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Demonstration of ordering in semiconducting (chalcopyrite) – (zinc blende) alloys

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Phase diagrams of alloys mixing the chalcopyrite crystal structure with the zinc-blende structure have been computed using a generalized antiferromagnetic Blume-Emery-Griffiths model in the tetrahedron approximation of the cluster-variational method. These phase diagrams are rich in transitions, including typically an order-disorder transition from chalcopyrite to zinc blende as a function of temperature for the undiluted chalcopyrite compound, a narrow miscibility gap between chalcopyrite and zinc-blende alloys at high temperatures, and a large miscibility gap at low temperatures. Additionally, for a range of energy parameters, novel $x = \frac{1}{2}$ stannite and other ordered phases are found. The calculated phase diagrams compare favorably with those obtained experimentally for the diluted magnetic semiconductors $(CuInTe_2)_{1-x}(MnTe)_{2x}$ and $(AgInTe_2)_{1-x}(MnTe)_{2x}$.

Much excitement has been generated recently by the growth of ordered ternary III-V compounds, e.g., the (001)-superlattice and chalcopyrite phases of $GaAsSb_2$.[1] Given the growth of these compounds on substrates, a basic question has been whether these compounds are equilibrium or metastable phases of the alloy. Yet many natural chalcopyrite compounds exist in nature, with many of them undergoing an equilibrium order-disorder transition as a function of temperature between the chalcopyrite to zinc-blende crystal types. The study of mixed *equilibrium* alloys of the chalcopyrite structure with the zinc-blende structure may well aid in the understanding of ordering in the more usual ternary III-V alloys.

Chalcopyrite compounds such as $ZnSnAs_2$ or $CuInTe_2$ can all be viewed as derivative compounds of zinc blende;[2] see Fig. 1. In a zinc-blende compound such as GaAs, the Ga and As atoms each independently occupy one set of face-centered-cubic (fcc) positions; see Fig. 1(a). In a chalcopyrite compound such as $ZnSnAs_2$ [see Fig. 1(b)], As atoms occupy one set of fcc positions and Zn and Sn the other. For this example, the cations originate from columns II and IV of the Periodic Table and the average valence of the pair (ZnSn) is III. Chalcopyrite (C) is an example of an average-valence compound and has a space group $I\bar{4}2d$ that is a subgroup of the zinc-blende (Z) space group $F\bar{4}3m$. Similarly, there exist chalcopyrite compounds derived from II-VI compounds, e.g., $CuInTe_2$.

Many chalcopyrite compounds undergo an order-disorder transition as a function of temperature to the zinc-blende form.[3] For example, in the disordered form of $ZnSnAs_2$, Zn and Sn atoms are randomly found on the cation fcc sublattice [large circles, Fig. 1(a)]. The existence of this order-disorder C-Z transition and the fact that both chalcopyrite and zinc blende have a single-anion fcc sublattice makes the transitions of the "mixed" (chalcopyrite)-(zinc blende) system a natural to study.

We model the transitions of the (chalcopyrite)-(zinc blende) (C-Z) system by using a simple lattice-gas model of the alloy. We assume first that the chalcopyrite (C) and zinc-blende (Z) compounds share a common anion D. We write schematically the chemical formulas for the chalcopyrite and zinc-blende parents as ABD_2 and CD, respectively, and the alloy system as either $(ABD_2)_{1-x}(CD)_{2x}$ or $[(AB)_{1-x}C_{2x}]D_2$. The lattice-gas assumption means that each site in an ideal fcc lattice is assumed to be singly occupied either by atom A, B, or C. A possible ordered phase derived from this alloy is stannite ($x = \frac{1}{2}$), e.g., Cu_2FeSnS_4,[2] having space group $I\bar{4}2m$ and shown in Fig. 1(c). Stannite is characterized by the same special-**k**

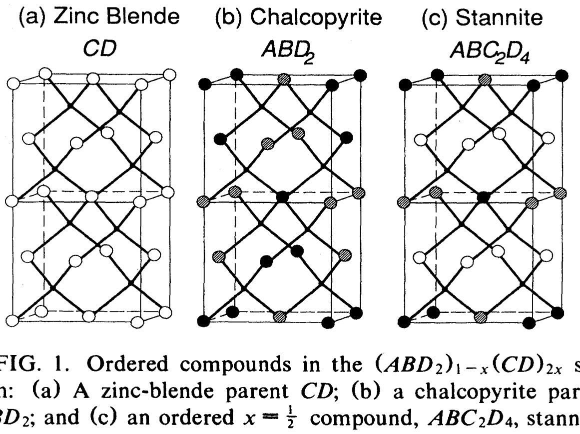

FIG. 1. Ordered compounds in the $(ABD_2)_{1-x}(CD)_{2x}$ system: (a) A zinc-blende parent CD; (b) a chalcopyrite parent ABD_2; and (c) an ordered $x = \frac{1}{2}$ compound, ABC_2D_4, stannite. Cations A, B, and C are shown as large solid, hatched, and open circles, respectively, and the anions D are shown as the smaller solid circles.

point as chalcopyrite.[4]

Note, in the absence of strain, this problem is related in symmetry to the alloy system $(AB)_{1-x}C_{2x}$, where atoms A, B, or C are on fcc sites.[5] We substitute this fcc alloy problem for our problem and assume also that atoms D never are on the "wrong" fcc sublattice. Including only the nearest-neighbor interactions between the sites on one fcc sublattice, we have

$$E = zN \sum_{\{\alpha,\beta\}} \varepsilon_{\alpha\beta} P^{\alpha\beta} , \tag{1}$$

where $z = 12$ is the coordination number, N is the number of sites in the fcc sublattice, $P^{\alpha\beta}$ is the pair probability, and the energies $\varepsilon_{\alpha\beta} = \varepsilon_{\beta\alpha}$ are the interaction energies of nearest-neighbor pairs. We reduce the number of interaction energies by using the well-known equivalence of this three-atom nearest-neighbor problem to a three-component spin model,[6] finding an energy E given by

$$E = J \sum_{\{i,j\}} S_i S_j - K \sum_{\{i,j\}} S_i^2 S_j^2 + L \sum_{\{i,j\}} (S_i^2 S_j + S_i S_j^2) , \tag{2}$$

where the spins $S_i = \{+1, -1, 0\}$ on sites $\{i,j\}$ map onto the atoms A, B, or C. The problem is thus characterized by three energy combinations:

$$4J = \varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB} , \tag{3a}$$

$$4K = -\varepsilon_{AA} - \varepsilon_{BB} - 2\varepsilon_{AB} - 4\varepsilon_{CC} + 4(\varepsilon_{AC} + \varepsilon_{BC}) , \tag{3b}$$

and

$$4L = (\varepsilon_{AA} - \varepsilon_{BB}) + 2(\varepsilon_{BC} - \varepsilon_{AC}) . \tag{3c}$$

Since the intention of this paper is to demonstrate new types of ordering for (C-Z) systems, we limit our discussion here to the evolution of the phase diagram within just a portion of the generalized energy space. Clearly, each physical system $(ABD_2)_{1-x}(CD)_{2x}$ has its own unique set of nearest-neighbor interaction energies $\{\varepsilon_{\alpha\beta}\}$. Yet we know only the combinations of energies of Eqs. (3) should be important in the determination of the phase diagram. We retain the Ising parameter J which controls transitions of the $x = 0$ compound ABD_2. J is positive, meaning that a chalcopyrite phase ABD_2 exists at low temperatures, and not the phases AD or BD. The parameter L controls the occupancies of C atoms on the different sublattices of the fcc lattice; we simplify the model and set L to zero. The parameter K controls the extent to which the parent chalcopyrite and zinc-blende compounds phase separate. For K positive, large miscibility bulges are found. For K negative, phase separation dominates less; additionally, arguments based on ground-state energies show that new phases should become stabilized with $K < 0$.[7] Thus the following is our choice for this paper: We vary two unique dimensionless energy scales, a renormalized temperature, $(k_B T)/J$, and a ratio, $R = K/J$, and study $R \leq 0$.

Negative values of R should be obtainable in physical systems, as is easily shown. For example, one of an infinite number of combinations of energy parameters which will yield $R = -1$ is $\varepsilon_{AA} = \varepsilon_{BB} = J > 0$ and $\varepsilon_{AB} = \varepsilon_{AC} = \varepsilon_{BC} = \varepsilon_{CC} = -J$. This particular choice of the ratio R represents an interesting *percolation* limit of the problem: $|J| = |K|$, so *all energies are equal in magnitude,* and for $T = 0$, the only variable of interest is the composition x which weights the relative amounts of atoms A, B, and C available from the compounds ABD_2 and CD. While it is unlikely that a physical system can be found that has exactly the percolation value $R = -1$, the existence of this special value of R is of physical interest because it controls the behavior of phase diagrams for neighboring values of R, $R \simeq -1$.

For the determination of the phase diagrams of this system, we employ the cluster-variation method (CVM) in the tetrahedron approximation.[8] We start with the general expression for the grand potential, $G = E - TS - \mu N x$, which is then minimized using Kikuchi's natural iteration scheme.[8] With this choice of thermodynamic potential, the chemical potential μ and temperature T are the natural variables of the problem. Phase boundaries as usual are found by searching for those special values of the chemical potential for which two or more phases coexist.

The symmetry of each region within the phase diagram is determined by careful examination of the site probabilities P_i^α, with $\alpha = A$, B, and C and $i = 1$, 2, 3, and 4. Order parameters which discriminate between two possible phases can be defined, e.g., the quantity

$$m_C = \tfrac{1}{4} \{ |P_1^A - P_1^B| + |P_2^A - P_2^B| + |P_3^A - P_3^B| + |P_4^A - P_4^B| \} \tag{4}$$

is nonzero within the C phase, but zero for a Z phase.

Turning now to results, we show in Fig. 2 computed phase diagrams obtained for four values of the energy parameter R. We start with the phase diagram found for $R = 0$, shown in Fig. 2(a), which is characteristic of both $R > 0$ and $R < 0$. First note on the axis $x = 0$ the location of the order-disorder transition of the parent chalcopyrite (C) system ABD_2 ($x = 0$) to the disordered zinc-blende (Z) form. This transition is first order; the order parameter m_C has a jump discontinuity to zero. With the dilution of the C compound ABD_2 by the Z compound CD, the temperature of the transition decreases. The two phases are separated by both a first-order transition and by a miscibility gap (shaded area). The opening of this miscibility gap found for even just a small nonzero value of the composition x is a characteristic feature of all studied (C-Z) systems.

For small values of temperature, a large miscibility gap separates the chalcopyrite ABD_2-rich phase from the zinc-blende CD-rich form. How this wide low-temperature miscibility gap evolves to become the narrow miscibility gap found for large temperatures depends dramatically on the value chosen for R. Unlike the case of a binary alloy, where the miscibility gap typically terminates at a critical point centered about $x \simeq \frac{1}{2}$, for $R = 0$, the critical point is found to be centered about $x = \frac{1}{3}$. Additionally, the narrow high-temperature miscibility-gap region shrinks to zero at $x = \frac{1}{2}$, becoming a critical-transition line (shown bold), which terminates at $x = \frac{2}{3}$ when it intersects the low-temperature miscibility-gap region.

Values of $R < 0$ characterize those (C-Z) systems for which new symmetry stannite (S) phases are found, e.g., see Figs. 2(b)–2(d). This phase stabilizes and increases in size as R is decreased. Thus in the phase diagrams of

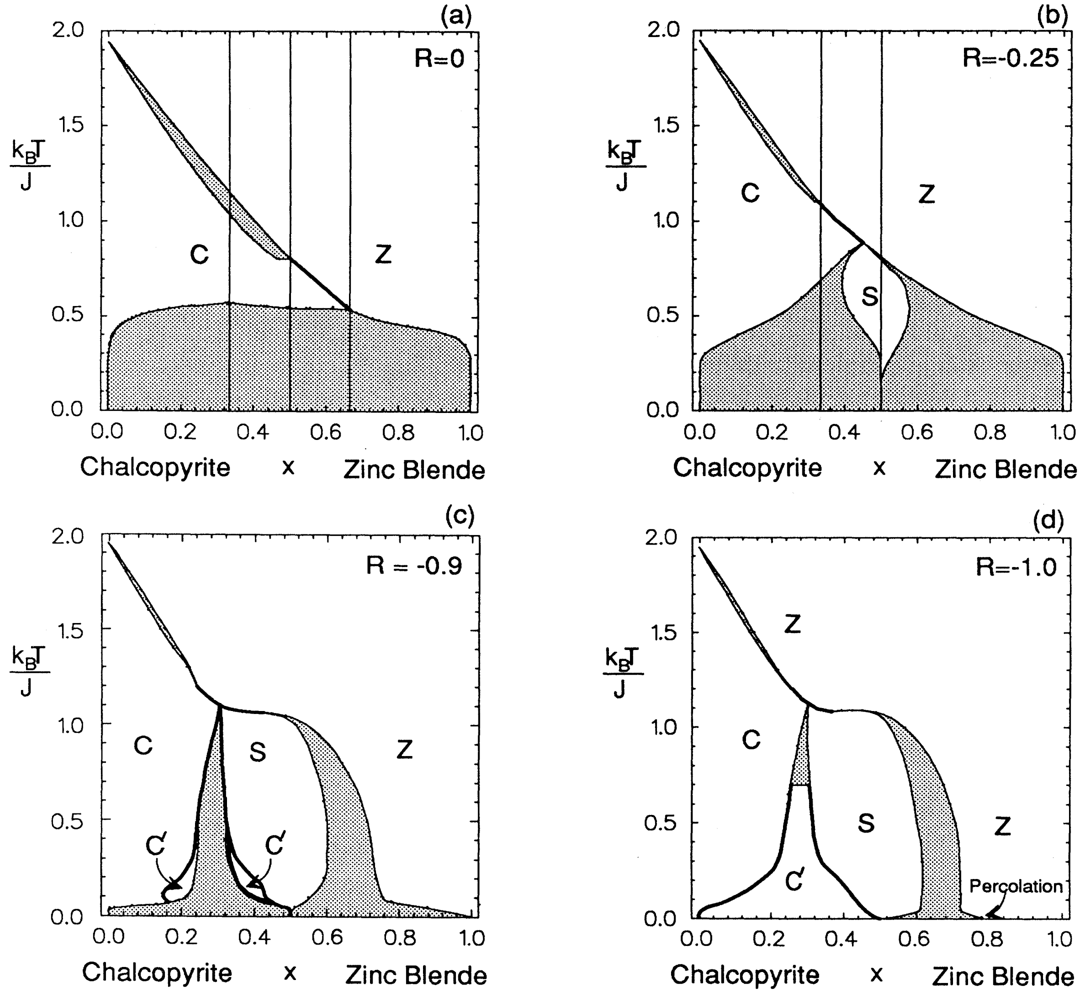

FIG. 2. Phase diagrams of the renormalized temperature k_BT/J vs composition x for the (chalcopyrite)-(zinc blende) system for the energy ratios (a) $R=0$; (b) $R=-0.25$; (c) $R=-0.9$; and (d) $R=-1$. Shown are chalcopyrite (C), stannite (S), and zinc-blende (Z) phases. Also indicated is a special "mixed-symmetry" transitional phase C', found for small values of the temperature.

temperature versus the composition x [see Figs. 2(b)-2(d)], *three* discrete phases are found at $T=0$, C ($x=0$), S ($x=\frac{1}{2}$), and Z ($x=1$). Additionally, as R decreases, the area enclosed inside the low-temperature miscibility bulge decreases and the high-temperature miscibility gap between the C and Z phases shrinks in width.

To understand $R\simeq-1$, we examine first the percolation limit $R=-1$, Fig. 2(d). Again, for percolation, since all energies are equal in magnitude, it *is* permissible, at $T=0$, to have alloy states, such as $(ABD_2)_{1-x}(CD)_{2x}$, with the composition x taking on any value between 0 and 1. The phase C' shown in Fig. 2(d) represents such a compromise: It is a special mixed transitional phase in which a C phase changes smoothly to a S phase without the need for a miscibility gap. The transitions (C-C') and (C'-S) occur continuously, as shown by the bold lines in Fig. 2(c) for $R=-0.9$ and in Fig. 2(d) for $R=-1$. In contrast, direct transitions (C-S) are first order and occur with a miscibility gap, e.g., the shaded region in Fig. 2(d). Interestingly, present also for $R=-1$ at $T=0$ is the more standard percolation limit: Pairs of atoms A and B with concentration $p=(1-x)$ being diluted by a fraction $(1-p)$ of pairs C_2 with atoms A, B, and C sitting on a fcc sublattice. The percolation limit for this problem is $p_c\simeq0.2$, or $x_p\simeq0.8$.[9] We find excellent agreement with this value, $x_p\simeq0.787$.

The phase diagram obtained for $R=-0.9$ is interesting because of the way in which the $T=0$ limit is obtained. Like $R=-0.25$ [Fig. 2(b)], at $T=0$, the only phases found are the ones expected by energetics: C, S, and Z. The mixed phase C' exists only for $T>0$, and is a clear precursor of the $R=-1$ phase diagram, Fig. 2(d).

Many (C-Z) alloy systems have been studied experimentally; we compare here only to two unusual diluted magnetic semiconductor (DMS) systems, $(\mathrm{CuInTe_2})_{1-x}$-$(\mathrm{MnTe})_{2x}$ (Refs. 10 and 11) and $(\mathrm{AgInTe_2})_{1-x}$-$(\mathrm{MnTe})_{2x}$,[11] and report more fully elsewhere.[7] DMS alloys are unusual because MnTe is only an "honorary" zinc-blende parent in that tetrahedral bonding occurs only up to a certain maximum value of the composition $x_{\max}$

(generally $\frac{1}{2} < x_{\max} < 1$), with MnTe itself having the rocksalt structure.[12] Equilibrium phase diagrams of many of these systems have been studied using a combination of differential thermal analysis and x-ray-diffraction techniques. Common features of these diagrams include a temperature-driven C-Z order-disorder transition at $x=0$ and an extended region at high temperatures of solubility of one phase within the other with the C-Z transition as a function of composition x being characterized by a small miscibility gap. There is also evidence for the existence of ordered phases at low temperatures and the midcomposition ranges, e.g., Aresti *et al.*[10] suggest that the existence of an $x=\frac{1}{2}$ stannite phase $\mathrm{CuMn_2InTe_4}$ and the possibility of mixed-symmetry alloys. Quintero *et al.*[11] present more complete phase diagrams, including regions which they label disordered α and ordered α' chalcopyrite and disordered β and ordered β' zinc blende. From the locations of these phases in their phase diagram and from their statement that the phases α' and β' differ from α and β by the ordering of Mn on the cation sublattice, we make the following assignation: $\alpha=C$, chalcopyrite; $\alpha'=C'$, mixed-symmetry phase; $\beta'=S$, stannite; and $\beta=Z$, zinc blende. We suspect their experiments to be described by values of R in the range $R \lesssim -1$.

In conclusion, the (chalcopyrite)-(zinc blende) system has been studied theoretically and has been shown to be an experimentally accessible semiconductor system that is unusually rich in ordering transitions. Further study is clearly warranted.[7]

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[1] H. R. Jen, M. J. Cherng, and G. B. Stringfellow, Appl. Phys. Lett. **48**, 1603 (1986).

[2] E. Parthé, *Crystal Chemistry of Tetrahedral Structures* (Gordon and Breach, New York, 1964).

[3] J. J. Brinsma, L. G. Giling, and J. Bloem, Phys. Status Solidi (a) **63**, 545 (1981).

[4] The order of the cations along the direction $\mathbf{k}=(1,0,\frac{1}{2})$ is $(AABB)$ for chalcopyrite and $(ACBC)$ for stannite.

[5] For a related problem, see Bing-Lin Gu, Kathie E. Newman, and P. A. Fedders, Phys. Rev. B **35**, 9135 (1987).

[6] M. Blume, V. J. Emery, and R. B. Griffiths, Phys. Rev. A **4**, 1071 (1971).

[7] K. E. Newman and X. Xiang (unpublished).

[8] R. Kikuchi, J. Chem. Phys. **60**, 1071 (1974); Acta Metall. **25**, 195 (1977).

[9] R. Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983).

[10] A. Aresti, L. Garbato, A. Geddo-Lehman, and P. Manca, in *Ternary and Multinary Compounds,* edited by S. K. Deb and A. Zunger (Materials Research Society, Pittsburgh, 1987), p. 497.

[11] M. Quintero, P. Grima, R. Tovar, G. S. Pérez, and J. C. Woolley, Phys. Status Solidi A **107**, 205 (1988).

[12] J. K. Furdyna, J. Appl. Phys. **64**, R29 (1988).