LaSb and CeSb are respectively 444·694 and 401·642 (a.u.)³. The experimental values of the cell volumes are 461·143 (a.u.)³ and 446·413 (a.u.)³ for LaSb and CeSb respectively. In LaSb, our calculated value of the cell volume agree with the experimental value whereas in CeSb the agreement is not so good. It may be noted from figures 5 and 6 that both the systems transform to the ST phase at high pressure. In LaSb the transition occurs at the cell volume of 351·135 (a.u.)³ and in CeSb it occurs at 306·425 (a.u.)³. According to the experimental results, the transition occurs at the cell volume of 357·416 (a.u.)³ for LaSb and 345·901 (a.u.)³ for CeSb. It may be pointed out that in LaSb, our calculated value of the cell volume at which the phase transition occurs agree with the experimental results. Whereas in CeSb, the predicted cell volume is found to be smaller than that of the experimental one. The discrepancies may be attributed to the limitations of the density functional approach (DFA) to the electronic structure for these systems. However, it may be noted that, our calculations are not fully relativistic. Further, we have not considered any spin splitting in our calculations.

We have also investigated the most favoured value of the c/a ratio in the ST phase for both LaSb and CeSb. To determine the said ratio, we have calculated the total energy as a function of c/a value in the ST phase keeping the cell volume fixed at 351·135 (a.u.)³ for LaSb and 306·425 (a.u.)³ for CeSb. The calculated results are plotted in figure 7 which shows that in LaSb, the most favoured c/a value is 0·837 and for CeSb, it is 0·802. The experimental values are 0·8157 for LaSb and 0·8161 for CeSb. In both cases, our calculated values agree with the experimental observations.

5. Summary and conclusion

The electronic structure and total energy of the rare earth compounds LaSb and CeSb are evaluated at two different structures. The results were used to get the equilibrium cell volume and to predict the possible structural transitions in these systems. Our calculations have shown that both LaSb and CeSb undergo a structural transition from NaCl to ST phase at high pressure. The calculated results agree with the experimental observation. We have also predicted the most favoured c/a ratio in these systems in the tetragonal phase. It may be noted from figure 3 that the narrow Ce $4f$ bands lie very close to the Fermi level and this gives rise to large density of states at the Fermi energy in CeSb. From our study we have found $s \rightarrow d$ and $s \rightarrow f$ electron transfer at high pressure in both compounds. This may be seen from table 1 where the d and f electron numbers have increased in the high pressure ST phase.

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