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The high-pressure behavior of AlSb

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Abstract

On the basis of the Gaussian nonlocal pseudopotential scheme, modifications of the structural and electronic properties of the indirect band-gap semiconductor AlSb with respect to the variation of the lattice constant are discussed. The results obtained for the valence and conduction band edge charge densities of this material for the zinc blende phase as a function of atomic volume up to 30% are used to analyze the bonding properties in AlSb. Trends in bonding are used to predict the pressure-induced structural phase transitions in AlSb from the zinc blende structure ($N_c=4$) to the insulating rock-salt structure of NaCl ($N_c=6$) or to a white-Sn-like structure ($N_c=6$). Analysis of the valence band edge charge densities as a function of volume shows that AlSb transforms at high pressure to the β-Sn phase, which is a free-electron-like metal.

Introduction

The main motivation for the present work is to study the change, under hydrostatic pressure, in the structural and electronic properties of a prototypical indirect gap semiconductor (AlSb) of the technologically important tetrahedrally bonded compound semiconductors. Systematic studies, both experimental and theoretical, of their electronic structures, optical properties and charge distributions at normal pressure have been widely reported elsewhere [1].

One approach [2] toward determining crystal structure is to calculate the total energy of a given system for various structural arrangements and separations of the cores. The preferred structure and core separations are then determined under the assumption that the system will have the configuration with the lowest total energy for a specific pressure or volume. Hence a calculation of the total energy is needed, and it must be precise, since the variation in energy with structure can be small. The use of a total energy calculation to search for the lowest-energy structure at a given volume and several properties of the low-pressure structural phase have been discussed elsewhere [3, 4]. This paper is an attempt to correlate this structural phase transition to the variation of the electronic charge densities. The electron pseudocharge densities derived from the nonlocal pseudopotential scheme (EPM) [5] have been found to be a useful probe for understanding the chemical bonds in these materials. In particular, the concept of the ionicity parameter of the chemical bond plays a central role in the semi-empirical interpretation and predictions of material properties, since most of these observable properties result from the type of interaction between atoms.

The investigation of chemical trends of solid state properties appears to be an extremely useful part of modern material research, especially when one tries to gain some information about the many interesting properties of binary compounds under pressure. Therefore, it seems more fundamental to relate the high-pressure behavior of the compounds to the type of bond between the nearest atoms by controlling the evolution with pressure of the bond character in terms of pseudocharge densities of the occupied valence bands, in an attempt to link the effect of high pressure to the lattice constant variation (volume) and thus to provide a real picture of the pressure-induced structural phase transitions in AlSb from the fourfold-coordinated crystal structure (ZB) to the sixfold one. The separation between crystal structures with coordination number $N_c=4$ and those with $N_c=6$ is determined by the competition between the covalent sp^3 bonding and the electrostatic

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interaction, which in its simplest form can be represented as an ionic Madelung interaction. It was one of the successes of the dielectric theory established by Phillips and Van Vechten [6] that it made it possible to ascribe, in a systematic manner, an ionicity value f_i to each compound. This ionic character obeys the equation $f_i + f_c = 1$, where f_c is the covalent character. In addition, a specific critical value ($f_i = 0.785$) was found to provide a complete separation between $N_c = 4$ and $N_c = 6$ structures, and a systematic classification of the structural phase transition with pressure can be derived for each compound according to the Phillips ionicity scale.

The great success of recent developments in this field, on an *ab initio* pseudopotential total energy scheme [2] and Murnaghan's equation of state, demonstrate the validity of this mechanism of the compositional $N_c = 4$ to $N_c = 6$ transition, since a semiquantitative phase diagram was deduced for different crystal structures of each compound as a function of decreasing volume (Fig. 1). Since in the tetrahedrally bonded semiconductors such as AlSb, the zinc blende (ZB) has the lowest minimum total energy, it is the most stable phase of these compounds at ambient pressure. As pressure is applied, the volume decreases, and the transition to the β-Sn phase occurs at relatively low pressure.

At zero pressure (normal volume), the covalent semiconductors are fourfold coordinated. The reason that the density is so low is that nearest neighbors are bound together through overlapping hybridized orbitals. In AlSb, these orbitals are the well-known sp^3 hybrids, with tetrahedral directionality. In terms of the charge distribution, this is consistent with delocalization of the charge in the covalent bond. Therefore, this covalent compound can be transformed — either through chemical shifts or under pressure — into a denser structure, which may be ionic or metallic. Thus, from this viewpoint, AlSb is not far away from either a metallic structure or an ionic structure. Thermodynamically the three structures are separated by the first-order phase transition, but microscopically the interactions that are responsible for the phase transition may be the same ones that are responsible for the chemical trends within the covalent structures themselves. This transformation can be obtained by decreasing the lattice volume of this compound. Therefore, in this context we have studied the calculated valence charge densities with respect to variation of the lattice volume. This variation could be linked to the effect of hydrostatic pressure. Thus, a particular aim of the present work is to discuss qualitatively the structural phase transitions in AlSb. The results show that the charge densities vary considerably as the lattice volume is varied. These results confirm that AlSb transforms into a β-Sn structure, and this phase is observed to be superconducting at high pressure.

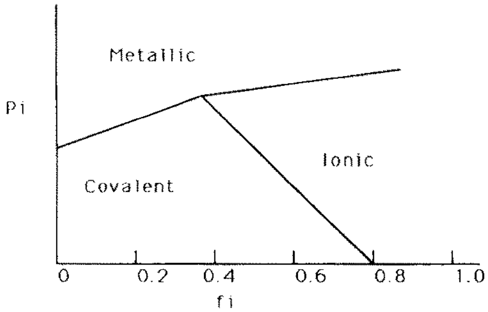

Fig. 1. Schematic thermochemical (P_i vs. f_i) phase diagram showing the covalent, ionic and metallic structures. Arbitrary units are used throughout.

Calculations

A modification of the crystal lattice that does not change its symmetry properties can be obtained by applying hydrostatic pressure to the crystal. An applied pressure changes the lattice parameters and hence produces shifts of the electronic states in the crystal. Therefore application of pressure provides a convenient technique for shifting the relative positions of some energy levels by a controlled amount. It is also evident that by applying sufficient pressure one can change the band extrema from one point of the Brillouin zone to another. It is easy to establish the connection between the symmetry of a level and its pressure dependence by considering the pseudopotential approximation. The pseudopotential Hamiltonian is then:

$$H = P^2/2m + V_p \tag{1}$$

V_p can be expressed in terms of the symmetric and antisymmetric pseudopotential form factors $V_L(G)$.

To investigate how a change in the lattice constant influences a state with a given symmetry, we use a number of symmetrized combinations of plane waves, construct the secular equation with the pseudopotential Hamiltonian, and, finally, show how the eigenvalues change when

$$a \longrightarrow a(1-\delta) \tag{2}$$

(δ is a small variation) and consequently when

$$V_{\mathrm{L}} \longrightarrow V_{\mathrm{L}} + \Delta V_{\mathrm{L}} \qquad (3)$$

Calculations of this type have been performed with considerable success [7–9].

We have observed that the variations ΔV_{L} tend to be positive under pressure, for all parameters involved.

For small changes in volume induced by the pressure, the calculational framework must remain valid, and the only physical quantities that change are the lattice constant and the pseudopotential form factors.

To compute the energy bands at high pressure, i.e., different primitive cell volumes and different Gs, the form factors must be scaled appropriately. We scaled the form factors in the following way. Let Ω' and G' be the primitive cell volume and the reciprocal lattice vector at a new pressure, respectively. Then the form factors are given by

$$V'(G') = (\Omega/\Omega')V(G') \qquad (4)$$

where Ω is the normal lattice cell volume.

When we substituted into the secular equation the values of δ appropriate to a given pressure and the corresponding positive ΔV_{L}, we found that the energy shift is more important to the positions of the top valence band Γ. The most important relative contribution is ΔV_{L} [8], which gives a large positive shift for Γ. The state at X is nearly constant with respect to Γ, because the different contributions to $\Delta_{\mathrm{X}} - \Delta_{\Gamma}$ tend to cancel. We noticed that the separation $E_{\mathrm{X}} - E_{\Gamma}$ remains nearly constant with pressure. Thus it seemed to us that the point Γ is the most important when pressure is applied. We have therefore carried out calculations of the electronic charge densities at this point for hypothetical pressure (very high pressure) in order to show how far our approximations are still valid.

The resulting pseudo-wave-functions $\Psi_{nk}(r)$, which are obtained by solving the secular equation, are used to compute the total valence charge density according to the following expression (n is the band index and k stands for wave vectors):

$$\rho_n(r) = e\Sigma_n |\Psi_{nk}(r)|^2 \qquad (5)$$

Results

AlSb occurs in the zinc blende structure, in which each atom has four nearest neighbors, arranged tetrahedrally. A (110) plane intersecting an atom also intersects two of its nearest neighbors. There are eight valence electrons per primitive cell and two valence electrons per energy band.

We now present the results of our calculated electron distribution for AlSb at ambient and high pressures. (All results are displayed in the (110) plane and along the <111> direction, using the same arbitrary units.)

The pseudocharge densities for the sum of the valence bands at the Γ point for AlSb are displayed in Fig. 2. We notice that the charge is practically concentrated at the bond center, where it reaches its maximum. It is displaced toward the Sb anion. This suggests that the bond has a covalent nature; thus the charge distribution is p-like for the sum of the four valence bands.

AlSb is a covalent semiconductor with a slight ionic character. This can be seen from the charge density at the bond center (covalent) and at the

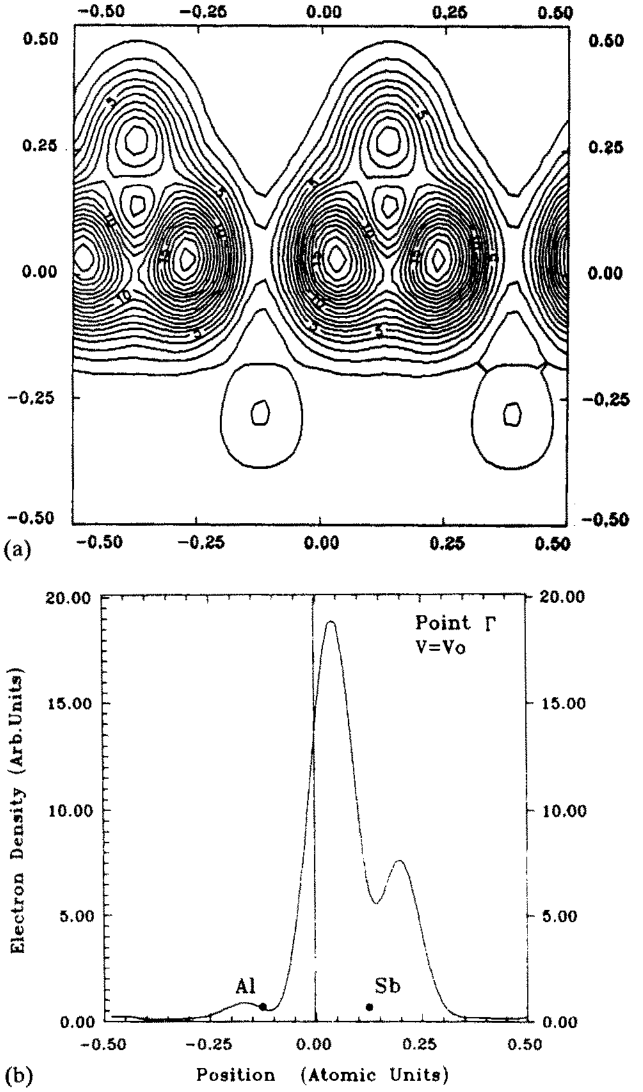

Fig. 2. The electron pseudocharge densities for the sum of the four valence bands for normal lattice volume V in AlSb: (a) in the (110) plane; (b) along the <111> direction.

atomic sites (ionic). This is consistent with the Phillips ionicity scale [6]. Covalent bonding is thus seen to be an important factor in the total valence charge density in AlSb. The potential is strong enough in the region between the two atoms to create an average bonding–antibonding energy gap E_g that is sufficiently larger than the band widths produced by bond–bond and antibond–antibond interactions to leave a residual or minimum gap between filled valence band and empty conduction band. This chemical trend associated with the covalent bond relates to the fact that AlSb is fourfold coordinated ($N_c = 4$) at ambient pressure, since the lowest structural phase is the zinc blende phase, which is not far away from the sixfold-coordinated structure ($N_c = 6$). The present study extends this investigation and explores the effect of hydrostatic pressure on AlSb. The effect of decreasing the lattice volume is to transform the crystal into a denser structure, which may be metallic or ionic ($N_c = 6$).

From analysis of the variations of the valence pseudocharge densities with respect to the variation of the lattice volume on the basis of the bonding properties, one can deduce the mechanism of the compositional $N_c = 4$ to $N_c = 6$ transition and consequently establish at least the first-order phase transformation that occurs in AlSb as a result of the transformation of the nature of the binding energy. The electron pseudocharge densities at the Γ point for $0.7V$, $0.6V$ and $0.5V$ are displayed in Figs. 3, 4 and 5, respectively.

Looking at these Figures, we notice that as the lattice volume decreases, there is a large amount of electronic charge transferred from the bonding region to the nonbonding region, indicating that AlSb becomes more metallic under pressure. The maximum of the charge density at the bond center decreases considerably, while the value of the charge distribution at the atom sites increases gradually, especially in the neighborhood of the cation site, where there is a slight charge buildup. However, the covalent bonding character is still strong at the transition volume. The strength of the covalent bonding can be understood by energy considerations. The relative stability of the diamond phase against the β-tin phase before transition results from the fact that the covalent electronic contribution (to the total energy) favoring the diamond phase more than compensates for the Ewald contribution, which favors the β-tin phase. The transition occurs when the Ewald contribution dominates over the covalent electronic contribution.

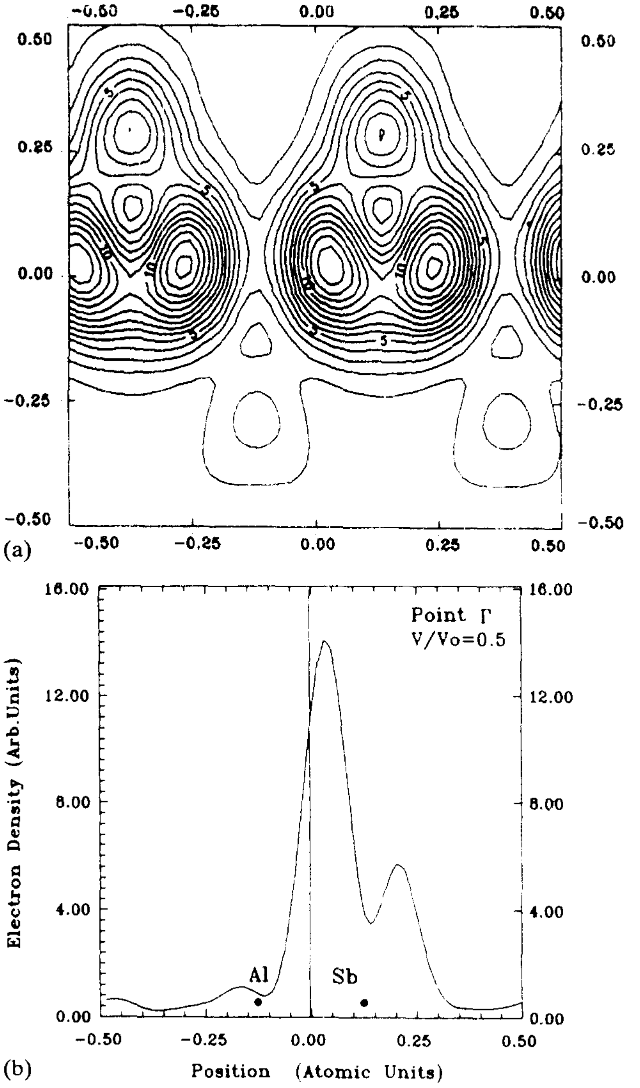

Fig. 3. The electron pseudocharge densities for the sum of the four valence bands for $0.7V$ in AlSb: (a) in the (110) plane; (b) along the <111> direction.

This change in bonding properties under high pressure is consistent with the modifications that occur in the band structure of this material (Fig. 6) and can be explained as follows: as pressure is applied, the volume decreases and the strong sp^3 covalent bonds that characterize this covalent structure at normal pressure are destroyed under increasing pressure, resulting in a metallic character. In terms of pseudocharge density, this means that the value of the distribution at the bond center decreases and the value at the atom sites increases (a uniform distribution). Therefore, the changes observed above in the nature of the chemical bonding as a consequence of decreasing volume are characteristic of a metallic phase. This conclusion for the high-pressure structural phase of AlSb is supported in our calculations by the indirect

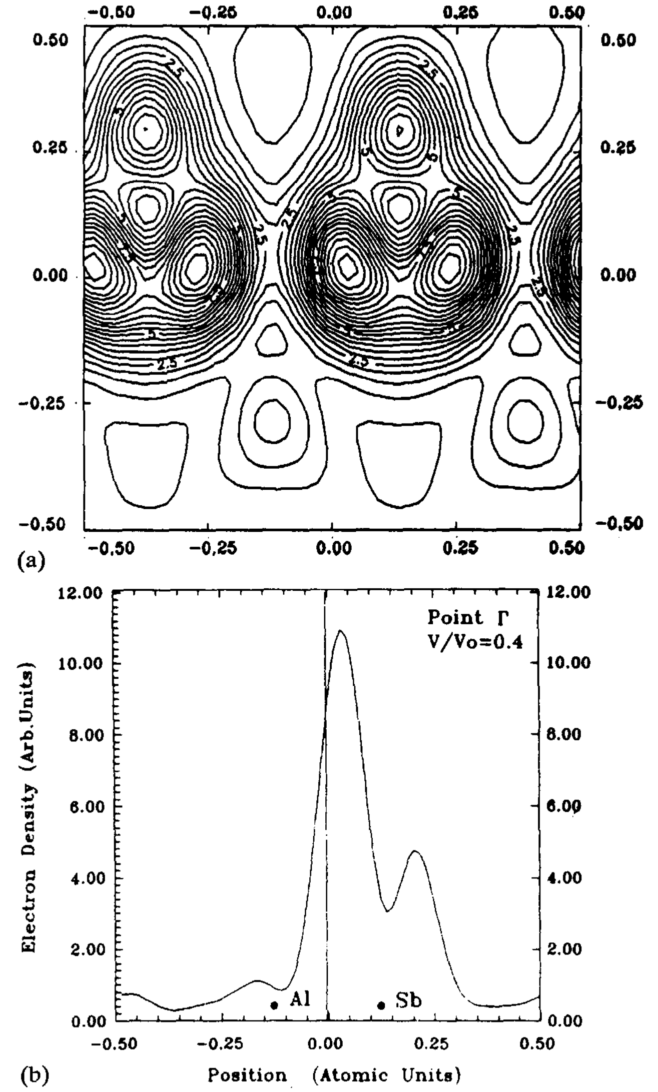

Fig. 4. The electron pseudocharge densities for the sum of the four valence bands for 0.6*V* in AlSb: (a) in the (110) plane; (b) along the <111> direction.

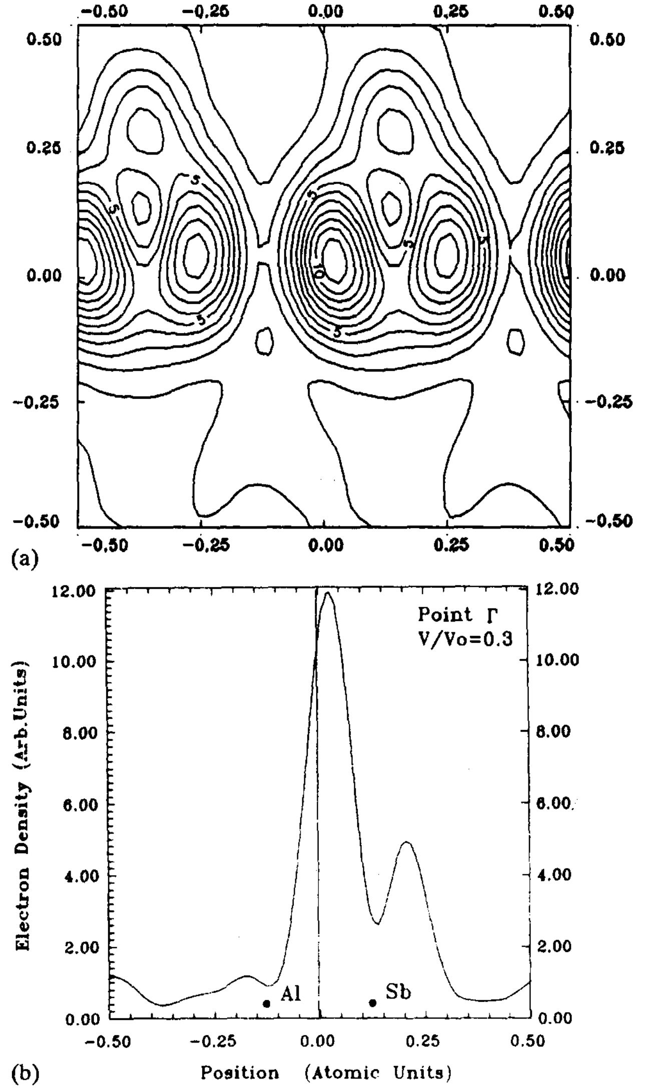

Fig. 5. The electron pseudocharge densities for the sum of the four valence bands for 0.5*V* in AlSb: (a) in the (110) plane; (b) along the <111> direction.

and direct band widths, in particular by the smallest energy gap between the valence and conduction band (Fig. 6), which decreases further with increasing pressure. The chemical explanation of this phenomenon is simple. In the zinc blende phase, AlSb has strong covalent bonds in addition to a small ionic character. As pressure is applied, the covalent bonds coexist with metallic bonding in the β-Sn phase at relatively low pressure. Further increases in the pressure force the bond charge to the atom sites, and in the most highly compressed phase, which we identify as β-Sn in AlSb, all the covalent character in AlSb will be suppressed, resulting in a free-electron metal, although the effect of this pressure may be to create an internal pressure, whose effect to first order is to expand the crystal, which results as well from the fact

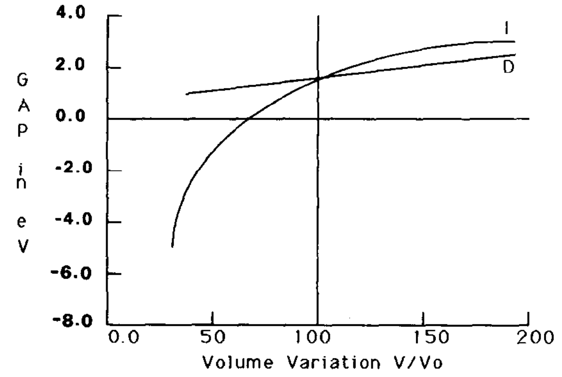

Fig. 6. The variation of the direct and indirect band gaps as a function of the volume. I = indirect gap; D = direct gap.

that the valence electrons are now repelled from the core regions by the exclusion principle. On the other hand, the valence and conduction bands of AlSb have also been affected essentially by the effect of pressure. As pressure is applied, the interatomic spacing of a set of atoms in the fourfold-coordinated structure decreases from its normal value, and the material is at first a semiconductor. As the volume decreases further, the bands broaden and the sp band gap decreases. Therefore, increases in pressure will make AlSb less semiconductor-like and may actually result in a metallic phase (the β-Sn phase) that exhibits a free-electron-like behavior.

In conclusion, the approximation used in our calculational framework gives results that are in good agreement with the results of Phillips ($f_i < 0.35$, for AlSb $f_i = 0.25$). Since the effect of hydrostatic pressure in AlSb is to transform this compound from a fourfold-coordinated structure into another, denser, structure, it is the β-Sn metallic phase at low pressure and very high pressure that is basically free-electron-like and seems to be a superconducting phase.

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