

Structural and electronic properties of spinel semiconductors: An *ab initio* pseudopotential study of MgIn_2S_4

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The structural properties of MgIn_2S_4 are studied from first principles within the local-density approximation, using norm-conserving pseudopotentials. Our results for the lattice constant, bulk modulus, and phonon frequencies are in good agreement with experiments. We also consider the relative stability of ordered and disordered structures. Contrary to experiment, our results would indicate the ordered structure to be the most stable. This failure is analyzed and suggestions about its possible source are given. The electronic properties of this compound are also discussed in terms of its electron charge-density distribution and density of states.

I. INTRODUCTION

Ternary semiconductors have recently attracted attention for the wide range of potential applications in device technology due to the presence of three different chemical components which allow, at least in principle, the tailoring of several important physical properties. The physics of these compounds spans many areas of fundamental and technological interest, such as magnetism, ferroelectricity, and superconductivity.^{1,2} Basic components of this family of materials are the chalcopyrites and the compounds with general formula $A^{\text{II}}B_2^{\text{III}}C_4^{\text{VI}}$. When $C=\text{O}$ or S the crystal is generally found in the cubic spinel structure. In the following we shall analyze in detail the physical properties of these materials with non-transition-metal B component. The lattice is characterized by the presence of different local atomic arrangements and by arrays of ordered vacancies which give rise to internal distortions. The latter are one of the common features of the ternaries. The same compound may show different polytype arrangements and/or structural phase transitions due to pressure and temperature. The presence of many competing nearly degenerate atomic configurations favors the presence of disordered phases and makes the growth and characterization of these materials rather difficult. On the theoretical side, the general trends of the microscopic structure can be qualitatively understood in terms of chemical quantities such as electronegativity differences.³ However, a more fundamental understanding based on a first-principles description of the forces acting among electrons and ions has long been considered an impracticable task because of the complexity of the crystal structure and the large number of electrons per unit cell. These difficulties are now being overcome due to the availability of powerful theoretical tools based on density-functional theory⁴ and to the steadily growing computer power from vector machines.

In this work we shall present the first detailed theoretical study of a ternary spinel compound. As a prototype,

we choose MgIn_2S_4 for which—beside predicting the equilibrium structural properties such as lattice constant and bulk modulus—we give a quantitative discussion of the relative stability of ordered and disordered phase. Attention is also paid to the interplay between structural and electronic properties, among which we report on density of electronic states and charge-density distribution. In Sec. II we discuss the crystal structure. Section III is devoted to the method of calculation and to the presentation of our results. Section IV contains our conclusions.

II. CRYSTAL STRUCTURE

The general formula $A^{\text{II}}B_2^{\text{III}}C_4^{\text{VI}}$, where $A=\text{Mg, Ca, Zn, Cd, Hg}$, $B=\text{Al, Ga, In}$, and $C=\text{O, S, Se, Te}$, corresponds to a number of different crystal structures. However, except for ZnIn_2S_4 , which displays a layered structure, most of them have a face-centered-cubic (fcc) anion sublattice whose tetrahedral and/or octahedral sites are partially filled with group-II and group-III cations. As mentioned above, the oxides and sulfides are generally found to be spinels, with one-third of the cations on tetrahedrally coordinated sites, and two-thirds on octahedrally coordinated ones. As in the case of chalcopyrite, two different cations occupy the corresponding sublattice giving rise to two nonequivalent cation-anion bonds. In Fig. 1 we display the normal spinel structure with the group-VI ions in their ideal position. The unit cell contains 14 atoms (two chemical formulas per cell) whose coordinates are reported in Table I. The presence of vacancies in the crystal structure gives rise to distortions in the anion sublattice. This fact, which is a common feature of this family of ternaries, is best defined in terms of the so-called *internal distortion parameter* u whose value is $\frac{3}{8}$ in the ideal fcc structure (see Table I). The symmetry of the crystal is cubic—space group O_h^7 —independent of the value of u .

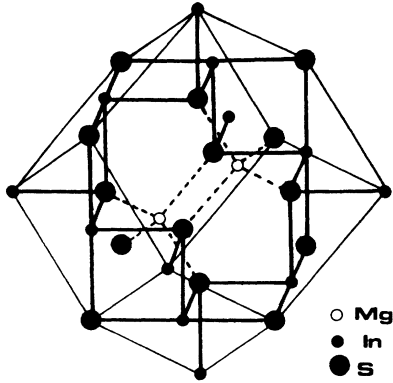


FIG. 1. Normal spinel structure.

Another important structural characteristic of the spinel compounds is given by the normality of the crystal, defined as the percentage of group-III atoms in tetrahedral sites. A convenient way to represent the cationic distribution is expressed by the formula

$$A_x B_{1-x} [A_{1-x} B_{1+x}] C_4,$$

where $0 \leq x \leq 1$ and the square brackets indicate atoms in the octahedral sites. The normal spinel structure corresponds to $x=1$, and the inverse one to $x=0$. At the microscopic level, each elementary cell can display a normality $x=1, \frac{1}{2}$, or 0 according to whether 0, 1, or 2 group-II atoms have octahedral coordination. Macroscopically, the simultaneous presence of different types of unit cells makes any value $0 \leq x \leq 1$ possible. In the inverse and partially inverse spinels, trivalent cations are still present in the octahedral holes, since the tetrahedral-octahedral site ratio is less than 1. In correspondence to the completely inverse cell there are six different degenerate arrangements of atoms, while there are eight corresponding to the partially inverse one. Accordingly—all the octahedral sites being equivalent—(partially) inverse spinels are intrinsically disordered. The inverse and partially inverse structures locally have a lower symmetry than the direct one (point groups D_{2h} and C_{3v} , respectively). Of course, in real materials, degenerate configurations occur with equal probability and cubic symmetry is recovered *on the average*.

TABLE I. Atomic positions in the unit cell in units of the lattice parameter a_0 .

	Mg	In	S
1	(0,0,0)	$(\frac{5}{8}, \frac{5}{8}, \frac{5}{8})$	$(-u, -u, u)$
2	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	$(\frac{7}{8}, \frac{7}{8}, \frac{5}{8})$	(u, u, u)
3		$(\frac{5}{8}, \frac{7}{8}, \frac{7}{8})$	$(-u, u, -u)$
4		$(\frac{7}{8}, \frac{5}{8}, \frac{7}{8})$	$(u, -u, -u)$
5			$(\frac{1}{4} + u, \frac{1}{4} + u, \frac{1}{4} - u)$
6			$(\frac{1}{4} - u, \frac{1}{4} - u, \frac{1}{4} - u)$
7			$(\frac{1}{4} + u, \frac{1}{4} - u, \frac{1}{4} + u)$
8			$(\frac{1}{4} - u, \frac{1}{4} + u, \frac{1}{4} + u)$

III. COMPUTATIONAL METHOD AND RESULTS

The present theoretical investigation is performed within the local-density approximation (LDA) to the density-functional theory⁴ (DFT). *Ab initio* norm-conserving pseudopotentials⁵ have been used to describe the electron-ion interaction. The electron-gas data used as input to the LDA are those by Ceperley and Alder as interpolated by Zunger and Perdew.⁶ Electronic wave functions have been expanded into a plane-wave (PW) basis set: After testing the sensitivity of our results to the size of the basis set,⁷ we decided to include in our calculation plane waves up to a kinetic energy of 9 Ry. This corresponds to ~ 900 PW's at equilibrium volume. The whole basis set has been treated exactly and no use of perturbation theory is made to diagonalize such matrices. The eigenvalue problem is managed using an efficient block version of Davidson's algorithm.⁸ The (4,4,4) Monkhorst-Pack mesh⁹ has been used for Brillouin-zone (BZ) integrations. In the case of cubic symmetry (direct structure) this corresponds to the set of the two Chadi-Cohen special points,¹⁰ while for D_{2h} and C_{3v} symmetries (inverse and partially inverse structures) the number of nonequivalent points in the irreducible wedge of the BZ is 6 and 5, respectively. Due to the smallness of the BZ in such a large unit-cell compound, the use of a larger set of \mathbf{k} points does not lead to any meaningful changes in our results.⁷ The equilibrium atomic positions have been determined using the Hellmann-Feynman forces acting on the individual ions, while the equilibrium lattice constants and the bulk moduli have been obtained fitting our results to the Murnaghan's equation of state.¹¹

A. Structural properties

In the direct spinel structure, the forces acting on the cations vanish by symmetry, while those acting on the anions give rise to the already mentioned internal distortion. As the symmetry of the crystal does not depend on the value of u , u can be thought of as the normal coordinate of a zone-center phonon of Γ_1 symmetry. When calculating the dependence of the crystal energy upon volume, we have optimized the anion positions for each value of the volume: as a by-product, we thus obtain the frequency of the above-mentioned phonon—which is Raman active—as well as the corresponding Grüneisen parameter.

In the case of inverse or partially inverse structures, we have calculated the crystal energy assuming that the crystal can be thought of as a collection of uncorrelated elementary cells. This amounts to assign to each cell the energy it would have in an ideal crystal made up by periodically repeated cells with identical local arrangement of cations. For (partially) inverse structures, as a consequence of the lower symmetry, forces act both on anions and cations when they are at their ideal positions, and every atomic position differs from the ideal one. The calculations for the inverse structure have been done optimizing *simultaneously* the lattice parameter and all the atomic positions. For the partially inverse structure, atomic positions have been optimized assuming the lat-

time parameter to be the average between those of the direct and totally inverse structures. The calculation of the phonon frequency ω_{Γ_1} is more difficult for (partially) inverse structures, because the local symmetry is no longer cubic and the system is intrinsically disordered. In order to calculate the ω_{Γ_1} in this case, we have taken advantage from the fact that the macroscopic symmetry continues to be cubic. For each atomic configuration in the (partially) inverse structure, we have projected out noncubic components of the forces acting on the ions. This gives by construction vanishing forces on the cations and forces acting on anions which have the same symmetry as in the direct structure. The calculation of ω_{Γ_1} for (partially) inverse structures is thus reduced to the corresponding calculation for the direct structure. Our results are reported in Table II.

The agreement with available experimental data is generally good. A comparison of the calculated values of u and ω_{Γ_1} with the experiment suggests that the actual crystal structure of this compound is not direct. In fact, the commonly accepted value for the normality of MgIn_2Se_4 is $x = 0.16$.^{12,13}

We have also evaluated the energy differences between the direct and the (partially) inverse structures. In order to display the importance of lattice relaxation on the relative stability of different structures these energy differences have been calculated in three ways: (a) assuming the arrangement of ions to be ideal fcc (i.e., ignoring both anionic and cationic relaxation); (b) allowing only anions to relax; and (c) including full relaxation of all the crystal constituents. Our results, collected in Table III, show that not only the energy differences dramatically depends on the lattice relaxation, but even the relative order of the inverse and partially inverse structures does so. In Table III we also report the mean-square displacements of cations, when they are allowed to relax. As a general trend we note that ionic relaxation is not negligible and that it acts in such a way as to substantially reduce the energy difference structures.

The most serious discrepancy between our calculations and experience concerns the normality of the structure. Our calculations would indicate that the normal structure is the most stable at zero temperature (correspond-

TABLE III. ΔE are the energy differences per cell (mRy) between direct and (partially) inverse structures. Δx are the cation mean-square displacements in a.u.

$E - E_{\text{dir}}$	ΔE^a	ΔE^b	ΔE^c	Δx_{Mg}	Δx_{In}
Inverse	88	22	18	0.0	0.025
Partially inverse	61	34	16	0.072	0.080

^aIons are as in ideal fcc structure.

^bOnly anions are relaxed.

^cBoth anions and cations are relaxed.

ing to $x = 1$), while the commonly accepted value at room temperature is $x = 0.16$.^{12,13} Assuming that the probability of finding an elementary cell in a given configuration is independent of the configuration of the neighboring cells, this probability would be given by a Boltzmann distribution according to the energy differences reported in the third column of Table III. As the energy difference between the direct and the inverse structures corresponds to a temperature of ≈ 3000 K, we conclude that our calculations would predict the normality at room temperature to be practically 1. Among the possible reasons for this failure, we quote numerical effects (such as the use of a relatively small basis set), the neglect of the phonon contribution to the free energy and—most seriously—the supposed lack of correlation between neighboring cell configurations. This amounts to assuming that the energy necessary to change the local configuration of a given cell equals the energy difference per cell between two hypothetical crystals made up by identical cells, independently of the configurations of the neighboring cells. In particular—in the case of (partially) inverse cells—no energy is assumed to be used to change the configuration of a cell into a degenerate one. In the following, this energy will be referred to as *intercell correlation energy*.

As for the numerical accuracy, we have verified that the energy differences quoted in Table III have converged, with respect to both the kinetic-energy cutoff of the PW basis set and the number of special \mathbf{k} points (which are the most common source of inaccuracy), to all the quoted figures.⁷ As for the vibrational contribution to the free energy, we observe that the phonon frequency we have calculated increases with decreasing normality, and so does the bulk modulus. This suggests that the vibrational entropy is greater for high normality, thus further stabilizing the direct structure. The quantitative evaluation of the intercell correlation energy demands a heavy computational effort since it requires even larger unit cells than used here. For this reason we postpone a detailed analysis of this quantity to future work. However, in order to get a qualitative estimate of the importance of intercell correlation energy, we have calculated the electrostatic energy of a fictitious crystal in which each atom is represented by a point charge of value equal to its chemical valence. This energy has been evaluated in two different cases. First—as in the previous *ab initio* calculation—we suppose the crystal made up of equal repeated cells; we then consider the case where each cell is surrounded by cells with same normality, but with different local arrangement of cations. The energy difference between the two cases is of the *same order of*

TABLE II. Calculated structural properties of MgIn_2S_4 . a_0 is the lattice parameter, B_0 the bulk modulus, and u_0 the internal distortion parameter. ω is the zone-center Γ_1 phonon frequency and γ is the corresponding Grüneisen parameter.

	a_0 (a.u.)	B_0 (Mbar)	u_0	ω (THz)	γ
Direct	19.89	0.79	0.381	10.5	1.3
Inverse	19.85	0.88	0.383	12.1	1.7
Partially inverse	19.87		0.382	11.2	
Expt.	20.24 ^a		0.382 ^b –3 ^a	11.2 ^c	

^aFrom Ref. 12.

^bFrom Ref. 13.

^cFrom Ref. 14.

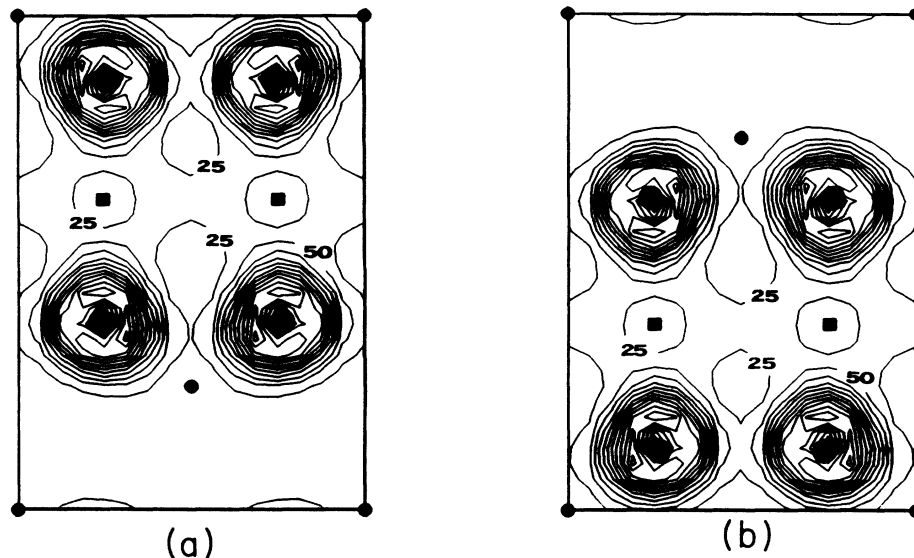


FIG. 2. MgIn_2S_4 in the normal spinel structure: total valence charge density on (a) $(1\bar{1}0)$ plane and (b) (110) plane (electron/cell). Dots indicate magnesium atoms, solid squares indium atoms, and solid circles sulfur atoms.

differences between cells of different normality. We conclude that the neglect of intercell correlation energy is the most serious source of inaccuracy of the present calculation and that its proper account is probably essential for a correct description of the relative stability of ordered and disordered phases.

B. Electronic properties

In Figs. 2–4 we report the electron charge-density distributions of MgIn_2S_4 in the various structures (direct, partially inverse, and inverse) we have studied, projected

onto the (110) and $(1\bar{1}0)$ planes: These planes are equivalent by symmetry for the direct structure, but they are not for the inverse and partially inverse ones. The partially inverse structure has been obtained interchanging atoms $\text{Mg}^{(1)}$ and $\text{In}^{(1)}$ (see Table I), while in the totally inverse one the couples $(\text{Mg}^{(1)}, \text{Mg}^{(2)})$ and $(\text{In}^{(3)}, \text{In}^{(4)})$ have been interchanged. According to the ionic character of this compound, most of the electronic charge is piled around the sulfur atoms. A partially covalent character of the bond emerges from the anionic anisotropic charge distributions (slightly pointing towards cations) and from the small charge piled around cations. This is

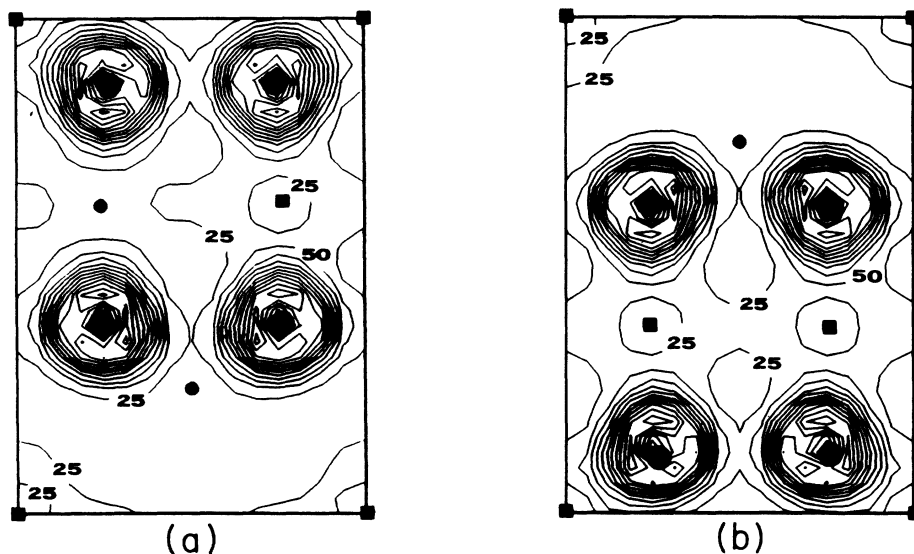


FIG. 3. MgIn_2S_4 in the partially inverse spinel structure: total valence charge density on (a) $(1\bar{1}0)$ plane and (b) (110) plane. Units and symbols are the same as in Fig. 2.

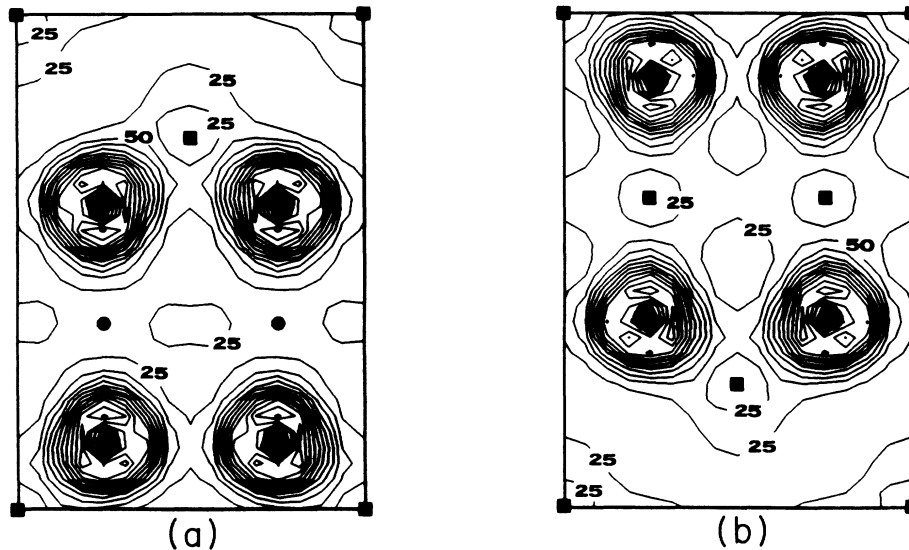


FIG. 4. MgIn_2S_4 in the inverse spinel structure: total valence charge density on (a) $(1\bar{1}0)$ plane and (b) (110) plane. Units and symbols are the same as in Fig. 2.

more evident for (partially) inverse structures, where the covalent character of the bond between anions and tetrahedrally coordinated group-II cations is more pronounced.

In Fig. 5 we display the density of valence states for the three structures considered here. This has been obtained diagonalizing the self-consistent Hamiltonian at a large number of special points in the Brillouin zone including the Γ point (10, 26, and 16 points for the direct, inverse, and partially inverse structures, respectively) and smearing the resulting histogram with a Gaussian of width $\Delta=0.2$ eV. The qualitative features of the density of states have been verified not to depend on the number of special points nor on the width of the smearing Gaussian. The main features emerging from a comparison of the three densities of states can be summarized as follows. (i) The density of states is more structured for the direct spinel due to the lack of any disorder. (ii) An intraband gap exists in all cases due to the energy separation between the sulfur $3s$ states from the remaining atomic states participating in the chemical bond. (iii) The density of states below the intraband gap is not affected by the normality as it mainly depends on the S - S distance, which is almost independent on the arrangement of cations. (iv) The same—though to a minor extent—holds for the high-lying portion of the upper band (near the band edge) which is mainly affected by the sulfur $3p$ orbitals. (v) The main differences manifest themselves in the low-lying portion of the upper band which depend more sensitively on the degree of hybridization between sulfur orbitals and orbitals from magnesium and indium. The most evident effect of inversion is a transfer of density of states from the upper to the lower band edge, with a reduction of the intraband gap from ~ 3.3 to ~ 2.5 eV.

In order to get a rough idea of the dependence of optical properties on normality, we have calculated the direct gap (occurring at the Γ point) for the three structures considered in this paper. Our calculations indicate that, contrary to previous theoretical results,¹⁵ the gap varies

linearly with the normality, going from ~ 1.9 eV for the totally inverse structure to ~ 2.4 for the direct one. These figures should be compared with an experimental value of 2.28 eV.¹³ Contrary to structural properties which are determined by valence bands only, our values

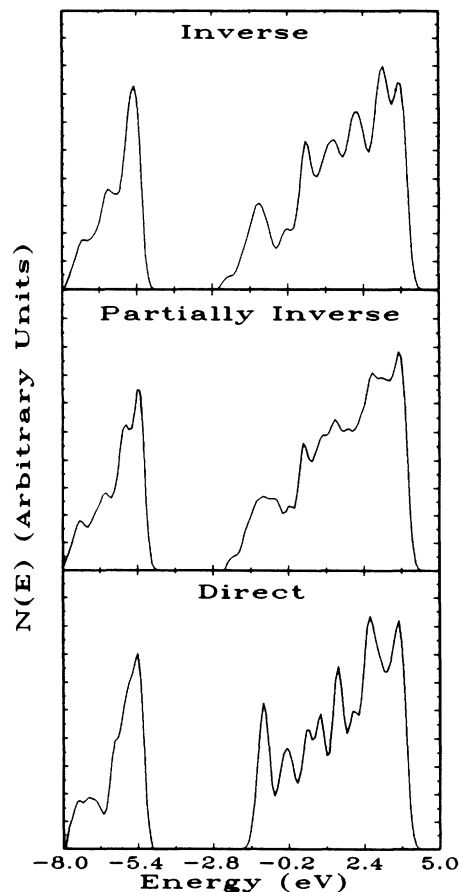


FIG. 5. Valence density of states of MgIn_2S_4 .

of the gap are not fully converged with respect to the size of the PW basis set; furthermore, DFT generally underestimates the gap. Therefore, the agreement of our calculated gaps with experiments is rather fortuitous and should not be taken as an indication that the actual crystal structure is direct. However, though the absolute values of the gaps are not reliable for the above reasons, we believe that our calculations do provide useful information about their dependence upon normality.

We finally mention that the typical excitation determining the gap is from a state localized around the anions (top of valence band) to a state mainly localized around octahedrally coordinated group-III cations.

IV. CONCLUSIONS

We have presented the first *ab initio* study of the structural and electronic properties of a ternary spinel semiconductor. Our results for the equilibrium lattice a_0 , bulk modulus B_0 , internal distortion parameter u , and one of the Raman-active frequencies ω_{Γ_1} are in good agreement with experiment. The agreement is closer when these quantities are calculated assuming an inverse or partially inverse structure, thus indicating that direct structure is not the one actually occurring in nature. This conclusion is contradicted by the calculation of the

relative stability of different structures which would indicate the direct one to be energetically favored. For the time being, we cannot draw any conclusion as to whether this failure is due to the approximations of our calculations or to the fact that—due to the kinetic of the crystal growth and/or to the preparation method—the crystal structure actually observed is not the most thermodynamically stable. Among the experimentally accessible quantities which are sensitive to the normality, we finally signal the quoted Raman-active ω_{Γ_1} frequency and the valence intraband gap which changes as much as 25% going from the direct to inverse structures.

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