Optical nonlinearity, band-structure parameters, and refractive indices of some mixed chalcopyrite crystals

L. K. Samanta,* D. K. Ghosh,† and G. C. Bhar,
Department of Physics, Burdwan University, Burdwan 713104, West Bengal, India
(Received 16 September 1985)

This paper describes for the first time a method of evaluation of some properties (such as the optical nonlinearity, lowest energy gap, band structure, and other relevant parameters) of mixed ternary semiconducting compounds. A comparison of the calculated results with the available experimental data on mixed chalcopyrite crystals is encouraging.

I. INTRODUCTION

The ternary chalcopyrites ($A^{II}B^{IV}C_2^{V}$ and $A^{I}B^{III}C_2^{VI}$) have shown considerable technological interest for efficient nonlinear optical conversion in a variety of optoelectronic device applications.[1] Using, particularly, $A^{I}B^{III}C_2^{VI}$ as absorber and a suitable binary as the window it is possible to construct heterojunction solar cells having enormous potential. Not only the single crystal but their solid solutions have created a lot of interest because of their possible applications in electro-optic devices. The mixed crystals are currently being used for the fabrication of lasers, detectors, and, very recently, for the new type of integrated optic devices[2] such as switches, modulators, and filters, etc. Yamamoto and Miyauchi[3] reported mixed crystals of $CuAl_{1-x}Ga_xS_2$ as useful light-emitting diode (LED) material covering the ultraviolet to green spectral range, while Mikkelsen and Kildal[4] showed that the phase matched second-harmonic generation (SHG) is possible using the $CdGe(As_{1-x}P_x)_2$ crystal pumped with a cw CO_2 laser. Because of the increasing trend of applications of the mixed crystals for a variety of applications, it is now a customary technique to change the cation/anion concentration of the single crystal. Among the key parameters for device control, nonlinearity is the most important which, in turn, is related to the refractive index. Again Tell *et al.*[5] and Galley *et al.*[6] have studied the valence-band structure of $CuGa_xIn_{1-x}S_2$ and $ZnSi(As_{1-x}P_x)_2$ crystals, respectively, and reported a spin-orbit splitting parameter ($\Delta_{s.o.}$) and crystal field splitting parameters (Δ_{cf}) for different concentrations. This paper describes for the first time the optical nonlinearities, refractive indices and band structure parameters of some useful mixed chalcopyrite crystals as the latter plays a dominant role in characterizing their optical properties.

Using the bond charge model of Levine[7] and introducing the necessary modifications which are essential for the evaluation of several parameters of the mixed crystals we have evaluated the nonlinear optical susceptibilities of $AgGa(S_xSe_{1-x})_2$, $AgIn(S_xSe_{1-x})_2$, $AgGa_xIn_{1-x}S_2$, $AgGa_xIn_{1-x}Se_2$ belonging to $A^{I}B^{III}C_2^{VI}$, $CdGe(P_xAs_{1-x})_2$, and $ZnGe(P_xAs_{1-x})_2$ to $A^{II}B^{IV}C_2^{V}$ group throughout the whole range of concentration. In this connection the spin-orbit splitting parameters $\Delta_{s.o.}$, the crystal field splitting Δ_{cf}, the lowest gap of the crystals with bowing parameters, and, finally, the refractive index values of a mixed pentenary have also been presented.

II. THEORY AND METHOD OF EVALUATION

Because of favorable nonlinear susceptibilities and favorable matching characteristics[8,9] the noble metal ternary compound, particularly with Ag, becomes very attractive. Good quality single crystals of the new and closely related ternary compound have been grown and some of their linear and nonlinear optical properties have been investigated. The second-order susceptibility and hence the nonlinear coefficient in a dielectric is closely related to the valence electron distribution. Out of the several approaches, such as the molecular orbital method of Jha and Bloembergen,[10] the charge transfer model of Tang and Flytzanis,[11] the dielectric theory of Phillips and Van Vechten,[12] and the bond charge model of Levine,[7] the latter is very useful in explaining the several linear and nonlinear properties and has been shown to give excellent agreement with experiment for a wide variety of simple and complex crystal structures. Using the bond charge model, the expression for Miller's delta comes out to be

$$\Delta_{ijk} = \sum F[\Delta_{ijk}(C) + \Delta_{ijk}(E_h)] , \tag{1}$$

where F, Δ, E_h, and C refer to a particular bond. Since in the sphalerite and sphalerite-related structure there is only one nonvanishing component of nonlinear coefficient we have omitted the subscript to Miller's Δ. Now

$$F\Delta(E_h) = \frac{G\chi^2 23.2 E_h^2 (v_\alpha - v_\beta)}{d^2 q\, N_b E_g^2 \chi_{av}^3} ,$$
$$F\Delta(C) = \frac{G\chi^2 600 \,|e|\, e^{-k_s d/2} b (Z_\alpha + Z_\beta) C}{d^2 q\, N_b E_g^2 \chi_{av}^3} , \tag{2}$$

χ_{av} being the average principal linear susceptibility of the crystal and all the quantities on right-hand side (RHS) of (2) refer to a particular bond. The quantity N_b denotes the number of particular bond types per cubic centimeters ϵ, the dielectric constant, f_c, the fractional covalent character of the bond, E_g being the Philips–Van Vechten (PV) gap, d, the bond length of the crystal and the bond charge being given by $q/e = n_v(1/\epsilon + \frac{1}{3}f_c)$. For evaluat-

ing the quantities like $\Delta(E_h)$ and $\Delta(C)$ for mixed crystals one has to take into account the relative contributions of different bonds. The contributions of d electrons have already been accounted for. As to the value of E_g(PV gap) we have neglected its bowing and this is justified because of its large value compared to the actual energy gap of the crystal. Thus χ_{av} of the mixed compound can be found as has already been done,[13] but χ of the bond in mixed varieties have been evaluated[14] by taking into account the weighted average of the bond. The bond length between the atoms in a mixed crystal have been evaluated by utilizing the relation of the form first suggested by Van Vechten and Bergstrasser,[15] i.e., for example, the bond length in AgS_xSe_{1-x} is given by $d=r_{Ag}+xr_S+(1-x)r_{Se}$ and thus helping one to calculate nonlinearity for the mixed crystals.

It is well known that the degeneracy of the p-like valence bands is completely lifted due to the simultaneous effect of the noncubic crystalline field and spin-orbit interaction in a chalcopyrite crystal thus showing the importance of the knowledge of the crystal field splitting (Δ_{cf}) and the spin-orbit splitting ($\Delta_{s.o.}$). Investigations show that the crystal field splitting Δ_{cf} of the valence bands in $A^{II}B^{IV}C_2^V$ crystals is dominated by the noncubic potential associated with the built-in lattice compression along the Z axis. The crystal field splitting of a valence band maxima may be written as $\Delta_{cf}=\frac{3}{2}b(2-c/a)$, where b is the deformation potential; c and a are the lattice parameters of the crystal. The above relation holds good for $A^{II}B^{IV}C_2^V$ compounds but the presence of d electrons in compounds with noble metal complicates the situation and these have been well accounted for, taking into consideration the contribution of d electrons separately in the deformation potential. Again the observation of spin-orbit splitting is one of the most reliable ways to find the nature of a transition as in atomic spectra. It also helps to understand the nature of transition on the high-energy side of the dominant peak as those from the same valence-band L state to higher L states in the conduction band. The spin-orbit splitting parameters $\Delta_{s.o.}$ have been evaluated for these mixed crystals using the relation as given by Hubner and Unger[16] and modifying accordingly for the mixed crystal where a linear variation of ionicity with x is considered. The atomic spin-orbit splitting of most of the elements are known[17] but problems arise in the case of Cu and Ag, whose atomic spin-orbit splittings are not properly known although Hubner[18] suggested a value. We have made a detailed study of $\Delta_{s.o.}$ for compounds containing the Cu and Ag elements, and since $\Delta_{s.o.}$ for quite a number of ternary compounds are known, we are able to evaluate Δ_{Cu} and Δ_{Ag} which, in turn, allows us to evaluate $\Delta_{s.o.}$ for these mixed crystals. Rowe and Shay[19] showed that the splitting of the Γ_{15} Zinc blende valence band can be explained under the combined action of Δ_{cf} and the spin-orbit splitting $\Delta_{s.o.}$ which again can be evaluated from the A,B,C transition energies as reported by Hopfield.[20] As $\Delta_{s.o.}$ and Δ_{cf} have already been known, so it is possible to calculate E_1, E_2 and hence the lowest gap of the compound. Again

$$E_1=E_A-E_B,\quad E_2=E_C-E_B$$

and

$$\Delta_{cf}=\tfrac{1}{2}[(E_1+E_2)-\{(CE_1+E_2)^2-6E_1E_2\}^{1/2}]\,,$$
$$\Delta_{s.o.}=\tfrac{1}{2}[(E_1+E_2)+\{(E_1+E_2)^2-6E_1E_2\}^{1/2}]\,, \tag{3}$$

with $E_0=\frac{1}{3}(E_A+E_B+E_C)$. This in turn helps one to estimate the bowing parameter of these crystals.

Lastly we have evaluated the refractive indices of these mixed crystals together with the pentenary $AgGa_yIn_{1-y}(S_xSe_{1-x})_2$ using the model suggested by Ghosh *et al.*[21]

III. RESULTS AND DISCUSSIONS

The results of our calculations of optical nonlinearity, band structure parameters and refractive indices of some mixed crystals are shown in the Table I. As the total nonlinearity (Δ) is the sum of $\Delta(C)$ and $\Delta(E_h)$, it is found that in case of mixed bonds of the type AgS_xSe_{1-x} both of the above parameters increase with the concentration whereas for (Ga_xIn_{1-x}−S,Se) a decreasing trend is observed. The relative magnitude and the rate of variation of $\Delta(C)$ and $\Delta(E_h)$ when considered for the whole crystal the total nonlinearity shows a slowly decreasing trend as one passes from lower to higher concentrations. The behavior of $\Delta(C)$ and $\Delta(E_h)$ values with composition is just the opposite for the other two silver mixed compounds because of higher contributions of $\Delta(E_h)$ and $\Delta(C)$ arising from larger ρ values[7] and the more ionic character of Ag-SeS bond but for the whole crystal considering the other contributions the general trend of decrease of Δ with x is maintained. This feature is in agreement with the experimental observation where $\Delta(AgGaSe_2)>\Delta(AgGaS_2)$ and $\Delta(AgInSe_2)>\Delta(AgInS_2)$ relevant to the higher refractive indices of the former material.

Considering $A^{II}B^{IV}C_2^V$ mixed quaternaries the opposite trend in the behavior of crystal nonlinearity is observed. Here the contributions from more covalent mixed bonds such as Ge-P_xAs_{1-x} is of the same sign as the other mixed bonds and the rate of cationic and anionic variation adjust themselves to yield the observed trend which again agrees with the experimental results.[7] The observed trend that the optical nonlinearity increases from sulphide to selenide and gallium to indium for the mixed Ag compounds leads to the choice of a suitable alloy composition to meet a specific device requirement. An effort has been made to establish a multivariate functional relationship for the crystal nonlinearity of a hypothetical mixed pentenary $AgGa_yIn_{1-y}(S_xSe_{1-x})_2$ in the form

$$\Delta(x,y)=\sum_{ij} a_{ij}x^iy^j\,.$$

A linear least-square fit (for $x=y$) truncated at the fourth term yields

$$\Delta(x)=0.919-0.5287x+0.5344x^2-0.25x^3\ldots\,. \tag{4}$$

Figure 1 shows a three-dimensional representation of the composition dependent nonlinearity normalized to that of $AgGaS_2$. It is evident from the figure that the crystal

TABLE I. Calculated values of nonlinearity, spin orbit splitting ($\Delta_{s.o.}$) crystal field splitting (Δ_{cf}), refractive index (n), and lowest band gap (E_g) at different concentrations together with the available experimental values of E_g.

Crystal	Concentration x	Nonlinearity $\Delta\times10^{-6}$ esu	$\Delta_{s.o.}$ (eV)	$-\Delta_{cf}$ (eV)	$E_{g\,cal}$ (eV)	$E_{g\,expt}$ (eV)	Refractive index n
$AgGa(S_xSe_{1-x})_2$	0.2	0.82	0.19	0.28	2.01	1.87[a]	2.49
	0.4	0.78	0.12	0.30	2.17	2.02[a]	2.46
	0.6	0.74	0.05	0.31	2.34	2.20[a]	2.43
	0.8	0.71	−0.02	0.32	2.48	2.37[a]	2.40
$AgIn(S_xSe_{1-x})_2$	0.2	0.79	0.26	0.11	1.37	1.36[b]	2.60
	0.4	0.75	0.18	0.12	1.50	1.47[b]	2.58
	0.6	0.74	0.11	0.12	1.63	1.61[b]	2.55
	0.8	0.71	0.04	0.12	1.79	1.75[b]	2.52
$AgGa_xIn_{1-x}S_2$	0.2	0.70	−0.05	0.16	1.99	1.97[c]	2.49
	0.4	0.69	−0.06	0.20	2.13	2.09[c]	2.46
	0.6	0.68	−0.07	0.24	2.30	2.22[c]	2.44
	0.8	0.67	−0.08	0.28	2.46	2.35[c]	2.41
$AgGa_xIn_{1-x}Se_2$	0.2	0.90	0.31	0.16	1.25	1.29[d]	2.63
	0.4	0.88	0.30	0.18	1.47	1.38[d]	2.58
	0.6	0.87	0.28	0.22	1.56	1.48[d]	2.57
	0.8	0.85	0.27	0.24	1.71	1.60[d]	2.54
$ZnGe(P_xAs_{1-x})_2$	0.2	0.55	0.30	0.06	1.38		3.29
	0.4	0.58	0.25	0.06	1.62		3.22
	0.6	0.61	0.20	0.06	1.86		3.16
	0.8	0.64	0.16	0.05	2.10		3.11
$CdGe(P_xAs_{1-x})_2$	0.2	0.69	0.32	0.22	0.79	0.80[a]	3.46
	0.4	0.72	0.28	0.21	1.03	1.03[a]	3.39
	0.6	0.75	0.23	0.21	1.26	1.26[a]	3.32
	0.8	0.79	0.18	0.20	1.49	1.49[a]	3.26

[a]Reference 4.
[b]L. Martinez, S. A. Lopez Rivera, and V. Sagredo, Nuovo Cimento **2D**, 1687 (1983).
[c]I. V. Bodnar, A. G. Karoza, and G. F. Smirnova, J. Appl. Spectros. **33**, 718 (1980) (in Russian).
[d]B. Santik, B. Celustka, S. Popevic, and B. Grzote-Plenkovic, Fizika **12**, Suppl-1, 80 (1980).

nonlinearity can be enhanced to a greater extent by increasing the indium content of the pentenary.

Again the band structure parameters $\Delta_{s.o.}$ and Δ_{cf} have been evaluated for these mixed crystals at different concentrations using the atomic spin-orbit splitting of Herman *et al.*[17] But for the compounds containing the noble metal elements like Cu and Ag one has to incorporate the contribution of d electrons. Using the experimental values of $\Delta_{s.o.}$ for a few compounds we have evaluated the atomic spin-orbit splitting of Cu and Ag which agrees closely with the values suggested by Hubner and Unger.[18] The variation of $\Delta_{s.o.}$ and Δ_{cf} with concentration also obeys Vagerd's law as was in the case of $ZnSi(As_{1-x}P_x)_2$.[6] In regard to the $AgGa_xIn_{1-x}S_2$ experimental value of $\Delta_{s.o.}$ for the parent compounds $AgGaS_2$ and $AgInS_2$ is zero whereas in our calculation we get a very small negative value. This might be due to the simultaneous appearance of two different cations although they have zero $\Delta_{s.o.}$ each separately. Considering the compound $AgGa(S_xSe_{1-x})_2$, $\Delta_{s.o.}$ for $AgGaS_2$ is zero, but the pres-

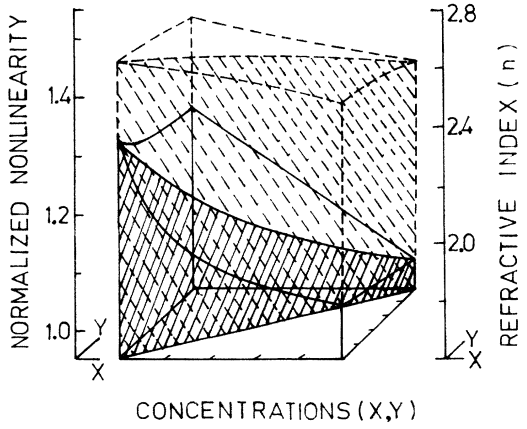

FIG. 1. A three-dimensional representation of normalized nonlinearity and refractive index as a function of concentrations (x,y). Solid line (——) denotes nonlinearity and dashed line (— — —) denotes the refractive index.

TABLE II. Theoretical and experiemental values of refractive indices at various concentrations of the pentenary system $AgGa_yIn_{1-y}(S_xSe^{1-x})_2$.

Concentration x	Concentration y	Lowest band gap E_g (eV)	Refractive indices n Calculated	Refractive indices n Experimental
0.0	0.0	1.25	2.63	2.63[a]
1.0	0.0	2.08	2.47	2.48[b]
1.0	0.4	2.27	2.44	2.40[c]
1.0	0.8	2.54	2.40	2.39[c]
1.0	0.92	2.63	2.35	2.38[c]
1.0	1.0	2.70	2.38	2.36[a]
0.4	0.4	1.71	2.54	
0.8	0.8	2.34	2.43	

[a]Reference 1.

[b]Reference 21.

[c]V. V. Badikov, I. N. Matveev, V. L. Panyutin, S. M. Pshenichnikov, A. E. Rozemson, S. V. Skrebneva, N. K. Trotsenko, and N. D. Ustinov, Sovt. J. Quant. Electron. **QE-10**, 1302 (1980).

ence of Se atoms within the mixed compound creates the similar situation. Regarding Δ_{cf} one has to carefully consider the contribution of p and d electrons separately through the term b_p and b_d and it is found that the calculated values agree well with the experimental values.

In regard to the bowing parameter we have evaluated the lowest band gap at different concentrations from the knowledge of $\Delta_{s.o.}$ and Δ_{cf} already evaluated. The lowest gap thus evaluated agrees well with the experimental results as shown in the Table I. In this connection it is interesting to observe that the bowing parameter calculated by the least-squares fitting technique shows close agreement with the available experimental values. It is also to be noted that there is almost no or low bowing when the anion concentration in a $AB(C_xD_{1-x})$ is varied but, on the other hand, considerable bowing is observed when either the A or B cation is varied and the bowing is more pronounced when the cation substituted comes from different rows.

Finally, the refractive indices of the pentenary compounds $AgGa_yIn_{1-y}(S_xSe_{1-x})_2$ at different concentrations using the calculated values of band gap described above are shown in the Table II and these have been compared with the experimental values. The agreement is encouraging. A three-dimensional representation of the evaluated refractive indices data has been shown in Fig. 1 for further clarity.

IV. CONCLUSION

In the present study we have been able to evaluate the optical nonlinearity, band-structure parameters, lowest energy gap of some important mixed crystals, thus allowing one to predict the refractive indices of some newly developed composite material, which, in turn, would be of immense help to crystal growers and optoelectronic device designers.

ACKNOWLEDGMENTS

The authors thank the Directorate of Aeronautics, Government of India for partial financial support. One of the authors (L.K.S.) wishes to acknowledge the University Grants Commission of India for providing him partial financial assistance for the work.

*Also at Department of Physics, Durgapur Government College, Durgapur-14 West Bengal, India.

†Also at Department of Physics, Ramananda College, Bishnupur, Bankura, West Bengal, India.

[1]J. L. Shay and J. H. Wernick, *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications* (Pergamon, New York, 1975).

[2]E. Garmire, in *Integrated Optics*, edited by T. Tamir (Springer, New York, 1979), p. 243.

[3]N. Yamamoto and T. Miyauchi, J. Phys. (Paris) Colloq. **36**, C3-155 (1975).

[4]J. C. Mikkelson, Jr. and H. Kildal, J. Appl. Phys. **49**, 428 (1978).

[5]B. Tell, J. L. Shay, H. M. Kasper, and R. L. Barns, Phys. Rev. B **10**, 1748 (1974).

[6]J. Galley, A. Des Chanvres, S. Gaillard, and C. Alibert, J. Phys. (Paris) Colloq. **36**, 123 (1975).

[7]B. F. Levine, J. Chem. Phys. **59**, 1463 (1973); Phys. Rev. B **7**, 2591 (1973).

[8]G. D. Boyd, H. M. Kasper, and J. H. Mcfee, IEEE J. Quant. Electron. **QE-7**, 563 (1971).

[9]G. D. Boyd, H. M. Kasper, and F. G. Storz, IEEE J. Quant. Electron. **QE-8**, 900 (1972).

[10]S. S. Jha and N. Bloembergen, Phys. Rev. **171**, 891 (1968).

[11]C. L. Tang and Chr. Flytzanis, Phys. Rev. B **4**, 2520 (1971).

[12]J. C. Phillips and J. A. Van Vechten, Phys. Rev. **183**, 709 (1969).

[13]L. K. Samanta and G. C. Bhar, Phys. Status Solidi (a) **41**, 331 (1977).

[14]D. K. Ghosh, Ph.D. dissertation, Burdwan University, 1984.

[15]J. A. Van Vechten and T. K. Bergstresser, Phys. Rev. B **1**, 3351 (1970).

[16]K. Hubner and K. Unger, Phys. Status Solidi (b) **50**, K105 (1972).

[17]F. Herman, C. D. Kuglin, K. F. Cuff, and R. L. Kortum, Phys. Rev. Lett. **11**, 541 (1963).

[18]K. Hubner and K. Unger, Phys. Status Solidi (b) **54**, K65 (1972).

[19]J. E. Rowe and J. L. Shay, Phys. Rev. B **3**, 451 (1971).

[20]J. J. Hopfield, J. Phys. Chem. Solids **15**, 97 (1960).

[21]D. K. Ghosh, L. K. Samanta, and G. C. Bhar, Infrared Phys. **24**, 43 (1984).