Predicting the temperature for the solid–solid phase transition in II–VI semiconductor alloys

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ABSTRACT

At atmospheric pressure, many of the II–VI semiconducting alloys are known to undergo a zinc-blende to wurtzite solid–solid transition. Experimental values for these transitions temperatures have only been reported for two alloys. We show here that chemical potentials for one of the components in a solid solution with the other can be used to estimate the transition temperature. The non-ideal behavior of the solvent component is addressed via an activity coefficient which is determined using the quasi-chemical model. The chemical potentials for each case, zinc-blende and wurtzite are then taken to be equal at the transition temperature. Predicted transition temperatures are reported here for ZnS, CdS, ZnSe, ZnTe, and CdSe. In the case of ZnS and CdS these values agree with the experimental. For ZnSe, ZnTe, and CdSe the values are above their respective melting points. This result suggests that there is no complete bulk transition below the melting point for these three alloys but calculations predict that the two phases are nearly isoenergetic.

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1. Introduction

The wide band gap II–VI semiconducting alloys are an important class of materials for electronic applications in that their band gaps can span the IR–visible–UV range. Several of these binary alloys have been identified as potential candidates for use in blue-green light emitting devices and solar cells [1]. Unfortunately, only CdTe can be effectively doped both p and n type as the other II–VI alloys exhibit a strong donor compensation effect for either p or n dopants [2–5]. This fact limits the applicability of these materials in semiconductor electronic devices. The exact origin for this compensation effect is a matter of significant debate with different explanations having been proposed throughout the years. Principal among these are that the effect stems from issues with impurities and native defects [4]. Additional detailed information on the thermal and structural nature of these materials, in the solid state, could lead to a better understanding of this compensation effect and in general expand the knowledge base for this important class of semiconducting materials.

One interesting property for some of the II–VI binaries is that at atmospheric pressure they undergo a solid–solid phase transition below the melting point. The room temperature state is the zinc-blende conformation while the high temperature solid state

is that of wurtzite. II–VI alloys known to be found in both solid phases include CdS, ZnS, ZnTe, ZnSe and CdSe [6]. The precise temperature for an abrupt transition is only known for ZnS [6,7], while a range for occurrence has been reported for CdS [6]. However, crystals for these materials are often not found in a structurally homogeneous state. Alternating layers of zinc-blende and wurtzite are known to occur [8,9]. To our knowledge, transition temperatures have not been reported for the other binary alloys mentioned above.

In this report it is shown that the transition temperature can be predicted by equating chemical potentials. This situation is sketched in Fig. 1. Here it is seen that the low temperature zinc-blende potential is favored, that is, the state with the lower chemical potential, at lower temperatures. The two potentials are equal at the transition temperature. Above the transition temperature the wurtzite state is favored.

To develop expressions for the chemical potentials, one of the binary components is assumed to act as the solvent in a solid solution with the other. Then, non-ideal effects in the potential are accounted for with an activity coefficient. These activity coefficients are then determined using the quasi-chemical model.

The quasi-chemical model requires the knowledge of an interchange energy w. Rather than leave this as an adjustable parameter we show that it can be computed using known thermal data for the components involved and reported structural data for the binary solid. Finally, when chemical potentials are then equated the transition temperature can be determined. The value computed here is within 2% of the experimentally reported value

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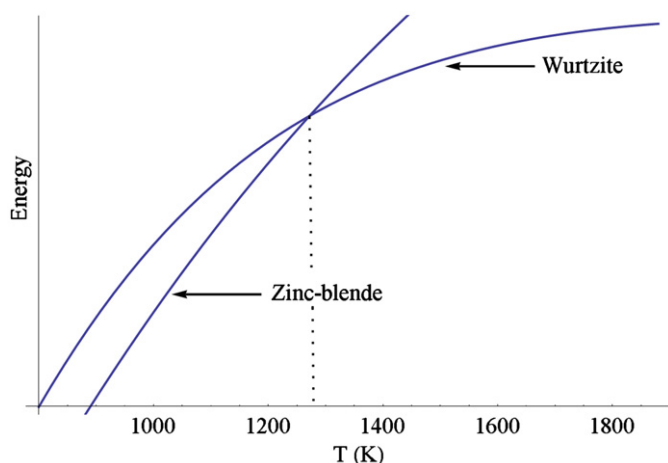 *E-mail address:* barlowd@erau.edu

Fig. 1. Schematic diagram showing approximate isobaric chemical potentials for the solid in the zinc-blende and wurtzite states. The vertical line identifies the transition temperature.

for ZnS. For CdS our computed value is within 2% of the high end of the reported range. For the remaining II–VI binaries considered here, ZnSe, ZnTe, and CdSe, the transition temperatures are also estimated using this method and reported here. These values are greater than the 1 atm melting temperature for all three materials. This result leads us to speculate that the two phases are nearly isoenergetic and that the zinc-blende and wurtzite structure types exists simultaneously in these alloys with no complete transition from zinc-blende to wurtzite below the melting point. To investigate this claim the derived expressions for the chemical potentials are used to compute the difference in potential between the two states at room temperature for each of the alloys. This difference is on the order of kT.

2. Theory

Here we model the binary alloy as a solid solution of two components A and B. Then we write for the chemical potential μ_z for one of the components within the solution in the zinc-blende phase as

$$\mu_z = \mu_z^o + kT\ln(x\gamma_z) \tag{1}$$

and likewise for the wurtzite phase:

$$\mu_w = \mu_w^o + kT\ln(x\gamma_w). \tag{2}$$

here k is Boltzmann's constant, T the absolute temperature, μ° the chemical potential of the pure component at the standard state, x the mole fraction of said component and γ the activity coefficient. When $\gamma=1$ the solution is ideal. In this study the mole fraction is held constant at $x=\frac{1}{2}$. At the transition temperature, T_t, the potential of Eq. (1) will equal that of Eq. (2) and the following will be true.

$$kT_t\ln(x\gamma_z) = \Delta\mu^o + kT_t\ln(x\gamma_w) \tag{3}$$

where$\Delta\mu^o = \mu_w^o - \mu_z^o$. In the non-ideal situation, considered here, the activity coefficients will be a function of the temperature. So in order to use Eq. (3) to estimate the transition temperature the activity coefficients and a value for the constant $\Delta\mu^\circ$ must be determined.

We express the activity coefficients using the quasi-chemical model as outlined by Guggenheim [10]. In this model for a solid solution of components A and B, the distribution of AB pairs in the solution has a temperature dependence given by a Boltzmann type distribution. Following Guggenheim we declare the following

$$\eta = e^{w/zkT} \tag{4}$$

where z is the number of nearest neighbors and w the interchange energy. In this study $z=4$. Now, the following quantity is also useful.

$$\beta = \left[1 + 4x(1-x)(\eta^2-1)\right]^{1/2} \tag{5}$$

With this, the activity coefficients, for the situation where $x=1/2$, can be given as [10].

$$\gamma = \left[\frac{2\beta}{(\beta+1)}\right]^{(1/2)z} \tag{6}$$

Since $x=\frac{1}{2}$ here the activity coefficient would be given by Eq. (6) for either component. In this analysis we need only focus on one component and then determine the interchange parameter w for the said component in each solid phase. Thus we will have an activity coefficient for the zinc-blende phase and another for the wurtzite state.

Guggenheim states that the interchange energy is the energy required to remove one atom of component A from the bulk of pure A and the same for an atom of component B and then interchange the two atoms [11]. We here propose a simple and direct way to compute this parameter using known experimental results for the thermal properties of the elements involved and structural properties of the binary alloy in each solid state.

To begin, the interchange energy is taken to be given by the following

$$w = -\left(\Delta H_{vap}^A + \Delta H_{vap}^B - 2\Delta H_{vap}^{AB}\right)/N_A \tag{7}$$

where ΔH_{vap} is the heat of vaporization in J/mol for component A, B or the mixture AB as denoted in Eq. (7). N_A is Avogadro's number. Heats of vaporization for the pure component elements are known however, an approximation is used to determine ΔH_{vap} for the AB mixture.

Several groups have suggested that lattice energies in a crystal are related to the lattice parameter a [12,13]. Phillips and van Vechtan [13] have suggested that an energy gap for a solid is proportional to $a^{-2.5}$. From this, Stringfellow [14] has proposed that the heat of sublimation for a solid be given by

$$\Delta H_{sub} = \frac{K}{a^{2.5}} \tag{8}$$

here K is a constant determined from fitting Eq. (8) to experimental data. A similar linear trend exists for experimental heat of vaporization data, ΔH_{vap}, for the II–VI elements considered here. This is shown in Fig. 2 below. Fitting the data to a straight line leads to a value for the constant K. Here we find that $K=1.21278 \times 10^6$ J Å$^{2.5}$/mol. Since lattice parameter data is available for CdS and ZnS in zinc-blende and the wurtzite state, Eq. (6) can be used to compute ΔH_{vap} for the binary in each phase and then an interchange energy can be computed for each state; w_z and w_w respectively. For the hexagonal wurtzite conformation where multiple lattice parameters are reported, the smallest of these is used in the computation of w_w. Now, activity coefficients can be computed using Eq. (6) for the component in each phase and then Eq. (3) can be used to determine the transition temperature.

Unfortunately the difference in chemical potentials for the pure component at standard state, $\Delta\mu^\circ$, is not known. However, this value can be approximated if we consider the first derivatives of the chemical potentials. Since the potentials of pure components at standard state are not a function of the temperature they are not involved in derivatives of μ. Consider the first derivatives
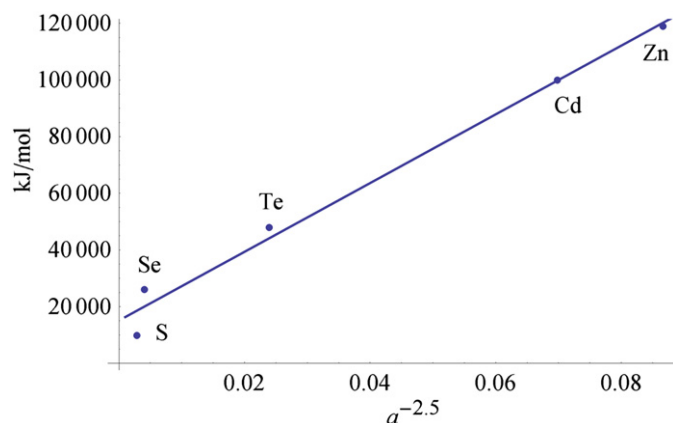
Fig. 2. Heat of vaporization data for selected group II metals and chalcogens plotted vs. their lattice constants raised to the power of -2.5, [7]. For a hexagonal lattice, the smallest of the reported lattice parameters is utilized. This data is fitted to the straight line depicted with the slope being K.

at the transition temperature

$$m_z = \left(\frac{d\mu_z}{dT}\right)_{T=T_t} \qquad (9)$$

$$m_w = \left(\frac{d\mu_w}{dT}\right)_{T=T_t} \qquad (10)$$

with Eqs. (9) and (10) we can write the following linear pseudo-potentials

$$\mu_w = m_w T + b_w \qquad (11)$$

$$\mu_z = m_z T + b_z \qquad (12)$$

Now it is assumed that the difference in zinc-blende and wurtzite potentials at the standard state temperature T_o can be given by the difference of Eqs. (11) and (12), that is

$$\mu_w(T_o) - \mu_z(T_o) = (m_w - m_z)T_o + b_w - b_z \qquad (13)$$

For our true potentials in Eqs. (1) and (2) at the standard state temperature we have

$$\mu_w(T_o) - \mu_z(T_o) = \Delta\mu^o + kT_o\ln\frac{\gamma_w(T_o)}{\gamma_z(T_o)} \qquad (14)$$

the pseudo-potentials of Eqs. (11) and (12) are taken to be equal at the transition temperature. This allows the difference of intercepts to be eliminated in Eq. (13) and then Eqs. (13) and (14) can be used to arrive at the following involving $\Delta\mu^\circ$.

$$(m_w - m_z)T_o + (m_z - m_w)T_t = \Delta\mu^o + kT_o\ln\frac{\gamma_w(T_o)}{\gamma_z(T_o)} \qquad (15)$$

By solving for $\Delta\mu^\circ$ in Eq. (15), and then using this in Eq. (3), along with the activity coefficient of Eq. (6) with the computed values for the interchange energy, the transition temperature can then be determined. The data used in the calculation of the activity coefficients is listed in Table 1

3. Results and conclusion

Plotting each side of Eq. (3) independently allows for the intercept to be found which is the transition temperature. These curves are shown for the cases of ZnS and CdS below in Figs. 3 and 4 respectively. The transitions temperatures computed here are listed in Table 1 along with the corresponding values reported from experiment. In the case of ZnS the temperature computed here is with 2% of the reported experimental value. For CdS the

Table 1
Data used in the calculation of the transition temperatures for selected II–VI alloys and the computed transition temperatures along with $\Delta\mu$ at 300 K.

Alloy	T_t (K) Ref [7]	T_m (K) Ref [6]	a (Å)	$\Delta\mu$ (J) at 300 K	w (J)
ZnS	1273[b] 1293[6] 1295[7]	2100	5.4109[c] 3.820[d]	6.8978×10^{-21}	-1.5479×10^{-19c} -7.1003×10^{-19d}
CdS	1089[b] 973–1073[6]	1750	5.83[c] 4.1348[d]	5.34238×10^{-21}	-1.3326×10^{-19c} -6.6717×10^{-19d}
CdSe	1634[a]	1512	6.084[c] 4.309[d]	5.54221×10^{-21}	-1.6517×10^{-19c} -1.0476×10^{-19d}
ZnSe	1868[a]	1790	5.6686[c] 4.01[d]	6.80175×10^{-21}	-1.8819×10^{-19c} -1.1573×10^{-19d}
ZnTe	2533[a]	1568	6.089[c] 4.27[d]	6.19824×10^{-21}	-2.3336×10^{-19c} -1.7046×10^{-19d}

[a] Predicted transition temperature is above the 1 atm melting point.
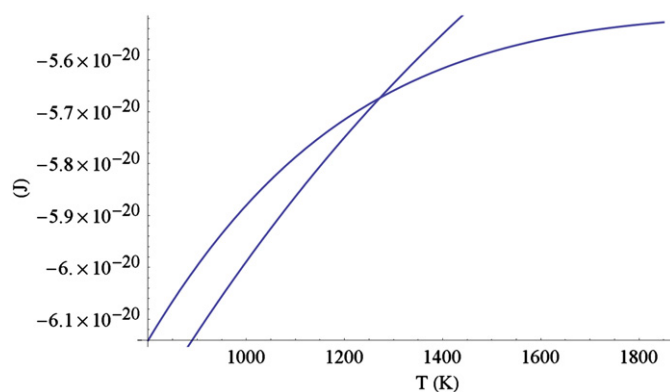[b] Value computed in this work.
[c] Zinc-blende.
[d] Wurtzite.

Fig. 3. Plot of the right and left side of Eq. (3) for the case of ZnS.
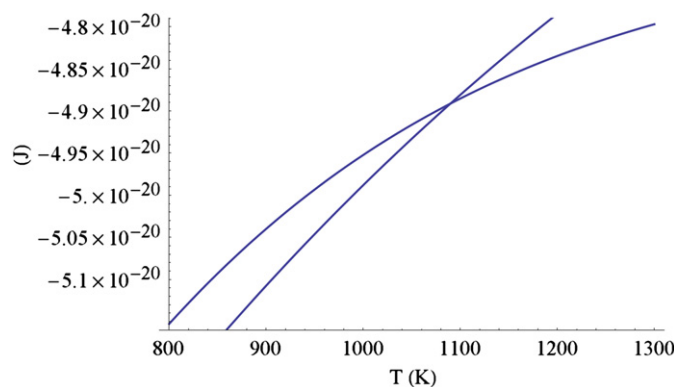

Fig. 4. Plot of the right and left side of Eq. (3) for the case of CdS.

value computed here is within 2% of the high side of the reported transition range.

It is interesting to consider the other II–VI alloys which are reportedly found in the zinc-blende and/or wurtzite state and for which we also have lattice parameter data. These are ZnSe, CdSe and ZnTe. To our knowledge, no transition temperatures have been reported for these alloys. The theoretical method outlined here finds a transition temperature in each case above the 1 atm melting point. These values are listed in Table 1. Considering this, it may well be that these materials do not undergo a complete bulk solid–solid phase transition ever at 1 atm. As mentioned

previously, the wurtzite phase is known to often appear in these alloys interspersed with the zinc-blende structure in the form of layers. If the chemical potentials for the two phases are separated energetically on the order of a thermal fluctuation up until the melting point then a portion of the material might shift into the wurtzite state. To investigate this possibility further $\Delta\mu$, the difference between the wurtzite and the zinc-blende chemical potentials at room temperature is computed for each alloy considered here. This is accomplished by computing $\Delta\mu^\circ$ with Eq. (15) using the estimated transition temperature and then using Eq. (14) with T_o replaced with 300 K. The results are listed in Table 1. It is clear that these energies are on the order of kT so that the two phases are almost isoenergetic for all the binary alloys considered here. It is interesting to note that CdS has the lowest value for $\Delta\mu$ at room temperature. It is no surprise then that a range of 973–1073 K, has been reported for the transition in this alloy. Here the estimated transition temperature is at the high side of that range. This agrees with the reported data in that all of the sample is predicted to be transformed to the wurtzite state above 1073 K.

References

[1] S. Colak, in: Mukesh Jain (Ed.), II–VI Semiconductor Compounds, World Scientific, Singapore, 1993, p. 397.
[2] Y. Marfaing, J. Cryst. Growth 161 (1996) 205.
[3] G. Mandel, Phys. Rev. 134 (4A) (1964) A1073.
[4] D.B. Laks, C.G. Van de Walle, G.F. Neumark, P.E. Blochl, S.T. Pantelides, Phys. Rev. B 45 (19) (1992) 10965.
[5] U.V. Desnica, I.D. Desnica, Vacuum 61 (2001) 361.
[6] N.Kh. Abrikosov, V.F. Bankina, L.V. Poretskaya, L.E. Shelimova, Semiconducting II–VI, IV–VI and V–VI Compounds, Plenum Press, New York, 1969, pp. 2–3.
[7] W.M. Haynes (Ed.), CRC Handbook of Chemistry and Physics, 92nd ed., CRC Press, Boca Raton, (2011–2012).
[8] N.Kh. Abrikosov, V.F. Bankina, L.V. Poretskaya, L.E. Shelimova, Semiconducting II–VI, IV–VI and V–VI Compounds, Plenum Press, New York, 1969, pp. 3–5.
[9] D.L. Fedorov, J. Lumin. 52 (1–4) (1992) 233.
[10] E.A. Guggenheim, Mixtures: The Theory of the Equilibrium Properties of Some Simple Classes of Mixtures Solutions and Alloys, Oxford, Clarendon Press, 1952, pp.38–40.
[11] E.A. Guggenheim, Mixtures: The Theory of the Equilibrium Properties of Some Simple Classes of Mixtures Solutions and Alloys, Oxford, Clarendon Press, 1952, pp.23–24.
[12] R.R. Reddy, M. Ravi Kumar, T.V.R. Rao, J. Phys. Chem. Solids 54 (5) (1993) 603.
[13] J.C. Phillips, J.A. Van Vechten, Phys. Rev. B 6 (2) (1970) 2147.
[14] G.B. Stringfellow, J. Phys. Chem. Solids 34 (1973) 1749.