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Order-disorder transition in ternary chalcopyrite compounds and pseudobinary alloys

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The order-disorder transition in ternary chalcopyrite-structure compounds and related pseudobinary alloys is discussed. An expression relating the critical transition temperature T_c to the difference in the band gap between ordered and disordered phases ΔE_g is proposed. The results are consistent with the values for T_c and ΔE_g of these ternary compounds previously reported. In addition, for the isovalent pseudobinary alloys, an order-disorder transition is predicted below about 130 K.

I. INTRODUCTION

It is a well-known fact that many semiconductors and their alloys undergo a solid-solid transition from a disordered to an ordered structure when the temperature is lowered below a critical value T_c.[1,2] This is because the different constituent atoms tend to occupy special sites in the lattice and, as a consequence, long-range order occurs in the resulting crystalline structure below T_c.

The pseudobinary $A_xB_{1-x}C$ alloys of binary isovalent AC and BC tetrahedral semiconductors have been traditionally considered to be substitutionally disordered at any temperature or composition.[3] However, recently crystal-growth experiments have shown the existence of ordered phases in strained-semiconductor alloys including systems such as $\mathrm{AlGaAs_2}$,[4] GeSi,[5] and $\mathrm{Ga_2AsSb}$.[6].

It has been suggested[5] that such ordering can be induced to occur in strained semiconductors by the substrate stress which drives the transition probably by increasing T_c. However, this ordering has not been observed in bulk crystals because of the low value of the transition temperature T_c.

Also, it has been pointed out[1] that although experimental or theoretical T_c data for these alloys have not been reported, there is a large class of tetrahedrally bonded semiconductors—the $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ and $A^{\mathrm{I}}B^{\mathrm{III}}C_2^{\mathrm{VI}}$ chalcopyrite-structure compounds—where T_c is known to be very high (from about 900 to 1400 K). In the chalcopyrite structure, each anion C has two A and two B cations as nearest neighbors. Above T_c, the A and B atoms disorder in the cation sublattice, giving rise to the zinc-blende structure. Since this antisite cation disorder is similar to that observed in isovalent pseudobinary alloys, information about this phenomenon in the alloys can be obtained from studies related to the factors controlling order-disorder transition in the chalcopyrite-structure compounds. In relation to these compounds, it has been found that they can separate into two groups: those that exhibit the chalcopyrite–zinc-blende transition before they melt, and those that remain in the chalcopyrite structure up to the melting point. Binsma, Giling, and Bloem[2] found that the order-disorder transition occurs only in compounds with a lattice constant ratio c/a larger than 1.95. Zunger[1] demonstrated, by considering the microscopic strain energies of ordered and disordered phases, that ordering occurs in compounds where the "anion displacement" μ (Ref. 7) is higher than a critical value, $\mu_c=0.265$. The analysis was extended to pseudobinary alloys and a classification of tetrahedral semiconductors, related to the order-disorder transition, into four equilibrium types was also given in Ref. 1.

In spite of these significant efforts devoted to understanding the phenomena of such a transition in ternary compounds, studies that predict T_c values that can be compared with experimental T_c data for these materials are very scarce.

In a recent article,[8] by using a semiempirical approach, which is an extension of a model proposed for the pseudobinary alloys,[9] the critical temperature T_c for the chalcopyrite–zinc-blende transition was determined. The model, although it predicts T_c values in good agreement with experimental data, seems to be inconsistent because an incorrect assumption was made concerning the relation of T_c and the difference ΔE_g in the energy gap between ordered and disordered phases.

Another unresolved problem, related to the order-disorder transition, is the fact that an ordered ABC_2 compound has an energy gap $E_g^{(0)}$ which is larger than its value in the disordered phase $E_g^{(D)}$ (i.e., $\Delta E_g=E_g^{(0)}-E_g^{(D)}>0$) but in alloys it is found that an ordered strain superlattice (e.g., $\mathrm{Al_xGa_{1-x}As_2}$) has a smaller gap than a disordered alloy of the same composition[10] (i.e., $\Delta E_g<0$ for pseudobinary alloys).

In the present work, an attempt is made to calculate, in a consistent manner, the critical temperature for the order-disorder transition in chalcopyrite-structure compounds. Then, the model has been extended to estimate T_c for the isovalent pseudobinary alloys. The results predict an order-disorder transition at low temperatures for these materials. The possible reasons for the low values expected for T_c are also discussed.

II. THEORY

As suggested by Van Vechten,[9] the difference in the band gap between the ordered chalcopyrite and the disordered zinc-blende phases ΔE_g is expected to be proportional to the extrinsic bowing parameter c_e. This is estimated here as

$$\Delta E_g = \alpha_{AB} c_e = \alpha_{AB} C^2 / A_0 \ , \tag{1}$$

where $A_0 \cong 1$ eV is the effective bandwidth parameter, C is defined as

$$C = 1.5 e^2 (Z_B / r_B - Z_A / r_A) \exp(-kR) \tag{2}$$

with A and B denoting the constituent elements of the ABC_2 ternary compound, k is a screening wave number related to the lattice constants of the compounds, and R is an arithmetic mean radius given by

$$R = (r_A + r_B + 2r_c)/4 \ , \tag{3}$$

where the r's denote the covalent radii of the constituent elements.[11]

The parameter α_{AB} is a correction factor introduced here because ΔE_g between chalcopyrite and zinc-blende structures is much less than that between the virtual-crystal approximation (VCA) of the pseudobinary alloy and binary-compound zinc-blende phases,[9] i.e.,

$$\Delta E_g = E_g^{(0)} - E_g^{(D)} = K(E_g^{(\mathrm{VCA})} - E_g^{(D)}) \ , \tag{4}$$

where $(1-K)\times 100$ is defined as the "% success of chalcopyrite mode."[9]

On the other hand, by taking into account that the difference in the band gap between the VCA of a pseudobinary $A_x B_{1-x} C$ and the true band gap in the disordered-pseudobinary-alloy phase is given by[11]

$$E_g^{(\mathrm{VCA})}(x) - E_g^{(D)}(x) = C_e x (1-x) \ , \tag{5}$$

and also by considering that for the chalcopyrite phase $x = 0.5$, we obtain Eq. (1) with $\alpha_{AB} = K/4$.

The critical temperature T_c and the difference ΔE_g in the fundamental energy gap between the ordered and disordered phases of the ternary compounds, according to calculations based in perturbation theory,[12] are related by the expression

$$T_c^{1/2} \ \alpha \ \Delta E_g \ . \tag{6}$$

Hence experimental or theoretical values of ΔE_g can be used to estimate order-disorder temperatures.

III. RESULTS AND DISCUSSION

The experimental data of $T_c^{1/2}$ for the ternary compounds versus the ΔE_g values obtained by using Eqs. (1)–(3) are plotted in Fig. 1. For the calculations a fixed value $\alpha_{AB} = 0.04$, which is of the same order as one estimated in Ref. 9 for these compounds, was used for all the ternary compounds. It is obvious from the curve that at first glance no fit can be obtained with use of the same value of α_{AB} for all the ternary compounds, because the points in the plot do not lie on the same straight line but are completely scattered. However, upon a closer examination of these points, it can be observed that compounds containing the same cations tend to lie on straight lines. These are indicated by dotted lines in Fig. 1 which do not represent a theoretical fit to the relation (6). In any case, this trend probably indicates that α_{AB} must be different for compounds containing different groups of cations and it should be very nearly the same for the ternary compounds which have the same cations. This seems to be consistent with the fact that the chalcopyrite–zinc-blende phase transition is related to atomic disorder in the cation sublattice but the anion sublattice is not expected to be affected by the transition.

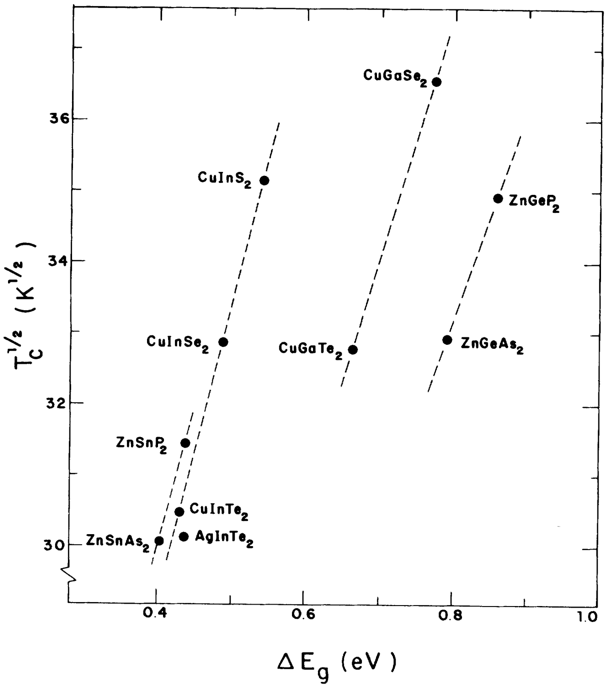

FIG. 1. Experimental data of $T_c^{1/2}$ vs the values of ΔE_g for several ternary compounds calculated by taking $\alpha_{AB} = 0.04$.

Furthermore, since the straight lines corresponding to compounds containing different groups of cations in Fig. 1 are very nearly parallel to one another, it is possible to fit $T_c^{1/2}$ versus ΔE_g by only one straight line, using α_{AB} as an adjustable parameter. This can be represented by an expression of the form

$$T_c^{1/2} = \beta \Delta E_g + T_0^{1/2} \tag{7}$$

where β and T_0 should be constants for all the ternary compounds.

Thus, under these conditions, we fit the T_c data and the theoretical ΔE_g values by a straight line. A good fit with $T_0 = 132.64$ K and $\beta = 43.941$ K$^{1/2}$eV^{-1} with a standard deviation $\sigma = 4.5$ K, as observed in Fig. 2, is obtained with the values $\alpha_{\text{Cu-In}} = 0.040$, $\alpha_{\text{Cu-Ca}} = 0.029$, $\alpha_{\text{Ag-In}} = 0.039$, $\alpha_{\text{Zn-Ge}} = 0.025$, and $\alpha_{\text{Zn-Sn}} = 0.042$. This indicates, taking into account that $\alpha = K/4$, that the chalcopyrite-structure approximation of the random phase is about 84%, 88%, 90%, and 83% accurate for CuInC_2^{VI}, AgInC_2^{VI}, ZnGeC_2^{V}, and ZnSnC_2^{V} compounds, respectively. These values are in good agreement with those estimated in Ref. 9 which are between 61% and 84% for these compounds.

The values of ΔE_g and T_c thus obtained for ternary

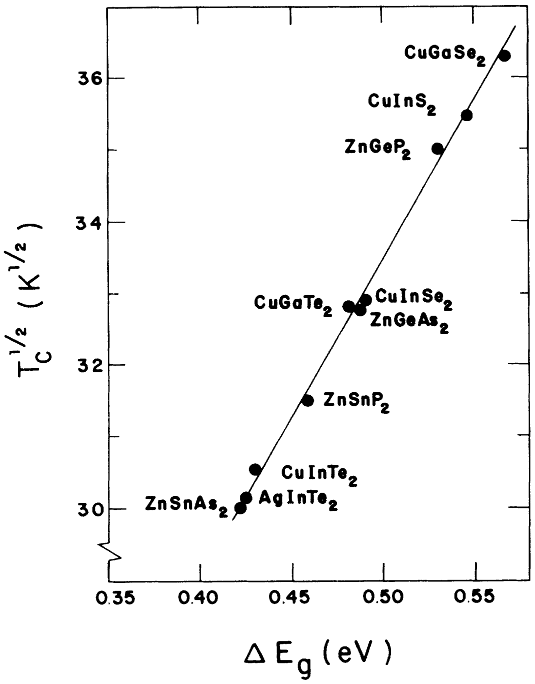

FIG. 2. A theoretical fit of the experimental data of $T_c^{1/2}$ and the corresponding calculated values of ΔE_g to Eq. (5). In the fit $\beta = 43.941$ K$^{1/2}$ eV^{-1} and $T_0 = 132.64$ K.

ABC_2 compounds are shown in Table I. The T_c experimental values have also been shown in this table for comparison.

TABLE I. Difference in the band gap between the chalcopyrite and zinc-blende phases ΔE_g and calculated critical transition temperature T_c of some $A^{\mathrm{I}}B^{\mathrm{III}}C_2^{\mathrm{VI}}$ and $A^{\mathrm{II}}B^{\mathrm{IV}}C_2^{\mathrm{V}}$ compounds. Experimental T_c values compiled in Ref. 8 are also shown in the table.

ABC_2 compound	ΔE_g (eV)	T_c (K) calculated	T_c (K) observed
$CuInTe_2$	0.432	930	933
$CuInSe_2$	0.488	1086	1083
$CuInS_2$	0.543	1252	1253
$CuGaTe_2$	0.483	1072	1078
$CuGaSe_2$	0.566	1324	1318
$CuGaS_2$	0.608	1462	
$AgInTe_2$	0.424	909	909
$AgInSe_2$	0.510	1151	
$AgInS_2$	0.553	1283	
$ZnSnSb_2$	0.365	759	
$ZnSnAs_2$	0.423	906	905
$ZnSnP_2$	0.457	998	993
$ZnGeAs_2$	0.488	1086	1085
$ZnGeP_2$	0.532	1218	1225

Because of the lack of experimental data on ΔE_g for ternary compounds, a comparison with calculated values is possible only for very limited cases. In $ZnSnP_2$ the energy gap varies from 1.25 to 1.66 eV depending on the Zn-Sn disorder.[13] This gives $\Delta E_g \cong 0.41$, which is in good agreement with $\Delta E_g \cong 0.46$ obtained in this work, especially if we take into account that the difference in the energy gap between homogeneous samples of chalcopyrite and zinc-blende phases must be slightly greater than between real samples in which both phases are present.

In $CuInS_2$ (Ref. 4) and $CuGaS_2$ (Ref. 15), a high-pressure-induced phase transition to a disordered crystalline structure was observed. In the recovered disordered samples, presumably with the zinc-blende structure,[16] a redshift of the energy gap (as compared with the chalcopyrite-structure samples) was also observed from the optical-absorption measurements of these two compounds. Indirect energy gaps of 1.07 and 1.9 eV for these compounds were obtained from the spectra. These values yield $\Delta E_g \cong 0.47$ and 0.60 eV for $CuInS_2$ and $CuGaS_2$, respectively, which are very close to $\Delta E_g \cong 0.54$ and 0.61 eV obtained in the present work.

On the other hand, the values of T_c calculated here are in good agreement with the experimental data reported fro most of the compounds. In the cases of $AgInSe_2$ and $AgInS_2$, the values of T_c are larger than the melting points 1043 and 1050 K, respectively.[17] This is consistent with the fact that no transition from chalcopyrite to zinc-blende phases is observed in these two compounds.

From Eq. (7) it is found that if $\Delta E_g = 0$, there is an order-disorder transition at $T_c = T_0 \cong 130$ K. Furthermore, the compounds with $T_c < 130$ K will have $\Delta E_g < 0$ (i.e., $E_g^{(0)} < E_g^{(D)}$). This is not observed in chalcopyrite-structure compounds since T_c is quite high. However, one could observe this in isovalent pseudobinary alloys where T_c is expected to be low. Thus, for example, a shift to higher energies in the band gap of $Al_xGa_{1-x}As$ quantum-well heterostructures (QWH's) has been observed after thermal annealing at relatively high temperatures (~900 °C) which induce compositional disorder in as-grown samples of such heterostructures.[10] The energy gap of disordered $Al_xGa_{1-x}As$ samples with compositions $x \cong 0.23$ and 0.35 is, respectively, 60 and 50 meV higher than its value in as-grown samples of the same compositions. These values, $\Delta E_g \cong -0.06$ and -0.05 eV, give, according to Eq. (7), $T_c \cong 79$ and 87 K for samples with compositions $x \cong 0.23$ and 0.35, respectively.

From Eq. (7) it is also observed that for $\Delta E_g = -0.262$ eV, the critical temperature T_c becomes equal to zero, indicating that alloys for which $E_g^{(D)} - E_g^{(0)} \gtrsim 0.26$ eV do not undergo the transition to the ordered phase but instead remain in the disordered phase at any temperature.

The existence of ordered phases at low temperatures in pseudobinary alloys can be explained, on the basis of formation-enthalpy considerations, by taking into account the destabilizing microscopic strain energy suggested by Srivastava, Martins, and Zunger.[18] According to these authors, the bond lengths $R_{AC}(x)$ and $R_{BC}(x)$ of the disordered phase deviate from the ideal values more than do the bond lengths of the ordered phase. Hence the strain energy term of the disordered phase exceeds that of the ordered. It means that the formation enthalpy of the disordered phase exceeds that of the ordered phase (i.e., $\Delta H^{(D)} > \Delta H^{(0)}$). Since isovalent pseudobinary alloys are disordered, except probably at very low temperatures, it can be inferred that the entropy gain upon disordering $-T\,\Delta S^{(D)}$, is able to stabilize this phase, i.e., $\Delta H^{(D)} - T\,\Delta S^{(D)} < \Delta H^{(0)}$. However, at very low temperature, due to the destabilizing microscopic strain energy term the entropy gain upon disordering term $(-T\,\Delta S^{(D)})$ will be insufficient to stabilize this phase and hence the material will not be disordered.

IV. CONCLUSION

In the present work, the order-disorder transition of both ternary chalcopyrite-structure compounds and related pseudobinary alloys is discussed. The transition temperature T_c can be given by a single relation in terms of the difference in the energy gap between ordered and disordered phases. The results are consistent with values for T_c and ΔE_g reported for the ternary compounds. In the case of isovalent pseudobinary alloys, where negative values of ΔE_g are expected, the theory predicts an order-disorder transition at temperatures below about 130 K. It is suggested that, although the formation enthalpy of the disordered phase exceeds that of the ordered phase, the entropy gain upon disordering stabilizes the disordered phase except at low temperatures where this gain will be found to be insufficient, hence leaving the material ordered.

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