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First-principles phase diagrams of pseudoternary
chalcopyrite —iinc-blende alloys

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The temperature-composition phase diagrams of the pseudoternary (CulnSe2)i (ZnSe)2 and (ZnSnP2)i (GaP)2 chalcopyrite —zinc-blende semiconducting alloys are obtained by a combina-tion of first-principles

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librium volume. The practical completeness of the expan-

sion is then examined by the ability of this set (J)to pre-

dict via Eq. (1) the energies AH(cr') of other structures o' not used in the Bt. For example, we have used LDA
to calculate AH(o) for six equimolar (CuSe)„(InSe)„
short-period (p = 1, 2) superlattices, not including the
chalcopyrite structure Retaining in Eq. (1) only the
empty-site energy Jo and the nearest-neighbor pair inter-action J2 produces a prediction of AH(CH) = —1183.4

meV/cation compared with the LDA value AH(CH) = —1163.0 meV/cation. This 20-meV prediction error can
be reduced to 0.4 meV if the nearest-neighbor four-body
term J4 is added. Further addition of second-, third-,
and fourth-neighbor pair interactions J,z

lead to a simi-

lar prediction error of 0.25 meV. We thus choose to retain only Jo, J2, and J4 in the Harniltonian of Eq. (1). Fit-ting these parameters to the AH(o) of seven superlat-tices results in the J2 and J4 values given in Table I. The

dominant interaction J2) 0 shows that the A' B" C

system is compound-forming (or "antiferromagnetic"). The order-disorder transition obtained in a Monte Carlo

(MC) simulation for CulnSeq is T, = 1120 K, in perfect agreement with the earlier result ~ ~ using up to fourth-neighbor pair interactions. The cluster-variation method (CVM) tetrahedron approximation leads to T, = 1224 K. The four-body term J4 acts to lower T, by as much as 300 K in both the MC and the CVM calculations. We will hence proceed using CVM with the interaction energies given in Table I.
The consideration of the pseudoternary

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1200—

(ZnSnP2) g (GaP)2„

hC

c0 800

O.
E
I-

400 CH2/ZB

~

CHi/ZB

substantial solubility. Additional metastable features are
presented for this ab initio phase diagram. The left
dashed line in Fig. 2(b) marks the chalcopyrite spin-odal, which is the upper-composition limit of metasta-
bility for the CH phase. The right dashed line is the
unstable second-order transition line inside the coexis-
tence region and marks the lower-composition limit for metastability of the zinc-blende phase. Between these
two lines we find BzF/Bx & 0, which implies that any
incipient phase separation will be preferred to a single-phase state. Since at x = 1/2 we found 0 & AH(ST) & AEvD & AE,»g (Fig. 1), the stannite structure could be
observed in (CulnSe2)q (ZnSe)z~ if long range atom-ic
diffusion were inhibited. The shaded region at x 1/2,

T (440 K shows this marginally metastable ST phase.

It should be observed if short-range atomic rearrange-
ments are allowed but long range atomic mi-gration (and

I I I I

0.0 0.2 0.4 0.6 0.8 1.0
ZnSnP2 X GaP

FIG. 3. First-principles phase diagram of (ZnSnP2)q
(GaP)2, using volume-dependent interactions. The different regions are described in the text.

hence, phase