

ENERGY BANDS AND OPTICAL PROPERTIES OF THE RANDOM
DEFECT SEMICONDUCTORS Ga_2S_3 , Ga_2Se_3 , Ga_2Te_3 AND
 In_2Te_3

G. Guizzetti^{†,††}, F. Meloni^{†,†††} and A. Baldereschi[†]

†) Laboratoire de Physique Appliquée, Ecole Polytechnique
Fédérale, Lausanne, Switzerland.

††) GNSM-CNR, Istituto di Fisica, Università di Pavia, Italy

†††) GNSM-CNR, Istituto di Fisica, Università di Cagliari, Italy

We study the electronic energies of the random zincblende compounds M_2X_3 by the dielectric theory and the virtual-crystal empirical pseudopotential method. The properties of these materials result to be intermediate between those of their III-V and II-VI analogs with weights 0.6 and 0.4, respectively. The main reflectivity peaks are interpreted as direct transitions at the points Γ , L and X. Weaker structures correspond to the predicted Γ -L and Γ -X pseudodirect gaps.

The III-VI binary compounds of $\text{M}=\text{Al}$, Ga , In and $\text{X}=\text{S}$, Se , Te generally have one of the two chemical formulas MX and M_2X_3 . While the MX compounds crystallize in layer structures, the M_2X_3 ones are tetrahedrally coordinated and their structures strongly resemble those of zincblende and wurtzite [1]. These crystals are the simplest example of semiconductors with completely satisfied chemical valencies but with a large number of vacant cation sites. The cation vacancies can be ordered (low temperature phase with very large unit cell) or fully random at higher temperatures. Although experimental work has been done on their structural, electrical, optical and vibrational properties no theoretical work has yet been published.

In this work we present the results of a theoretical investigation of the compounds Ga_2S_3 , Ga_2Se_3 , Ga_2Te_3 and In_2Te_3 which at high temperature have the simplest possible structure, i.e. random sphalerite. The fundamental interband transition energies are first estimated from the Phillips-VanVechten dielectric theory [2] by appropriately averaging the properties of III-V and II-VI analogs and then they are calculated by the empirical pseudopotential method taking the cation disorder into account via the virtual-crystal approximation. The results of the two methods are similar and indicate that the properties of M_2X_3 compounds are a weighted average between those of the III-V and II-VI analogs with weights 0.6 and 0.4, respectively. The most intense reflectivity peaks correspond to the calculated direct interband energies at the points Γ , L and X of the Brillouin zone. Some weak structures in the reflectivity spectra could be interpreted as indirect Γ -X and Γ -L virtual-crystal transitions which are allowed by cation disorder even without phonon assistance (non-direct or pseudo-direct transitions).

We first calculate the main optical gaps E_0 , E_1 , E_2 and the indirect Γ -L, Γ -X transition energies from the Phillips-VanVechten dielectric theory by assimilating the M_2X_3 crystals to virtual tetrahedral AB compounds. The virtual system is defined as a zincblende

crystal obtained by averaging, with weights x and $(1-x)$, respectively, the "isoelectronic" III-V and II-VI analogs, i.e. GaP-ZnS for Ga_2S_3 , GaAs-ZnSe for Ga_2Se_3 , GaSb-ZnTe for Ga_2Te_3 and InSb-CdTe for In_2Te_3 . Following the basic assumptions of the dielectric theory, the weighting factor x is determined from the observed optical dielectric constants. The only value available is $\epsilon_\infty(\text{In}_2\text{Te}_3) \approx 10.3$ [3] from which we derive $x \approx 0.52$. Better overall agreement with the experimental optical data of all compounds is obtained with a somewhat larger value of x and therefore we have decided to use $x = 0.6$. The resulting average values of the ionic energy gap C and of the d-character correction factor D_{av} are given in the Table together with the spin-orbit splitting Δ_0 and the lattice constant a . All values of a are taken from [1] except a (Ga_2S_3) = 5.24 Å which is an average taken from [4]. Published values of the lattice constant of Ga_2S_3 range from 5.17 Å [5] to 5.42 Å [6]. The predictions of the dielectric theory for the fundamental energy gaps are also given in the Table and will be discussed later on.

Table Values of the parameters used in the calculations and of the calculated transition energies in eV. Experimental transition energies correspond to the position of the strongest reflectivity peaks corrected for spin-orbit effects. All data are from [9] except those indicated (a) which are from [10].

Crystal	$a(\text{\AA})$	$C(\text{eV})$	D_{av}	$\Delta_0(\text{meV})$		E_0	E_1	E_{2A}	E_{2B}	$\Gamma\text{-L}$	$\Gamma\text{-X}$
Ga_2S_3	5.24	4.5	1.14	100	diel.	3.4	4.7	6.5	6.8	3.7	4.6
					pseud.	2.6	4.5	6.1	6.3	3.7	4.2
					exp.	2.6	4.5	6.7	6.7		
Ga_2Se_3	5.41	4.0	1.21	380	diel.	2.0	3.8	5.9	6.2	2.8	3.9
					pseud.	2.0	4.1	5.8	6.2	3.4	4.2
					exp.	2.1	3.9	6.3	6.3		
Ga_2Te_3	5.87	3.0	1.27	850	diel.	1.3	3.0	4.7	4.9	1.9	2.6
					pseud.	1.4	2.9	4.4	5.1	2.2	3.1
					exp.	1.4	2.8	4.5	5.4		
In_2Te_3	6.14	3.2	1.37	860	diel.	0.6	2.7	4.5	4.8	1.8	2.9
					pseud.	1.3	2.9	4.2	5.2	2.3	3.4
					exp.	1.4	2.4	4.3	5.2		
						(a)	(a)	(a)			

We now calculate the energy bands of the M_2X_3 random-sphalerite compounds by the empirical pseudopotential method. The cation vacancy disorder will be handled via the virtual crystal approximation (VCA) [7] which in the past has been successfully used to treat the cation disorder in homogeneous III-V and II-VI semiconducting alloys. Deviations from the VCA are expected to be larger in our case since we average between group III cations and vacancies (i.e. we average over both the long-range and the short-range parts of the atomic potentials) whereas for homogeneous alloys the average is between atoms of the same valence (i.e. over the short-range part only). We replace the M_2X_3 crystal with its VCA perfect-zincblende analog in which all cation sites are occupied with "atoms" whose potential is 2/3 that

of the real cation M. The empirical pseudopotential calculations have been performed with the method and the local atomic pseudopotentials proposed in [8] except for the S atom whose γ parameter has been increased from 1.853 a.u. to 1.93 a.u. in order to improve the agreement with experimental data for Ga_2S_3 . We use Penn model for the diagonal valence screening and simulate ionic charge-transfer screening with effective anion and cation charges Z_a^* , Z_c^* which are determined by a fit to the lowest energy gap E_0 . The values used are $Z_a^* = 5.3$, $Z_c^* = 2.7$ except for In_2Te_3 where we use $Z_a^* = 5.2$, $Z_c^* = 2.8$. The resulting energy gaps are given in the Table where they are compared with experimental data [9,10]. The VCA energy bands of Ga_2Se_3 and In_2Te_3 are represented in the Figure.

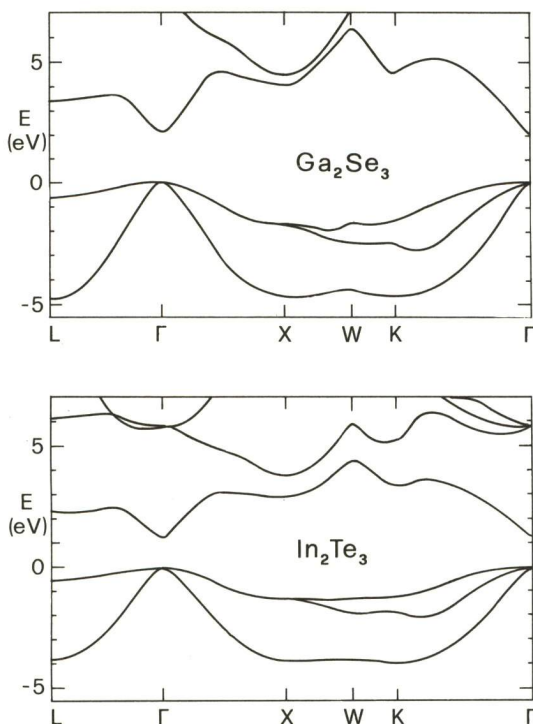


Figure Pseudopotential energy bands of Ga_2Se_3 and In_2Te_3

The theoretical results reported in the Table do not contain the effects of structural disorder. These can be included by treating the potential fluctuations by perturbation theory as explained for homogeneous alloys in [11]. The effects of the short-range potential disorder are in the range 10 - 100 meV [11] and can be neglected for our purposes, those of long range disorder can be estimated by comparing chalcopyrite compounds with their III-V or II-VI analogs as explained in [12] and should not exceed 0.3 eV. The latter figure must be kept in mind when comparing theoretical and experimental energy gaps. Cation-vacancy disorder is also expected to produce qualitative effects. Similar to amorphous semiconductors [13] and homogeneous semiconducting alloys [14], disorder will allow non-di-

rect or pseudo-direct optical transitions, i.e. zero-phonon non-vertical optical transitions. The optical spectra of random M_2X_3 compounds can therefore present structures corresponding to transitions which in VCA are indirect and therefore forbidden. This is the reason why in the Table we have included the indirect Γ -L and Γ -X energy gaps.

According to our calculations all materials are direct at the Γ point including Ga_2S_3 which is intermediate between GaP and ZnS which are indirect and direct, respectively. The direct energy gaps obtained from the pseudopotential calculation generally differ from the dielectric ones by not more than 10%. This agreement on four materials with rather different lattice constant and ionicity is very satisfactory since the dielectric results should be much less sensitive on structural approximations. Notable exceptions are the E_0 gaps in In_2Te_3 and Ga_2S_3 . In the former case the dielectric result must be considered less accurate since it is very sensitive to the parameter D_{av} (reducing D_{av} to 1.36, the value of E_0 increases to 0.7 eV). The disagreement for Ga_2S_3 is not understood at present. The pseudopotential result has been adjusted to the experimental value quoted in the Table and which to our knowledge is the only available for the random sphalerite phase. The optical threshold measured in the ordered wurtzite structure is 3.4 eV [15] which is the dielectric result.

The indirect-gaps predicted by the two models show larger differences ($\leq 20\%$). Extending the statistical analysis made by VanVechten [2] the dielectric results should be more accurate. In the Table we have not reported the experimental values of the non-direct gaps. The reflectivity spectra indeed show structures at the predicted energies [9] but these are broad and weak.

According to our interpretation of the reflectivity peaks, spin-orbit splittings have been observed only in the spectrum of In_2Te_3 and at the E_0 gap in Ga_2Te_3 . It is not yet established if in all other cases the splittings have not been resolved because of the intrinsic vacancy disorder or due to the poor quality of the samples. The former explanation is supported by the infrared reflectivity spectra [3,4] which show richer structures for the ordered phases.

- 1) N.A.Goryunova: The Chemistry of Diamond Like Semiconductors ed. J.C.Anderson (Chapman and Hall, London 1965) pp. 154-156
- 2) J.C.Phillips: Bonds and Bands in Semiconductors (Academic, New York 1973). J.A.VanVechten: Phys.Rev. 182 (1969) 891; *ibid.* 187 (1969) 1007.
- 3) E.Finkman and J.Tauc: Phys. Rev. Letters 31 (1973) 890.
- 4) E.Finkman, J.Tauc, R.Kershaw, A.Wold: Phys.Rev.B11 (1975) 3785.
- 5) L.G.Musaeva, G.A. Akhundov, A.E. Bakhyshev and N.M.Gasanli: *phys. stat. sol. (b)* 60 (1973) K1.
- 6) R.W.G.Wyckoff: Crystal Structures (Intersc.NY. 1964) Vol.2,p.22.
- 7) R.Hill: J.Phys.C 7 (1974) 521 and references therein.
- 8) F.Aymerich, F.Meloni and G.Mula: Phys.Rev.B15 (1977) 3980.
- 9) V.V.Sobolev: *phys.stat.sol. (b)* 43 (1971) K71.
- 10) D.L.Greenaway and M.Cardona: Proc. Int. Conf. Phys. Semicond. at Exeter (Inst. Physics, London 1962) p.666.
- 11) A.Baldereschi and K.Maschke: Solid State Commun. 16 (1975) 99.
- 12) W.Andreoni, A.Baldereschi, R.Car: Solid State Comm. 27 (1978)821.
- 13) N.F.Mott and E.A.Davis: Electronic Processes in Non-crystalline Materials (Clarendon, Oxford 1971) § 7.6.
- 14) A.Onton: J.Luminescence 7 (1973) 95.
- 15) V.P.Mushinskii et al: *phys. stat. sol. (b)* 83 (1977) K 149.