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Pseudopotential Calculation of the Band Structure of $CdIn_2S_4$

F. Meloni and G. Mula

Istituto di Fisica dell'Università, Cagliari, Italy

and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale della Ricerche, Italy

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The band structure of the spinel-type semiconductor $CdIn_2S_4$ has been calculated by the empirical-pseudopotential method. The form factors have been determined to agree with the values previously chosen by Cohen and Bergstresser for semiconductors with diamond and zinc-blende structures. Because of the large number of atoms per unit cell, a simplified model of the actual crystal structure has been developed, thus obtaining a feasible way to get meaningful results and to make direct comparisons with the band structures of many well-known elementary and binary semiconductors. The band structure obtained with the use of our model, and the results of the full calculations made for symmetry points, are discussed and compared with the available experimental information.

1. INTRODUCTION

During the last decade pseudopotential theory[1] proved to be a very useful basis for the study of the optical properties of a large class of solids. In fact, there are now several methods[2–5] to determine the pseudopotential to be used in actual calculations, depending on whether one wants to make a kind of *a priori* calculation or to obtain, by comparison with optical data, very accurate band structures. A notable point is that there are no great differences[6,7] between the pseudopotentials computed from first principles and the ones empirically determined, so that the gross features of a band structure can now be predicted with sufficient reliability; furthermore, as shown by very recent calculations[7–11] based on the empirical-pseudopotential method (EPM), quite good results can be obtained by associating a pseudopotential with each ion, independent of its chemical state, so that it is now possible to build good pseudopotentials even for complex structures like, e.g., ternary compounds. For these reasons we have chosen to investigate the band structure of spinel-type semiconductors by using the EPM. We expect these calculations to give reliable results, even in absence of detailed experimental information, of course, apart from possible "sensitive"[12] energy levels.

In this paper we report on a theoretical study of the band structure of the spinel-type semiconductor $CdIn_2S_4$; the form factors of our pseudopotential are those empirically determined by Cohen and Bergstresser[7] (CB) and modified to take into account the variation of the lattice constant, as explained in Sec. 2. This choice has been made essentially for two reasons: There is no other way to get a reliable approximation to the sulphur form factors, which are not given in the tables by Animalu and Heine,[5] and we regard the use of empirical form factors as more likely to get good results, because of taking into account crystalline effects such as charge redistribution and of a more realistic screening of the ionic potentials.

A preliminary analysis of the band structure of spinel-type semiconductors has been made recently by Rehwald,[13] who classified the electronic states on the basis of group theory and got first-order values of the energy levels at Γ in the nearly-free-electron approximation. The main difficulty in making a more accurate computation lies, of course, in the large number (64) of the valence electrons per unit cell, so that the order of the secular determinants to be solved is very high and requires a great deal of computer work. Moreover, the usual convergence difficulties are enhanced, so that it was felt that an approximation to the actual crystal structure leading to a lower number of valence electrons per unit cell could be a very effective way to get useful results without excessive labor. The details of this approximation and the band structure obtained with this approach are given in Sec. 3, while in Sec. 4 the results of unsimplified calculations made for symmetry points are compared with the available experimental information and a discussion is given of the validity of our approximation.

2. PSEUDOPOTENTIAL HAMILTONIAN

The pseudopotential Hamiltonian we have used can be written, as usual,

$$H=(\hbar^2/2m)\nabla^2+V(\vec{r}), \tag{1}$$

where V can be expressed as a Fourier series

$$V(\vec{r})=\textstyle\sum_q\left[S_q(\mathrm{S})F_q(\mathrm{S})+S_q(\mathrm{In})F_q(\mathrm{In})+S_q(\mathrm{Cd})F_q(\mathrm{Cd})\right]e^{-i\vec{q}\cdot\vec{r}}. \tag{2}$$

The structure factors S_q can be determined from the position of the atoms in the unit cell and are listed in Table I. The parameter u, which enters the coordinates of sulphur atoms, has been taken to be exactly $\frac{3}{8}$. For normalization purpose, in our table, each structure factor is divided by the number of atoms per unit cell of the element under consideration. Of course, the same number multiplies the corresponding form factor.

TABLE I. Structure factors $S_q=[\sum_i \exp i\vec{q}\cdot\vec{R}_i]/n$ for each element of the compound. See Sec. 2.

$\vec{q}/(2\pi/a)$ \ S_q	Cd	In	S
(1, 1, 1)	$-\frac{1}{2}\sqrt{2}\,\epsilon$[a]	$\frac{1}{2}\epsilon$	0
(2, 0, 0)	0	0	0
(2, 2, 0)	−1	0	0
(3, 1, 1)	$-\frac{1}{2}\sqrt{2}\,\epsilon$	$-\frac{1}{2}\epsilon$	0
(2, 2, 2)	0	1	−1
(4, 0, 0)	−1	1	1
(3, 3, 1)	$\frac{1}{2}\sqrt{2}\,\epsilon$	$-\frac{1}{2}\epsilon$	0
(4, 2, 0)	0	0	0
(4, 2, 2)	1	0	0
(3, 3, 3)	$\frac{1}{2}\sqrt{2}\,\epsilon$	$\frac{1}{2}\epsilon$	0
(4, 4, 0)	1	1	1
(5, 3, 1)	$\frac{1}{2}\sqrt{2}\,\epsilon$	$-\frac{1}{2}\epsilon$	0
(6, 0, 0)	0	0	0
(5, 3, 3)	$-\frac{1}{2}\sqrt{2}\,\epsilon$	$-\frac{1}{2}\epsilon$	0
(6, 2, 2)	0	1	−1

[a] $\epsilon=\cos\vec{q}\cdot\vec{\tau}/|\cos\vec{q}\cdot\vec{\tau}|$, where $\tau=\frac{1}{8}a\,(1,1,1)$.

TABLE II. Pseudopotential form factors, in Rydbergs, derived from the values of CB, by interpolation and renormalization, as shown in Sec. 2.

$\vec{q}/(2\pi/a)$ \ F_q	Cd	In	S
(1, 1, 1)	−0.0215	−0.0743	···
(2, 2, 0)	−0.0110	···	···
(3, 1, 1)	−0.0040	−0.0294	···
(2, 2, 2)	···	−0.0235	−0.2300
(4, 0, 0)	0.0063	−0.0071	−0.2250
(3, 3, 1)	0.0100	0.0044	···
(4, 2, 2)	0.0120	···	···
(3, 3, 3)	0.0130	0.0213	0.0078
(4, 4, 0)	0.0140	0.0254	···
(5, 3, 1)	0.0130	0.0260	···
(6, 2, 0)	0.0042	···	···
(5, 3, 3)	0.0000	0.0260	···
(6, 2, 2)	···	0.0260	0.0150

The form factors F_q are taken from those of CB after proper corrections for the variation of the lattice constant and of the atomic volume, as suggested by Animalu and Heine.[5] Parallel corrections have been made for the variation of the dielectric function, using the expression and the table in Ref. 6, putting for each element the number of screening electrons equal to 4, i.e., to the average number of electrons per atom, including vacancies. The values so computed are shown in Table II.

As can be seen from Fig. 1 the necessary interpolation procedure for determining the F_q's for the crystal parameters of the $\mathrm{CdIn_2S_4}$ leads to fairly unambiguous results for the cadmium and indium potentials, while for the sulphur form factors, both for the absence of Heine-Abarenkov[4]-type calculations and for the fact that only two values can be directly taken from CB, there is a large uncertainty for the intermediate q values. For these reasons the dashed interpolation curve of Fig. 1 can only be considered as purely indicative. The effect of this indetermination will be discussed in Sec. 4.

3. SIMPLIFIED ENERGY-BAND CALCULATIONS

As is known[13] the primitive rhombohedral unit cell of cadmium indium sulphide contains two Cd, four In, and eight S atoms, i.e., 64 valence electrons: Therefore to attain the same convergence degree of the calculations of CB it would be necessary to use at least 1000 plane waves for the expansion of the wave function. Such an expansion is not a simple matter, even with modern computers, so that we studied a way of tackling the problem that could give reliable results without too much effort.

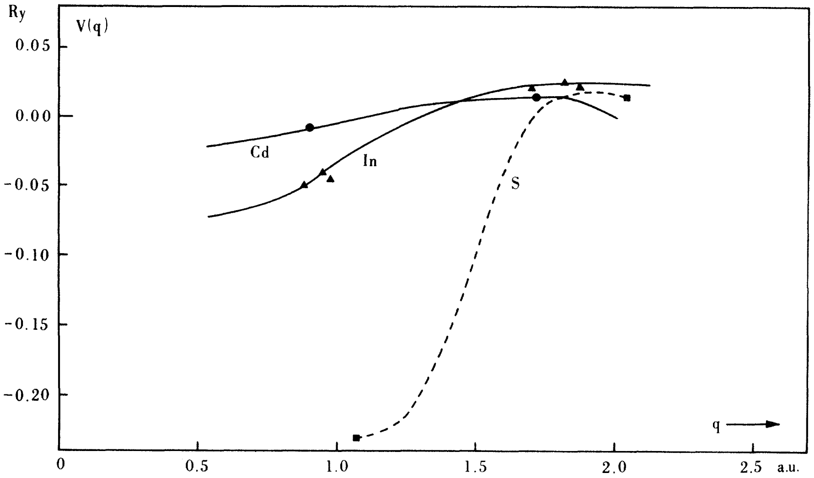

FIG. 1. Interpolation curves for form factors. The heavy dots are the values taken from CB after proper renormalization. (See text.)

Our approximation consists in building a fictitious unit cell smaller than the actual one; we chose to take as unit cell that one of the anion sublattice, which is essentially a fcc lattice with half the lattice constant of the spinel. So we have one S, $\frac{1}{2}$ In, and $\frac{1}{4}$ Cd atoms per unit cell, i.e., 8 valence electrons instead of 64, and the use of about 100 plane waves is now enough to get convergent results to within 0.1 eV; of course, fractional numbers of atoms mean nothing: One has to average over the actual unit cell and the best way to do it is to use the same Fourier coefficients as in an exact calculation, only remembering that, because of the halving of the lattice constant, there is a series of q values which are no longer allowed.

Table III gives the details of the conversion, together with the values of the Fourier coefficients utilized for the calculation. It should be noted that our approximation is entirely equivalent to representing the energy bands of $CdIn_2S_4$ in a large reciprocal-lattice zone eight times greater than the true Brillouin zone (BZ) and to retain only the Fouier coefficients which do not break the continuity of the $E(\vec{k})$ inside the large zone.

The results obtained with the use of the values in Table III are shown in Fig. 2. These results were obtained with the technique first devised by Brust,[12] putting $E_1 = 7$, $E_2 = 11.5$, and $E_M = 1.8$, in units of $(2\pi/a)^2$, that is by using about 50 plane waves. No significant variation has been found with the use of more plane waves, up to 113 for $\vec{K} = 0$.

TABLE III. Fourier coefficients, in Rydbergs, for the approximate structure of $CdIn_2S_4$ (see text).

Actual structure $a_1 = a$		Approximate structure $a_2 = a/2$	
$\vec{q}/(2\pi/a_1)$		$\vec{q}/(2\pi/a_2)$	V_q
(2, 2, 2)	→	(1, 1, 1)	0.207
(4, 0, 0)	→	(2, 0, 0)	−0.240
(4, 4, 0)	→	(2, 2, 0)	0.047
(6, 2, 2)	→	(3, 1, 1)	0.009

As should be expected the general shape of this approximate band structure resembles very much that one of the zinc-blende-type semiconductors. Throughout the large zone there is an energy gap between the fourth and the fifth band which corresponds to a gap between the 32nd and the 33rd band in the reduced zone, that is, to a gap between the filled and the empty bands.

Additional information on the band structure in the reduced zone can be gained by partial reduction; as is known,[14] the X and L points of the large zone correspond to Γ points in the reduced one, so that we can guess the position of some upper levels at Γ simply by inspection. Then, also in the reduced zone, the direct gap at Γ should be between Γ_{15} and Γ_1 states and of about 3.0 eV; owing to the shape of the first conduction band one should expect a marked increase in the density of states for energies slightly above 3 eV.

4. FINAL RESULTS AND DISCUSSION

Till now the experimental information about the optical properties of $CdIn_2S_4$ above the absorption edge is rather poor and can be summarized in the following points[15,16]: The lowest energy gap is of 2.2 eV and is an indirect one; the lowest direct transition occurs at about 3.1 eV; three other reflection peaks can be seen at about 4.5, 5.0, and 5.5 eV. The band structure computed on the basis of our model allows for an interpretation of these features: In fact, as we already pointed out, the peak structure at energies between 3 and 6 eV can be attributed to the folding of the first conduction band of the large zone into the reduced zone; we recall that a large zone is equivalent to eight times the

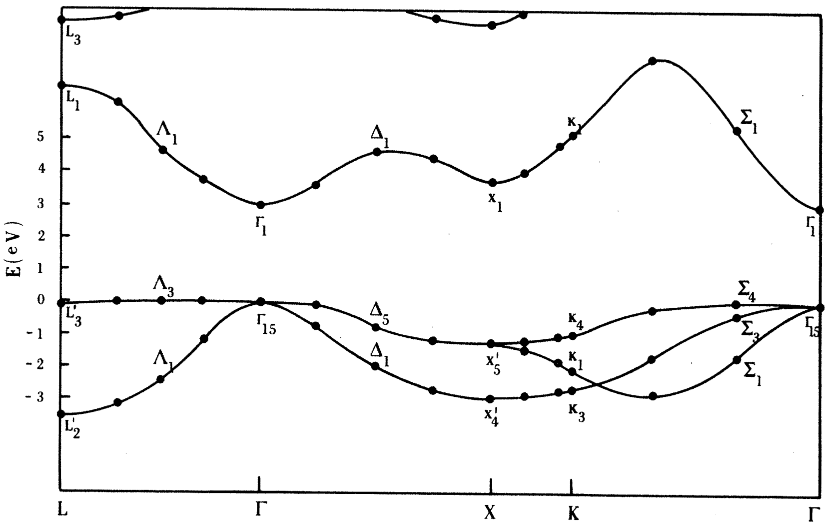

FIG. 2. Large-zone band structure of $CdIn_2S_4$. (See text.)

BZ. Moreover the occurrence of an indirect gap can be easily understood by taking into account the perturbation due to the neglected Fourier coefficients: Including coefficients such as $V(1, 1, 1)$ or $V(2, 2, 0)$ gives rise to energy splittings, respectively, at the points $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ or $(\frac{1}{2}, \frac{1}{2}, 0)$ in the large zone. Thus it can be seen that the point which is more likely to become the minimum of the conduction band is the point L of the reduced zone, since the related Fourier coefficient, namely, $V(1, 1, 1)$, is by far the largest one of the coefficients neglected in our approximation. Therefore we can suggest that the indirect absorption edge corresponds to a Γ-L transition.

To get more detailed results we made full calculations of the energy bands of $CdIn_2S_4$, that is, we took into account all the Fourier coefficients of the pseudopotential up to $V(6, 2, 2)$, for several points in the BZ and using up to 113 plane waves at $\vec{K} = 0$. The results for the symmetry points Γ, X, and L appear convergent to within 0.5 eV, whereas those ones for general points are practically useless. In fact, on increasing the number of plane waves the shift of the Fermi level is several times greater for general points than for symmetry points. Thus the use of only ~ 100 plane waves is not enough to get satisfying results for all the BZ; nevertheless we can make a useful comparison with the preceding results.

In Fig. 3 we report an indicative band structure of $CdIn_2S_4$: The energy levels at Γ, X, and L, computed with $E_1 = 11.5$, $E_2 = 21.5$, and $E_M = 9$, in units of $(2\pi/a)^2$, are joined together by smooth lines, taking into account the compatibility relations. The agree-

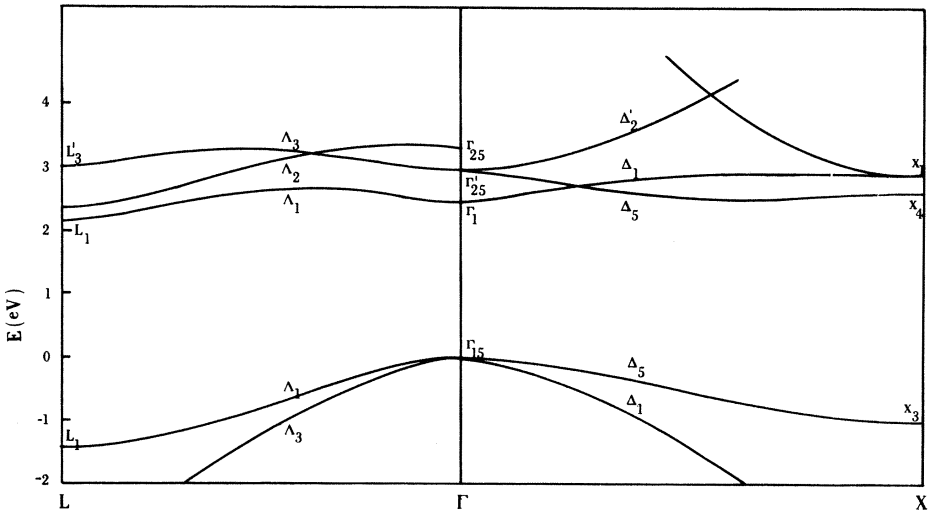

FIG. 3. Reduced-zone band structure of $CdIn_2S_4$.

ment between our two band structures is quite gratifying: The direct gap of lowest energy is between Γ_{15} and Γ_1 states in both cases and is of comparable magnitude (2.5 against 3.0 eV). Moreover, the minimum of the conduction band occurs at L, as we have suggested. We see that this indirect gap is of about 2.1 eV, in good agreement with the experimental result of 2.2 eV[15]; it must be pointed out, however, that this close agreement should not be regarded as particularly meaningful because of the relatively large arbitrariness of the interpolation curve for the sulphur pseudopotential. In fact, while our band structures are practically unchanged by a different, but reasonable, choice of the interpolation curves for indium and cadmium pseudopotentials, we can see from Fig. 1 that the differences between reasonable interpolation curves for the sulphur pseudopotentials may be significant.

We made no attempt to get a best fit by adjusting the sulphur pseudopotential, but we found that a substantial lowering of the curve causes a lowering of the energy gap too. Nevertheless the general appearance of the band structure is unaltered, so that we feel that our interpolation curve is a good one and could be used satisfactorily for other ternary sulphur compounds.

In conclusion we say that our simplified approach allows a straightforward use of the EPM for such complex structures and correctly gives the qualitative features and some quantitative results for the energy bands. Its success clearly shows its close connection with the physical reality and points out the usefulness of comparing complex structures like spinel with the simple structures from which they can be thought to derive. On this basis the use in our calculation of form factors taken from binary compounds can be fully justified. Our complete calculations for the symmetry points of the real structure both confirm the validity of our model and the correctness of our pseudopotentials so that the extension of our approach to other semiconductors with the same or similar structure seems particularly promising. Work is in progress in this direction.

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