

Band structure of CsSnBr₃

I. Lefebvre, P. E. Lippens, M. Lannoo, and G. Allan

*Laboratoire de Physique des Solides, Institut Supérieur d'Electronique du Nord,
41 boulevard Vauban, 59046 Lille CEDEX, France*

(Received 16 May 1990)

The band structure of cubic CsSnBr₃ is determined by an empirical pseudopotential method. Independent of the choice of the parameters used in the calculation, cubic CsSnBr₃ is shown to be a zero-band-gap semiconductor. Based on this result, a new interpretation of the experimental data is proposed.

CsSnBr₃ crystals exhibit interesting electronic properties because of the phase transitions as a function of the temperature around 0°C.¹ At room temperature the structure is cubic, and becomes slightly distorted as the temperature decreases. The electronic structure of the cubic phase has been already investigated both experimentally and theoretically. However, some ambiguities appear in the determination of its electrical character. Parry *et al.*² have proposed that cubic CsSnBr₃ is a semimetal. This result is obtained from an extended-Hückel-method calculation. As pointed out by the authors, the resulting band structure depends upon the choice of parameters and does not always show a semimetallic character. The experimental data given in their paper do not clearly show this character. In addition, it is well known that the extended-Hückel method does not provide a good description of the conduction band, in contrast with pseudopotential calculations.³ Thus, we make use here of the latter approach, which is more adequate for a determination of the electrical behavior of CsSnBr₃. Other experimental data have been reported by Clark *et al.*⁴ which will also be discussed in this paper.

The empirical pseudopotential method has been extensively used in the calculation of band structures. This approach provides a good description of the valence band and of the lowest conduction bands. A lot of papers concerning this method have been published.⁵ We just detail its application to the case of cubic CsSnBr₃.

The one-electron pseudopotential can be written as a function of the form factors $V_i(q)$ where i denotes the atomic site in the unit cell and q is the reciprocal-lattice vector. The calculation of the band structure of CsSnBr₃ requires the knowledge of three different form factors. They can be calculated from the analytical relation proposed by Falicov and Lin:⁶

$$V_i(q) = \frac{\alpha(q^2 - \beta)}{1 + \exp[\gamma(q^2 - \delta)]}, \quad (1)$$

where α , β , γ , and δ are the form-factor parameters. Different sets of parameters have been reported in the literature for Sn.⁷⁻¹² The variations of the form factors as a function of q obtained from these parameters are found in the dashed area plotted in Fig. 1. For Cs we have used the set of parameters given by Harrison.¹² No reliable parameters have been found for Br. However, it

has been shown¹³ that the elements in a same column of the Periodic Table exhibit similar variations of $\Omega_i V_i(q)$ as a function of q , where Ω_i is the volume of the atom i . Thus, we have calculated the parameters of Br from those of iodine.^{14,15} The values of the parameters are given in Table I and the variations of the form factors in Fig. 2.

We have plotted the band structures of CsSnBr₃ obtained from the present pseudopotential calculation in Fig. 3(a), and from the extended-Hückel-method calculation of Parry *et al.* in Fig. 3(b). The differences in the predicted electrical behaviors can be seen by comparison of these two figures, and in particular from the differences in the values of the highest valence band at the point M_1 . The position of the Fermi level is found to be between the

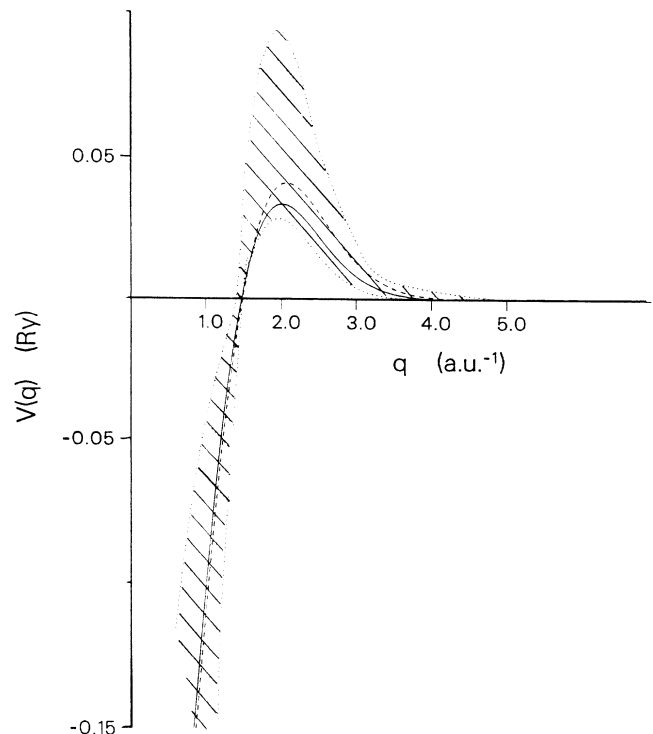


FIG. 1. Form factors for Sn atoms. The dashed area contains the values of Refs. 7-12. The straight line represents the variations of the form factor obtained from Table I.

TABLE I. Parameters used in the calculation of the form factors [Eq. (1)].

	α	β	γ	δ
Cs	0.65	0.46	5.00	-0.15
Sn	0.74	2.16	0.55	-2.70
Br	6.35	2.20	0.51	-6.30

R_{15} and M_5 levels in the calculation of Parry *et al.* and at the R_{15} point in the present calculation. We consider the origin of the energies at the R_{15} point. The M_1 point is found at about -1.5 eV in our calculation and at about 0.1 eV in the calculation of Parry *et al.* Thus, those authors have found that cubic CsSnBr_3 is a semimetal in contrast with the present pseudopotential calculation which shows that cubic CsSnBr_3 is a zero-band-gap semiconductor. As one can notice in Fig. 1 for Sn, other sets of parameters can be used in our calculation. We have considered numerous sets for the three atoms of CsSnBr_3 , and only slight changes in the band structure have been observed. For the clarity of this paper we do not analyze here the effect of the parameters. However, in all the cases cubic CsSnBr_3 is found to be a zero-band-gap semiconductor. It is worth noticing that this result is obtained by neglecting some effects such as spin-orbit coupling. The degeneracy at the R point results from the symmetry of the cubic lattice. As pointed out by Parry *et al.* the spin-orbit coupling could remove this degenera-

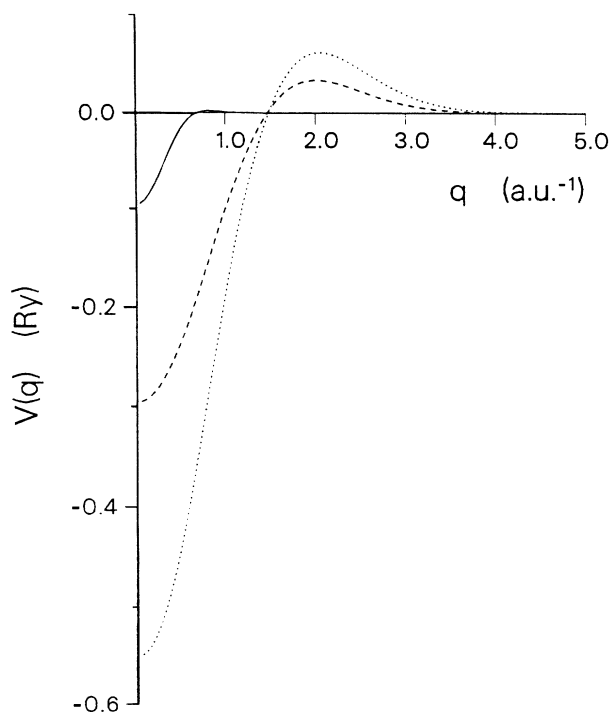


FIG. 2. Form factors calculated from the parameters of Table I. The solid line is for Cs, the dotted line for Sn, and the dashed line for Br.

cy and open a band gap. Thus, the real value of the band gap is quite possibly small. We conclude that the cubic CsSnBr_3 is a semiconductor with a zero or a narrow band gap.

The comparison with the experimental data is not simple because there is no unambiguous evidence of the electrical character of CsSnBr_3 . We compare some published experimental data with the present results.

The photoelectron spectra obtained by Parry *et al.*² provide interesting information concerning the electronic

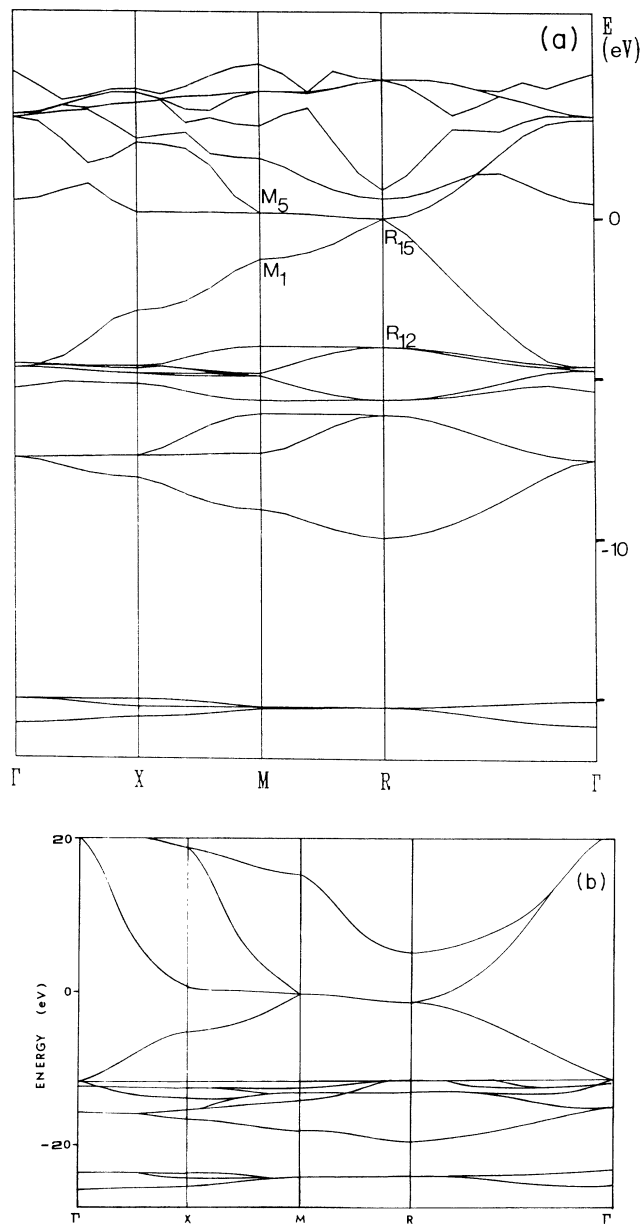


FIG. 3. Band structure of CsSnBr_3 obtained by the present pseudopotential calculation (a), and by the extended-Hückel-method calculation of Parry *et al.* (b). The origin of the energies is taken at the point R_{15} in the two figures. We have only indicated the points of the band structure used in the text.

density of states in the valence band. The spectra exhibit five main peaks at about -27 , -21 , -18 , -12 , and -5 eV (see Fig. 2 in Ref. 2). These values are given relative to the experimentally determined Fermi level. A direct comparison of these data with the results of the present pseudopotential calculation can be made by aligning the experimental and theoretical Fermi levels. In our calculation the Fermi level is found at the point R_{15} of the top of the valence band. The three lowest and nearly flat bands which are found from our calculation at about -16 eV can be compared to the peak at -18 eV. The energy difference can be attributed to the uncertainty in the position of the experimental peak which is not well resolved. The nearly flat bands at -5 eV correspond to the peak of the density of states at the same energy. The three other peaks, as noticed by Parry *et al.* can be assigned to states which do not significantly participate in the bonding of CsSnBr_3 because of their compact structure. The effect of the corresponding orbitals is not included in the calculation of the form factors. Thus, these three peaks cannot be predicted from our calculation. The comparison between the experimental data and the band structure calculated by Parry *et al.* [Fig. 3(b)] is more difficult. The Fermi level is found by those authors between the levels at points R_{15} and M_5 . The alignment of the Fermi levels does not provide a correct agreement between the calculated density of states and the experimental data. The peaks are found to be at -24 and -12 eV instead of -18 and -5 eV, respectively. Thus, there is a shift of about 6 eV. This problem has already been pointed out by Parry *et al.* in their paper. For a correct comparison, these authors have aligned the highest energy peaks obtained in experiments with those of their calculation instead of the Fermi levels. In that case, a correct agreement is observed. The reason for this discrepancy is inherent to the use of the extended-Hückel method. This method gives a correct description of the bands formed from bonding states, but not of the bands which include a large contribution of the antibonding states. In particular, it has been shown that the width of the latter bands is strongly overestimated by that kind of calculation.³ The same effect is observed in the calculated band structure of Parry *et al.* for energies higher than about -10 eV, as can be seen by comparison of Figs. 3(a) and 3(b). Thus, the description of the valence band, and, in particular, the position of the main peaks relative to the Fermi level, is correctly predicted by our calculation.

In their paper Clark *et al.*⁴ have reported measurements of the optical absorption, of the luminescence, and of the electrical conductivity of CsSnBr_3 . The quantitative interpretation of their results requires complicated calculations, and we just suggest some qualitative explanations. The most interesting results concern the variations of the electrical conductivity as a function of temperature. The authors have observed that the conductivity increases with the temperature up to about 303 K, and then decreases for higher temperatures. A phase transition (cubic \leftrightarrow tetragonal) has been observed by Mori and Saito¹ at 292 K and could explain this abrupt change in conductivity. In the range 160–303 K, CsSnBr_3 exhibits

the behavior of a semiconductor with a small band gap (≈ 0.34 eV). The phase transition yields modifications of the crystal symmetry. Mori and Saito have shown that the point group of CsSnBr_3 changes from O_h to D_{4h} at 292 K with decreasing temperature. Thus, the irreducible representations (E, T_1, T_2) of the O_h group are split into the representations ($A_1 + B_1, A_2 + E, B_2 + E$) of the D_{4h} group, respectively. This transformation will remove the degeneracy of the point R_{15} and open a band gap. This assumption is consistent with the small value of the gap which is observed experimentally. For temperature higher than about 300 K the conductivity strongly decreases. This is consistent with the semimetallic behavior proposed by Parry *et al.* as well as with our calculation if we consider the existence of impurities. Impurities are expected to introduce energy levels at about 0 eV and give a metallic character to the zero-band-gap semiconductor. In the experiments of Clark *et al.* the presence of impurities has been effectively shown by the values of the conductivity at low temperatures.

At room temperature, the optical-absorption spectra exhibit a threshold at about 1.8 eV, and the luminescence curve a peak at about 1.7 eV. As can be seen in Fig. 3(b) such a transition cannot be predicted from the band structure of Parry *et al.* On the other hand, our calculation clearly shows that the transition between the point M_1 of the highest valence band (≈ -1.5 eV) and the point M_5 of the lowest conduction band (≈ 0.2 eV) could explain these optical features. This assumption is confirmed by the fact that optical transitions are forbidden at the threefold degenerated R_{15} point but are allowed between points M_1 and M_5 . A simple calculation of the optical-absorption coefficient can be made by assuming no energy dispersion between points R_{15} and M_5 , and a parabolic curve between points R_{15} and M_1 . The absorption coefficient is shown to strongly increase at the energy of the transition $M_1 \rightarrow M_5$, as observed experimentally. In fact, all the directions in the momentum space must be taken into account for a realistic calculation. However, similar variations of the absorption coefficient are expected for energies lower than 2 eV.

Our discussion of the experimental data is based on the calculated band structure of Fig. 3(a) and is mainly qualitative. A more rigorous interpretation requires the calculation of the conductivity and the optical-absorption coefficient in the different phases of the crystal. The influence of the impurities should also be taken into account. However, the good agreement between our pseudopotential calculation and the experimental data confirms our description of the band structure. In contrast to the extended-Hückel calculation of Parry *et al.*, the position of the main features of the density of states relative to the position of the Fermi level, and the optical transition at about 1.7 eV can be predicted. In addition, the pseudopotential method is well known to give a better description of the band structure than the extended-Hückel method. Thus, cubic CsSnBr_3 must be a semiconductor with a zero or a narrow band gap. The phase transitions, which occur when the temperature decreases, are expected to increase the value of the band gap.

- ¹M. Mori and H. Saito, *J. Phys. C* **19**, 2391 (1986).
- ²D. E. Parry, M. J. Tricker, and J. D. Donaldson, *J. Solid State Chem.* **28**, 401 (1979).
- ³R. P. Messmer, *Chem. Phys. Lett.* **11**, 589 (1971).
- ⁴S. J. Clark, C. D. Flint, and J. D. Donaldson, *J. Phys. Chem. Solids* **42**, 133 (1981).
- ⁵See, for example, V. Heine, M. L. Cohen, and D. Weire, *Solid State Physics* (Academic, New York, 1970), Vol. 24.
- ⁶L. M. Falicov and P. J. Lin, *Phys. Rev.* **141**, 562 (1966).
- ⁷C. Y. Fong and M. L. Cohen, *Phys. Rev. B* **5**, 3095 (1972).
- ⁸M. Schluter and C. Schluter, *Phys. Status Solidi B* **57**, 147 (1973).
- ⁹G. Mula and F. Aymerich, *Phys. Status Solidi B* **51**, 35 (1972).
- ¹⁰M. J. Powell, W. Y. Liang, and D. J. Chadi, *J. Phys. C* **11**, 885 (1978).
- ¹¹R. Car, G. Guicci, and L. Quatapelle, *Phys. Status Solidi B* **86**, 471 (1978).
- ¹²W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).
- ¹³V. Heine, M. L. Cohen, and D. Weire, in Ref. 5, pp. 237–240.
- ¹⁴C. Schluter and M. Schluter, *Phys. Rev. B* **9**, 4 (1974).
- ¹⁵M. Schluter, M. L. Cohen, S. E. Kohn, and C. Y. Fong, *Phys. Status Solidi B* **78**, 737 (1976).