

## Variation of the energy gap with composition in $A^I B^{\text{III}} C_2^{\text{VI}}$ chalcopyrite-structure alloys

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The nonlinear variation of the fundamental energy gap  $E_g$  as a function of composition  $x$  observed in  $A^I B^{\text{III}} C_2^{\text{VI}}$  chalcopyrite-structure alloys is discussed. The downward optical-bowing parameter  $c$  observed in these alloys is analyzed in terms of current models given in the literature. A relationship between  $c$  and the difference in electronegativities  $\Delta X$  of the atoms mixed to form the alloy is obtained. Also, an expression to predict the  $E_g$ -vs- $x$  curve for these alloys is proposed and good agreement with experimental data is found.

### I. INTRODUCTION

The  $A^I B^{\text{III}} C_2^{\text{VI}}$  chalcopyrite-structure alloys have recently attracted considerable interest because of their potential applications in optoelectronic devices.<sup>1,2</sup> These materials are substitutional alloys formed from pairs of  $A^I B^{\text{III}} C_2^{\text{VI}}$  semiconductor compounds with the chalcopyrite structure. Two types of alloys can be obtained, namely those with mixed cations (i.e.,  $A_x A'_{1-x} B C_2$  or  $A B_x B'_{1-x} C_2$ ) and those with mixed anions [i.e.,  $A B (C_x C'_{1-x})_2$ ]. This substitution gives rise to a disorder in the respective cation or anion sublattices.

Studies of various types made on these materials show that in general such alloys are solid solutions across the whole composition range and that they have well-defined band structures in which the energy gaps and other related parameters vary continuously with composition between their values of the end compounds.<sup>3-8</sup> Also, it is observed that the optical energy gap  $E_g$  varies with the composition  $x$  according to the equation

$$E_g(x) = a + bx + cx^2, \quad (1)$$

where  $c$ , the nonlinear coefficient, is a measure of the downward bowing.

Although some plausible attempts have been made in order to correlate the bowing parameter  $c$  with relevant physical parameters of these alloys,<sup>9,10</sup> no quantitative analysis capable of explaining successfully the values of  $c$  observed in these materials has been reported. It has been suggested<sup>10</sup> by an analysis that considers the influence of the anion displacement on the band gap of such alloys that  $c$  will be appreciable in mixed-cation alloys (e.g.,  $\text{Ag}_x \text{Cu}_{1-x} \text{InS}_2$  or  $\text{CuIn}_x \text{Ga}_{1-x} \text{Se}_2$ ) but very small in mixed-anion alloys [e.g.,  $\text{CuIn}(\text{Se}_x \text{S}_{1-x})_2$ ]. However, this suggestion does not agree well with experimental data, which show that for these alloys  $c$  varies from 0 to about 0.5 eV for the case of mixed anions while it was found to be about 0.20 or less for the case of mixed cations.<sup>3,5,8,11-15</sup>

In the present work we attempt to point out that the nonlinear variation of the energy gap versus composition observed in these alloys can be related to the difference in electronegativities of the two atoms that are mixed to

form the alloys. The analysis allows us to express  $c$  in a simple way and gives an expression to determine the  $E_g$ -vs- $x$  curve for these alloys. A good agreement is found with the data for both mixed-cation and mixed-anion  $A^I B^{\text{III}} C_2^{\text{VI}}$  alloys reported in the literature.

### II. THEORY

It has been pointed out<sup>16,17</sup> that the optical-bowing parameter  $c$ , observed in semiconductor alloys, can be separated into a contribution  $c_I$  due to order effects and a contribution  $c_{II}$  due to disorder effects. According to Van Vechten and Bergstresser,<sup>16</sup> the  $c_{II}$  contribution, which is related to the difference of electronegativities of the alloyed atoms, plays a dominant role in determining  $c$  in the case of the  $A_x B_{1-x} C$  alloys. However, Bernard and Zunger,<sup>17</sup> based on first-principles calculations of the electronic structure of  $A_x B_{1-x} C$  zinc-blende-structure alloys, have recently concluded that the optical bowing is due to order effects arising principally from an internal structural relaxation effect. Furthermore, they claim that the scaling between  $c$  and  $\Delta X$  does not constitute a proof of the relevance of the disorder since the order contribution  $c_I$  also scales with the electronegativity difference.

In the case of the present chalcopyrite-structure alloys, no calculation like that reported in Ref. 17 has been published, and so no definitive conclusions about the relevance of order or disorder effects can be given at present. However, since in any case a correlation between  $c$  and  $\Delta X$  is expected to occur according to the results of Ref. 17, we plot in Fig. 1 the experimental data of  $c$  for the  $A^I B^{\text{III}} C_2^{\text{VI}}$  alloys reported in the literature<sup>8,11-15</sup> versus  $\Delta X$ , using the Phillips electronegativity values<sup>18</sup> given in Table I. It is observed that the points tend to stay on a straight line. The best fit to the data is shown in the figure by the dashed line; however, since it is expected, according to the model, that the bowing must disappear when  $\Delta X$  vanishes, an attempt was also made to adjust the data under this condition. A good fit, as shown in the figure by the solid straight line, is obtained by the expression

$$c = \frac{5}{4} \Delta X \text{ eV} . \quad (2)$$

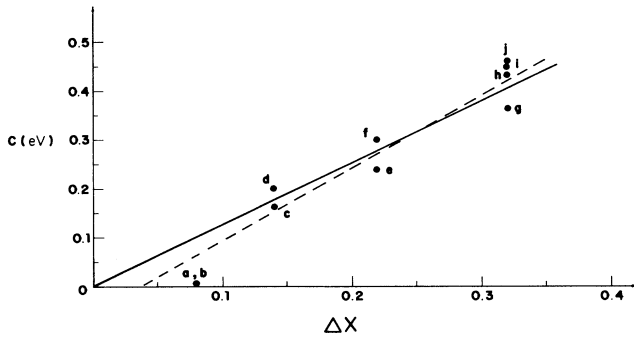


FIG. 1. Experimental downward bowing parameter for  $A^I B^{III} C_2^{VI}$  alloys as a function of the difference in electronegativity of mixed cations or mixed anions to form the alloy. *a*,  $\text{CuIn}(\text{S}_x \text{Se}_{1-x})_2$  (Ref. 14); *b*,  $\text{CuGa}(\text{S}_x \text{Se}_{1-x})_2$  (Ref. 15); *c*,  $\text{Cu}(\text{Ga}_x \text{In}_{1-x})\text{Se}_2$  (Ref. 11); *d*,  $\text{Cu}(\text{Ga}_x \text{In}_{1-x})\text{S}_2$  (Ref. 12); *e*,  $\text{Ag}_x \text{Cu}_{1-x} \text{InTe}_2$  (Ref. 13); *f*,  $\text{Ag}_x \text{Cu}_{1-x} \text{InSe}_2$  (Ref. 11); *g*,  $\text{AgIn}(\text{Se}_x \text{Te}_{1-x})_2$  (Ref. 8); *h*,  $\text{CuIn}(\text{Se}_x \text{Te}_{1-x})_2$  (Ref. 13); *i*,  $\text{CuGa}(\text{Se}_x \text{Te}_{1-x})_2$  (Ref. 13); *j*,  $\text{AgGa}(\text{Se}_x \text{Te}_{1-x})_2$  (Ref. 8).

Taking into account that the reduction in the energy gap of the alloy, measured with respect to the values of  $E_g$  obtained by a linear extrapolation from the band gaps of the extrema compounds, is given by<sup>10</sup>

$$\Delta E_g(x) = E_g^{\text{linear}}(x) - E_g(x) = cx(1-x) \quad (3)$$

and also by considering that in the case of a linear variation of  $E_g$  vs  $x$  the energy gap can be expressed as

$$E_g^{\text{linear}}(x) = E_g(0) + [E_g(1) - E_g(0)]x, \quad (4)$$

where  $E_g(0)$  and  $E_g(1)$  are the energy gaps of the end compounds (i.e., of samples with composition  $x=0$  and 1, respectively), we finally obtain

$$E_g(x) = E_g(0) + [E_g(1) - E_g(0) - \frac{5}{4}(1-x)\Delta X]x. \quad (5)$$

This expression is used to calculate the energy gap as a function of composition in  $A^I B^{III} C_2^{VI}$  chalcopyrite-structure alloys.

TABLE I. Phillips electronegativities (from Ref. 18).

$A^I$	$B^{III}$	$C^{VI}$
Cu 0.79	Ga 1.13	S 1.87
Ag 0.57	In 0.99	Se 1.79
		Te 1.47

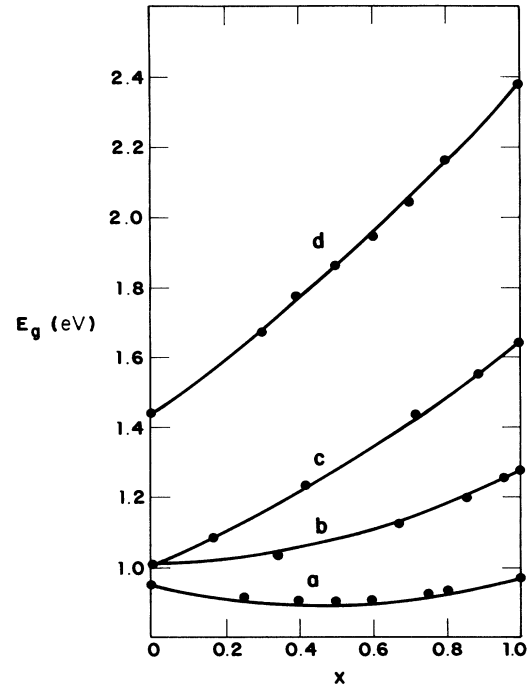


FIG. 2. Variation of the energy gap as a function of composition for mixed cation  $A^I B^{III} C_2^{VI}$  alloys (solid circles). Theoretical values, according Eq. (5), are represented by solid curves. *a*,  $\text{Ag}_x \text{Cu}_{1-x} \text{InTe}_2$  (Ref. 13); *b*,  $\text{Ag}_x \text{Cu}_{1-x} \text{InSe}_2$  (Ref. 11); *c*,  $\text{CuGa}_x \text{In}_{1-x} \text{Se}_2$  (Ref. 11); *d*,  $\text{CuGa}_x \text{In}_{1-x} \text{S}_2$  (Ref. 12).

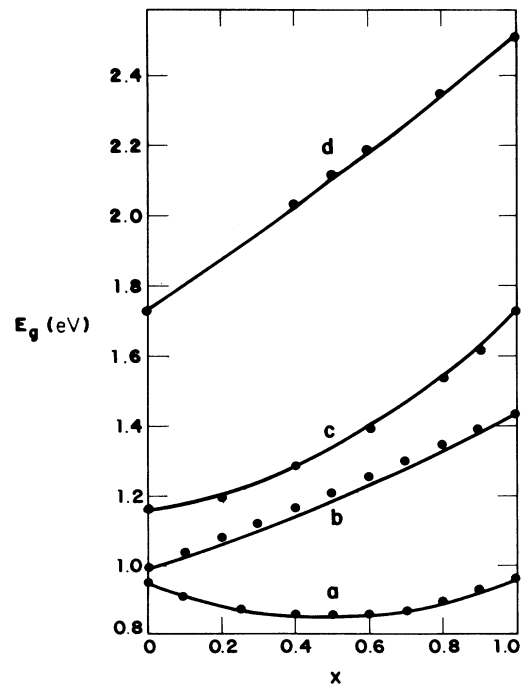


FIG. 3. Variation of the energy gap as a function of composition for mixed anion  $A^I B^{III} C_2^{VI}$  alloys (solid circles). Theoretical values, according to Eq. (5), are represented by solid curves. *a*,  $\text{CuIn}(\text{Se}_x \text{Te}_{1-x})_2$  (Ref. 13); *b*,  $\text{CuIn}(\text{S}_x \text{Se}_{1-x})_2$  (Ref. 14); *c*,  $\text{AgGa}(\text{Se}_x \text{Te}_{1-x})_2$  (Ref. 8); *d*,  $\text{CuGa}(\text{S}_x \text{Se}_{1-x})_2$  (Ref. 15).

### III. COMPARISON WITH EXPERIMENTAL DATA

Curves of  $E_g$  vs  $x$  for several  $A^I B^{III} C_2^{VI}$  alloys have been reported.<sup>8,11-15</sup> Some of these curves, represented by circles, for both mixed-cation and mixed-anion alloys, are plotted in Figs. 2 and 3, respectively. Theoretical  $E_g$  values, according to Eq. (5), are also indicated in these figures by solid curves. As observed, a very good agreement is found in all cases, which shows the applicability of the model for these alloys.

### IV. CONCLUSIONS

It is suggested that the downward optical-bowing parameter observed in the curve of the fundamental energy gap with a composition of  $A^I B^{III} C_2^{VI}$  chalcopyrite-structure alloys can be related to the difference in Phillips electronegativities of cations or anions mixed to form the alloy. This fact gives us an expression to predict the  $E_g$ -vs- $x$  curve for such alloys. The results agree well with the data reported in the literature.

At present, the origin of such bowing is not clear. For pseudobinary  $A_x B_{1-x} C$  alloys, Van Vechten and Bergstresser<sup>16</sup> have suggested that a disorder-effect contribution is mainly responsible for the nonlinear behavior

observed in the  $E_g$ -vs- $x$  curve of these alloys. However, Bernard and Zunger<sup>17</sup> have recently suggested a physical mechanism for  $c$  that differs from that offered in Ref. 16. These authors analyze the optical bowing in terms of three contributions: (i) a volume deformation of the band structure due to the replacement of the lattice constants of the binary constituents by that of the alloys, (ii) a chemical-electronegativity contribution due to charge exchange in the alloy relative to its constituent binary subsystems, and (iii) a structural contribution due to the relaxation of the anion bond lengths in the alloys. They also conclude that the disorder contribution to the bowing parameter is very small in the case of zinc-blende-structure pseudobinary alloys. Although this model agrees well with observations in these alloys, no definitive conclusions can be given in the present case since no calculations have been reported for chalcopyrite-structure alloys. For this reason, the possibility of a disorder-effect contribution to the optical bowing of these alloys cannot be completely ruled out.

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- <sup>1</sup>J. M. Stewart, W. S. Chen, W. E. Devany, and R. A. Mickelsen, in *Ternary and Multinary Compounds*, edited by S. K. Deb and A. Zunger (Materials Research Society, Pittsburgh, 1987), pp. 59-64.
- <sup>2</sup>C. Paorici, L. Zanotti, N. Romeo, G. Sberveglieri, and L. Taricone, *Solar Energy Mater.* **1**, 3 (1979).
- <sup>3</sup>J. Avon, K. Yooder, and J. C. Woolley, *Nuovo Cimento D* **2**, 1858 (1983).
- <sup>4</sup>T. F. Ciszek, C. D. Evans, and S. K. Deb, in *Ternary and Multinary Compounds* (Ref. 1), pp. 195-200.
- <sup>5</sup>M. Quintero and J. C. Woolley, *J. Appl. Phys.* **55**, 2925 (1984).
- <sup>6</sup>P. Grima, M. Quintero, C. Rincón, G. Sánchez Pérez, and J. C. Woolley, *Solid State Commun.* **67**, 81 (1988).
- <sup>7</sup>I. A. Aksenov, L. A. Makovetskaya, G. P. Popelnyuk, and I. P. Shilovich, *Phys. Status Solidi A* **105**, K97 (1988).
- <sup>8</sup>S. Chantraphorn, T. Panmatarile, S. Pramatus, A. Prichavudhi, R. Kritayarinka, J.-O. Benaranda, V. Sa-yakanith, and J. C. Woolley, *J. Appl. Phys.* **57**, 1791 (1985).
- <sup>9</sup>A. Zunger and J. E. Jaffe, *Phys. Rev. Lett.* **51**, 662 (1983).
- <sup>10</sup>J. E. Jaffe and A. Zunger, *Phys. Rev. B* **29**, 1882 (1984).
- <sup>11</sup>R. Bacewicz, J. R. Durrant, T. F. Ciszek, and S. K. Deb, in *Ternary and Multinary Compounds* (Ref. 1), pp. 155-160.
- <sup>12</sup>I. V. Bodnar and I. Lukomskii, *Phys. Status Solidi A* **98**, K165 (1986).
- <sup>13</sup>M. Quintero, R. Tovar, E. Guerrero, F. Sánchez, and J. C. Woolley, *Phys. Status Solidi* (to be published).
- <sup>14</sup>I. V. Bodnar, B. V. Korzun, and A. I. Lukomskii, *Phys. Status Solidi B* **105**, K143 (1981).
- <sup>15</sup>L. Roa, C. Rincón, J. González, and M. Quintero, *J. Phys. Chem. Solids* **51**, 551 (1990).
- <sup>16</sup>J. Van Vechten and T. K. Bergstresser, *Phys. Rev. B* **1**, 3351 (1970).
- <sup>17</sup>J. E. Bernard and A. Zunger, *Phys. Rev. B* **36**, 3199 (1987).
- <sup>18</sup>J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).