

Order-disorder transformation in ternary tetrahedral semiconductors

Alex Zunger

Citation: *Applied Physics Letters* **50**, 164 (1987); doi: 10.1063/1.97649

View online: <http://dx.doi.org/10.1063/1.97649>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/50/3?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Kinetics of order–disorder transformations in alloys. III](#)

J. Chem. Phys. **71**, 2844 (1979); 10.1063/1.438674

[Kinetics of order–disorder transformations in alloys. II](#)

J. Chem. Phys. **69**, 5006 (1978); 10.1063/1.436491

[Order-disorder transformation in gold-modified \$\beta\$ -brass](#)

J. Appl. Phys. **43**, 4495 (1972); 10.1063/1.1660951

[The Order-Disorder Transformation in Cu₃Au at High Pressure](#)

J. Appl. Phys. **38**, 103 (1967); 10.1063/1.1708937

[Contribution of Lattice Vibrations to the Order-Disorder Transformation in Alloys](#)

J. Chem. Phys. **33**, 1299 (1960); 10.1063/1.1731404

Frustrated by old technology? Is your AFM dead and can't be repaired? Sick of bad customer support?



It is time to upgrade your AFM
Minimum \$20,000 trade-in discount for purchases before August 31st

Asylum Research is today's technology leader in AFM

dropmyoldAFM@oxinst.com

OXFORD INSTRUMENTS
The Business of Science®

Order-disorder transformation in ternary tetrahedral semiconductors

Alex Zunger

Solar Energy Research Institute, Golden, Colorado 80401

(Received 8 October 1986; accepted for publication 18 November 1986)

The recently discovered order-disorder transformations in pseudobinary semiconductor alloys $A_x B_{1-x} C$ are shown to belong to a broader class of such transformations in $A_n B_{4-n} C_4$ semiconducting compounds (e.g., chalcopyrites, for $n = 2$). Strain energy, set up by the atomic size mismatch between the $A-C$ and $B-C$ bonds, is shown to control the nature of the state of order in chalcopyrites and pseudobinary alloys alike. These considerations lead to a classification of all bulk tetrahedral semiconductors into four classes of order-disorder characteristics.

The thermodynamic ground state of pseudobinary $A_x B_{1-x} C$ alloys of binary isovalent AC and BC tetrahedral semiconductors has traditionally been considered to be substitutionally disordered, having no stable and long-range ordered $A_n B_{4-n} C_4$ -like phase at any temperature or composition x .¹ Recently, however, Srivastava *et al.*² and Mbaye *et al.*³ have proposed on the basis of their first-principles total energy and phase diagram calculations that, whereas at high temperature ($T > T_c$) such systems are indeed stable in a disordered phase, at lower temperatures ($T < T_c$) an ordered phase² or a clustered (pseudo-ordered) phase³ can become the ground state. More recently, careful crystal growth experiments have dramatically demonstrated the existence of hitherto unknown ordered stoichiometric ternary "alloys," including systems such as $GaAlAs_2$,⁴ $SiGe$,^{5,6} $InGaAs_2$,⁷ and Ga_2AsSb .⁸ The question of whether such systems are thermodynamically stable in the ordered phase (or just metastable) remains, however, elusive: recent calculations by Wood *et al.*⁹ suggest $GaAlAs_2$ to be thermodynamically unstable towards disproportionation, whereas epitaxially grown $SiGe$ was predicted⁶ to be stable in its ordered phase only due to substrate strain. Clearly, the issue of stability of such ordered phases is difficult to settle experimentally because the critical temperature T_c for order-disorder transitions can be so low that atomic mobilities are insufficient to grow fully ordered samples in conventional semiconductor crystal growth techniques. In this letter I point to the fact that there exists a large class of tetrahedrally bonded semiconductors—the ABC_2 chalcopyrites and pnictides—where T_c is known to be very high (only 0–200 °C below the melting temperature T_M), and that experimental and theoretical studies of the physical factors controlling order-disorder transformations in these systems can be used to gain insight into the analogous phenomena in *isovalent* pseudobinary alloys (where T_c is very low).

In addition to the pseudobinary isovalent semiconductor alloys,^{4–8} there are at least four other classes of tetrahedral semiconductors which exhibit order-disorder transformations as a function of temperature: (i) the $A^{IV}B^{III}C_2^{VI}$ and $A^{II}B^{IV}C_2^V$ chalcopyrite-type crystals,^{10–13} (ii) alloys of $(A^{III}C^V)-B^{IV}$ heterovalent semiconductors¹⁴ (e.g., $GaAsGe$), (iii) alloys of $A_3^{III}C_2^V$ pnictides (Cd_3As_2 - Zn_3As_2 ^{15(a)} and Cd_3P_2 - Zn_3P_2 ^{15(b)}), and (iv) heterovalent $(A^{II}C^{VI})-(B^{III}D^V)$ alloys¹⁶ (e.g., $CdTe$ - $InAs$). For all but the first class, the experimental data are yet incomplete: for class (ii) T_c is not certain, and for classes (iii) and (iv) the

structure of the ordered phase is not known. I will therefore concentrate in what follows on class (i).

In the ordered ABC_2 chalcopyrite structure¹⁰ each anion C has two A and two B atoms as nearest neighbors; the space group is $I\bar{4}2d$ ($E1_1$ -type). Above T_c the x-ray diffraction peaks characteristic of the chalcopyrite phase disappear¹⁰ as the A and B atoms disorder on the cation sublattices, giving rise to the zinc-blende $F\bar{4}3m$ space group ($B3$ type). Hence, chalcopyrites above T_c are analogous to isovalent $A_{0.5}B_{0.5}C$ alloys at room temperature. Table I divides all known chalcopyrite-type compounds (entries without asterisks) into two groups: those that exhibit an order-disorder (chalcopyrite to zinc blende) transition before they melt ("disordering type," shown to the left), and those that remain ordered until they melt ("nondisordering," shown to the right). Clearly, since the A and B atoms in chalcopyrites belong to *different* columns in the periodic table, their interaction is stronger than in *isovalent* pseudobinary alloys, hence T_c in chalcopyrites is sufficiently high to conveniently observe and (reversibly) characterize order-disorder transitions, both during and after growth. A cursory look at the compounds listed on either side of Table I reveals no obvious reason for their classification as disordering and nondisordering: both $A^{IV}B^{III}C_2^{VI}$ (chalcopyrite) and $A^{II}B^{IV}C_2^V$ (pnictide) compounds, low-melting or high-melting compounds, and covalent or partially ionic compounds can exhibit either type of behavior.

To relate the order-disorder characteristics of such compounds to their atomic structure, we first consider the equilibrium structure of the ordered ABC_2 phase. We have previously demonstrated^{2,3,6} that the formation enthalpy $\Delta H^{(O)}$ of the order (O) ternary phase contains (i) a destabilizing microscopic strain (ms) energy term ΔE_{ms} , reflecting the failure of a given tetrahedral structure to accommodate simultaneously both ideal bond angles and ideal bond lengths d_{AC} and d_{BC} (as in pure binary AC and BC compounds), and (ii) a chemical piece ΔE_{chem} , reflecting (stabilizing or destabilizing) interactions at fixed volume (e.g., $A-B$ charge transfer, polarization, etc.):

$$\Delta H^{(O)} = \Delta E_{ms} + \Delta E_{chem} \quad (1)$$

The first term is related to the atomic structure at equilibrium: If the C atom in ABC_2 were exactly at the center of the tetrahedron having two A and two B atoms at its corners, one would have an equal bond length ($R_{AC} = R_{BC} = \sqrt{3/4} a$) but *strained* structure (since *ideal* d_{AC} and d_{BC} bond lengths are generally unequal). In actuality, the common atom (C)

TABLE I. Observed and predicted order-disorder characteristics of ABC_2 compounds. T_c and T_M are transition and melting temperatures, respectively (in K). $O-D$ (O) denotes compounds that undergo order-disorder transitions (remain ordered) below T_M . Asterisk denote hypothetical compounds. Compounds to the right (left) are predicted to be disordering (nondisordering).

Disordering systems						Nondisordering systems					
ABC_2 compound	T_M^a	$(c/a)^b$	Observed			u_{calc}^c	ABC_2 compound	T_M^a	$(c/a)^b$	Obs.	u_{calc}^c
			$O-D$	T_c							
CuAlS ₂	~1573	1.96	0.264	AgAlS ₂	...	1.772	O^c	0.288	
CuAlSe ₂	~1473	1.954	0.264	AgAlSe ₂	...	1.793	O^c	0.287	
CuAlTe ₂	...	1.975	0.263	AgAlTe ₂	...	1.878	...	0.285	
CuGaS ₂	1553	1.959	0.264	AgGaS ₂	< 1313	1.789	O^c	0.288	
CuGaSe ₂	~1313	1.966	$O-D^c$...	0.264	AgGaSe ₂	1123	1.793	O^c	0.287	
CuGaTe ₂	1143	1.987	$O-D^c$...	0.263	AgGaTe ₂	993	1.897	O^c	0.285	
CuInS ₂	~1298	2.016	$O-D^c$	1253	0.236	MgSiP ₂	...	1.769	...	0.284	
CuInSe ₂	1263	2.008	$O-D^d$	1083	0.237	MgSiAs ₂ *	0.284	
CuInTe ₂	1053	2.000	$O-D^d$	950	0.237	MgSiSb ₂ *	0.281	
AgInS ₂	...	1.91	0.262	MgGeAs ₂ *	0.276	
AgInSe ₂	~1046	1.919	$O-D^d$	~1046	0.261	MgGeSb ₂ *	0.275	
AgInTe ₂	953	1.962	$O-D^d$	910	0.261	ZnSiP ₂	< 1643	1.933	O^a	0.272	
MgSnP ₂ *	0.250	ZnSiAs ₂	1369	1.940	O^a	0.271	
MgSnAs ₂ *	0.250	ZnSiSb ₂ *	0.270	
MgSnSb ₂ *	0.250	CdSiP ₂	1393	1.839	O^a	0.296	
ZnGeP ₂	1148	1.96	$O-D^d$	1225(?)	0.264	CdSiAs ₂	> 1123	1.84	O^a	0.294	
ZnGeAs ₂	~1148	1.966	$O-D^d$	1085(?)	0.264	CdSiSb ₂ *	0.291	
ZnGeSb ₂ *	0.263	CdGeP ₂	~1049	1.877	O^a	0.288	
ZnSnP ₂	1203	2.00	$O-D^d$	993	0.236	CdGeAs ₂	~943	1.886	...	0.287	
ZnSnAs ₂	1048	2.00	$O-D^d$	~910	0.236	CdGeSb ₂ *	0.285	
ZnSnSb ₂	...	2.00	$O-D^d$...	0.237						
CdSnP ₂	843	1.951	(?)	...	0.262						
CdSnAs ₂	~869	1.956	$O-D^d$	~860	0.261						

^a Compiled in Ref. 10.

^b Compiled in Refs. 10 and 12.

^c Reference 12.

^d Compiled in Refs. 10 and 13.

^e Calculated in Ref. 11 (Tables II and VII).

is displaced¹¹ so that it is closer to one pair of atoms (say, A) than the other (B), giving rise to a finite "displacement parameter"

$$u - 1/4 = (R_{AC}^2 - R_{BC}^2)/a^2 \quad (2)$$

(zero in the zinc-blende structure), and consequently to "bond alternation" ($R_{AC} \neq R_{BC}$) where, in the chalcopyrite structure,¹¹ $R_{AC} = [u^2 + (1 + \eta^2)/16]^{1/2}a^2$, $R_{BC} = [(u - 1/2)^2 + (1 + \eta^2)/16]^{1/2}a^2$, and where the tetragonal deformation is $\eta \equiv c/2a$. (Note that u and $u - 1/2$ are interchanged when A and B are.) Jaffe and Zunger¹¹ observed that these u values can be successfully predicted for all known chalcopyrite crystals in a simple semiclassical model, postulating that at equilibrium the three structural parameters (a, u, η) of ABC_2 assume the values that minimize ΔE_{ms} , a quantity that measures the strain imposed by the departure of $R_{AC}(a, u, \eta)$ and $R_{BC}(a, u, \eta)$ from the sum of the atomic tetrahedral radii $d_{AC} = R_A^0 + R_C^0$ and $d_{BC} = R_B^0 + R_C^0$, respectively. In this "conservation of tetrahedral bonds" model,¹¹ one has $u \approx 1/4 + 3/4(d_{AC}^2 - d_{BC}^2)/(d_{AC} + d_{BC})^2$.

There is a significant qualitative difference between bond lengths in ordered and disordered phases: whereas the ordered ABC_2 structure has only two distinct (R_{AC} and R_{BC}) bond lengths, the disordered phase can have a *distribution* of bond lengths, reflecting different possible local environments. This affects the relative strain energies in ordered and disordered phases as follows. Limiting our discussion to first neighbors on fcc lattice, the common C atom may have around it in the disordered phase five local environments (A_4, A_3B, A_2B_2, AB_3 , or B_4 denoted $n = 0, 1, 2, 3$, and 4,

respectively), with relative probabilities $P^{(n)}(x)$. The *average* bond length in the disordered phase is then a statistical mixture of the bond lengths $R_{AC}^{(n)}$ and $R_{BC}^{(n)}$ of pure $A_nB_{4-n}C_4$ "clusters," i.e.,²

$$R_{AC}^{(D)}(x) = \sum_{n=0}^4 w^{(n)} P^{(n)}(x) R_{AC}^{(n)}[a(x)] \quad (3)$$

[with a similar expression for $R_{BC}^{(D)}(x)$], where $w^{(n)}$ is the number of bonds in the $A_nB_{4-n}C_4$ structure. Srivastava *et al.*² demonstrated that the bond lengths $R_{AC}^{(D)}(x)$ and $R_{BC}^{(D)}(x)$ of the *disordered* phase deviate from the ideal values d_{AC} and d_{BC} , respectively, more than do the bond lengths $R_{AC}^{(n)}$ and $R_{BC}^{(n)}$ of the *ordered* phases, simply because the superposition principle underlying Eq. (3) makes it impossible for all bonds to approach *simultaneously* the ideal values. Hence, the microscopic strain energy ΔE_{ms} of the disordered phase exceeds that of the ordered phase or, $\Delta H^{(D)}(x) > \Delta H^{(O)}(x)$. The difference $\Delta H^{(O)} - \Delta H^{(D)}$ increases as the disparity between the two bonds $A-C$ and $B-C$ increases, i.e., as $|u - 1/4|$ increases. This analysis suggests that for a sufficiently large displacement parameter ($u > u_c$), the enthalpy of the disordered phase $\Delta H^{(D)}$ would be so large that even the entropy gain $-T\Delta S^{(D)}$ upon disordering will be insufficient to stabilize this phase before it melts (i.e., $\Delta H^{(O)} < \Delta H^{(D)} - T\Delta S^{(D)}$, for $T < T_M$), hence the system will be nondisordering.

This model then suggests a new way of thinking about the problem: to examine the idea of strain-induced preference for order over disorder, I search for a critical value u_c (or its complement, $1/2 - u_c$) consistent with this prediction. I find (Table I) for $u_c = 0.265$ (or $1/2 - u_c = 0.235$)

that in all 23 cases where data exist (with no exception!) *all disordering type compounds have $u < u_c$ (or $u > 1/2 - u_c$) and all nondisordering compounds have $u > u_c$* . This remarkable result implies that we can predict the order-disorder characteristics for ABC_2 compounds for which no such data exist as yet (nine compounds in Table I), or even for compounds which have not yet been synthesized¹¹ (11 compounds in Table I, predicted in Ref. 11 to exist and denoted in Table I by an asterisk) solely from the knowledge of the atomic radii. A similar correlation exists between order-disorder characteristics and the experimental tetragonal deformation ratio $c/a \cong 2\eta$ given in Table I ($2\eta < 1.95$ implies nondisordering; $2\eta > 1.95$ implies disordering, $AgInS_2$ and $AgInSe_2$ being the only possible exceptions), as recognized by Binsma *et al.*¹² Whereas such a phenomenological correlation can be expected in light of our analysis [η can be approximately related to u through¹¹ $u \cong 1/2 - 1/4(2\eta^2 - 1)$, giving $2\eta_c = 1.941$ for our $u_c = 0.265$], the relation of 2η to disorder is not as obvious, and requires the measurement of c/a (or, a fit to orbital radii with rather nonintuitive fitting parameters¹²).

The foregoing analysis can be extended to pseudobinary $A_xB_{1-x}C$ alloys.^{2,4} Calculations¹⁷ of u show $GaAlP_2$, $GaAlAs_2$, and $GaAlSb_2$ ($u = 0.250$) to be of the disordering type. Indeed, Zn diffusion experiments show $T_c < 773$ K in $AlGaAs$ superlattices.¹⁸ Since this exceeds the growth temperature for which ordering was observed,⁴ the latter, most likely, does not represent *thermodynamic* ordering, in agreement with recent calculations.⁹ In contrast, $InGaP_2$ ($u = 0.278$), $InGaAs_2$ ($u = 0.277$), and $InGaSb_2$ ($u = 0.275$) are predicted to be too strained in the disordered phase (in agreement with Ref. 2). I therefore suggest that it is useful to classify all pseudobinary $A_xB_{1-x}C$ systems according to whether $u > u_c$ or $u < u_c$. This implies a classification of order-disorder behavior in all tetrahedral semiconductors into four equilibrium types, depending also on the sign of ΔE_{chem} . (I) If $u < u_c$ and $\Delta E_{chem} < 0$ the system can order at $T < T_c$ (including the impractical case where T_c is lower than conventional growth temperatures, or even $T_c \cong 0$) but it disorders at $T > T_c$, showing there are solid solutions. The disordering chalcopyrites (Table I) such as $CuInSe_2$, as well as¹⁵ $Cd_xC_2^{VI}-Zn_{1-x}C_2^{VI}$ and possibly $Cd_xMn_{1-x}Te$,¹⁹ belong to this type (metallurgical example: $CuAu$). (II) If $u < u_c$ and $\Delta E_{chem} > 0$, the system will not order thermodynamically as a single phase, showing instead multiple-phase regions below the miscibility gap (MG) temperature T_{MG} and a disordered solid solution above it. $A^{III}P_xAs_{1-x}$, $Al_xGa_{1-x}C^V$ and Si_xGe_{1-x} belong to this class (metallurgical examples: KRb , $CsRb$). T_{MG} will simply scale with the size mismatch²⁰ (proportional to $|u - 1/4|$). (III) If $u > u_c$ but $\Delta E_{chem} < 0$, the system orders at all $T < T_M$, showing limited solid solubility and strong compound formation. The nondisordering chalcopyrites (Table I, e.g., $AgAlS_2$), as well as²¹ SiC , belong to this class (metallurgical examples: NaK , $MgZn$, $NaCs$). Comparing this type to type I above shows that for systems with *attractive* chemical interactions $\Delta E_{chem} < 0$, a large strain ($u > u_c$) *stabilizes* the ordered phases (in contrast to the implication of simpler models used in semiconductors²⁰ which suggest strain to be invariably destabilizing). Finally, (IV), if $u > u_c$

and $\Delta E_{chem} > 0$ we encounter two possibilities: (a) formation of a wide miscibility gap with no solid solubility and no compound formation (e.g., $A^{III}P_xSb_{1-x}$, $AgCu$), and (b) "strain-induced selection of species." In the latter case³ no formal long-range order exists, but a given ordered species, say $A_nB_{4-n}C_4$ is strongly favored statistically (in excess of what a random distribution would grant) at the composition $x = x_n = n/4$ over the other species ($A_mB_{4-m}C_4$) with $m \neq n$. It is likely that this is the case for $GaAs_xSb_{1-x}$ ⁸ and ($A^{II}C^{VI}$)-($B^{III}D^V$) systems.¹⁵

Our approach hence places order-disorder transformations in "pseudobinary" alloys in the broader context of similar transformations in ternary tetrahedral compounds. It also suggests predictions for the reduction Δ in the band gap upon disorder since²² $\Delta H^{(O)} - \Delta H^{(D)} \propto \Delta^2$, one expects $T_c = (\Delta H^{(O)} - \Delta H^{(D)})/\Delta S = \text{const } \Delta^2$. Using the data for chalcopyrites (e.g., $\Delta = 0.41$ eV,²³ $T_c = 993$ K¹⁰ in $ZnSnP_2$) one gets $\text{const} \cong 1.69 \times 10^{-4}$ eV²/K. Using the T_c data from Table I, one then predicts $\Delta \cong 0.4$ eV for most disordering chalcopyrites, and that a disorder-induced reduction in the band gap of $\Delta \geq 225$ meV is necessary in tetrahedral semiconductors for having T_c at or above room temperature. Measurements of Δ can hence be used to deduce order-disorder temperatures.

- ¹O. Madelung, *Physics of III-V Compounds* (Wiley, New York, 1969), pp. 269-398; J. C. Woolley, in *Compounds Semiconductors*, edited by R. K. Willardson and H. L. Goering (Reinhold, New York, 1962), pp. 3-33.
- ²G. P. Srivastava, J. L. Martins, and A. Zunger, *Phys. Rev. B* **31**, 2561 (1985).
- ³A. A. Mbaye, L. G. Ferreira, and A. Zunger, *Phys. Rev. Lett.* (in press).
- ⁴T. S. Kuan, T. F. Kuech, W. I. Wang, and E. L. Wilkie, *Phys. Rev. Lett.* **54**, 201 (1985).
- ⁵A. Ourmazd and J. C. Bean, *Phys. Rev. Lett.* **55**, 765 (1985).
- ⁶J. L. Martins and A. Zunger, *Phys. Rev. Lett.* **56**, 1400 (1986).
- ⁷H. Nakayama and H. Fujita, in *GaAs and Related Compounds 1985*, edited by M. Fujimoto, *Inst. Phys. Conf. Ser.* **79** (Adam Hilliger, Bristol, 1986), p. 289.
- ⁸H. R. Jen, M. J. Cherny, and G. B. Stringfellow, *Appl. Phys. Lett.* **48**, 1603 (1986).
- ⁹D. M. Wood, S. H. Wei, and A. Zunger (unpublished).
- ¹⁰J. L. Shay and J. H. Wernick, *Ternary Chalcopyrites* (Pergamon, Oxford, 1975).
- ¹¹J. E. Jaffe and A. Zunger, *Phys. Rev. B* **29**, 1882 (1984).
- ¹²J. J. Binsma, L. J. Giding, and J. Bloem, *Phys. Status Solidi A* **63**, 595 (1981).
- ¹³O. Madelung, M. Schulz, and H. Weiss, eds., *Landolt Börnstein New Series* (Springer, Berlin, 1985), Vol. 17h, pp. 27 and 68.
- ¹⁴J. E. Greene and A. H. Eltoukhy, *Surf. Interface Anal.* **3**, 34 (1981); K. E. Newman and J. D. Dow, *Phys. Rev. B* **27**, 7495 (1983).
- ¹⁵(a) G. A. Castellion and L. C. Beegle, *J. Phys. Chem. Solids* **26**, 767 (1965); (b) K. Masumoto, S. Isomura, and K. Sasaki, *Phys. Status Solidi A* **6**, 515 (1971); J. Berak and Z. Pruchnik, *Roczniki Chemii (Ann. Soc. Chim. Polonorum)* **45**, 1425 (1971). I thank Dr. J. Meakin for drawing my attention to these references.
- ¹⁶E. N. Khabarov and V. A. Liopo, *Acta Crystallogr. Sec. A* **31**, S92 (1975); N. A. Semikolenova, L. A. Skorobogatova, and E. N. Khabarov, *Sov. Phys. Semicond.* **8**, 976 (1975).
- ¹⁷J. E. Jaffe and A. Zunger, *Phys. Rev. Lett.* **51**, 662 (1983).
- ¹⁸W. D. Laidig, N. Holonyak, J. J. Coleman, and P. D. Dapkus, *J. Electron. Mater.* **11**, 1 (1982).
- ¹⁹S. H. Wei and A. Zunger, *Phys. Rev. Lett.* **56**, 2391 (1986).
- ²⁰L. M. Foster, *J. Electrochem. Soc.* **121**, 1662 (1974).
- ²¹J. L. Martins and A. Zunger, *J. Mater. Res.* **1**, 523 (1986).
- ²²J. A. Van Vechten, in *Semiconductors Handbook*, edited by S. P. Keller (North-Holland, Amsterdam, 1980), Vol. 3, p. 1.
- ²³M. A. Ryan, D. Williamson, J. A. Turner, and B. A. Parkinson, *J. Electrochem. Soc.* **132**, 134c (1985) and unpublished.