Influence of concentration on the structural-phase-transition pressure of the II-VI ternary alloy $Zn_x Cd_{1-x} S$

Alain Béliveau and Cosmo Carlone

Département de Physique and Centre de Recherche sur la Physique du Solide, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

Measurements in a diamond-anvil cell of the critical-pressure-inducing structural phase transition have been performed on the ternary compound $Zn_x Cd_{1-x} S$ for the full range $0 \leq x \leq 1$. The results show an above-the-line variation of the critical pressure with concentration lies above the linear curve, typical of such ternary alloys. This behavior is described using simple thermodynamic considerations that also yield predictions for the variation of P_c with concentration for the family of II-VI ternary crystals.

I. INTRODUCTION

The study of the physical properties of solids under pressure is an important part of the understanding of bonding. Among the most spectacular changes induced by pressure lies the solid-solid phase transition. Numerous experimental and theoretical investigations are available on the subject. For semiconductors, it is well established that most IV and III-V crystals will transform from a diamond or zinc-blende phase to a metallic (β-tin) or rocksalt phase, while for the commonly studied II-VI semiconductors, the transition is from the zinc-blende (or wurtzite) phase to an insulating or semiconducting rocksalt structure.

Many recent advances in materials science involve ternary compounds, for they allow the precise selection of specific properties. The stability and the bonding character of such alloys is of great interest. Though intensive theoretical and experimental work[1] has been performed at atmospherical pressure on the physical properties of this family of solids, few studies exist on the effect of pressure on ternary alloys. Most of the properties of these alloys can be interpolated from the properties of the end (binary) compounds. This seems also to be the case for the critical pressure inducing a phase transition; Göni et al.[2] have reported a linear variation of this critical pressure as a function of concentration x for the solid solution $Ga_x In_{1-x} P$, while Liu, Spain, and Skelton[3] clearly observed an above-the-line variation in $Ga_x In_{1-x} Sb$. For the II-VI family, Webb et al.[4] reported a linear variation in $Zn_x Cd_{1-x} Te$ and Strössner et al.[5] observed no systematic variation in the critical pressure of $Cd_x Mn_{1-x} Te$ ($0 \leq x \leq 0.6$) while a clear variation was seen by Qadri et al.[6] for the same compound.

It is risky to bring out some specific trends from such scant data, nevertheless one can state that linear or an above-the-line variation of the critical pressure with concentration is more frequently observed than sublinear variation in semiconducting solid solutions. To add to these data, we have undertaken a study of the behavior of this critical pressure in $Zn_x Cd_{1-x} S$. Our investigation shows that the solid solution $Zn_x Cd_{1-x} S$ displays an above-the-line variation of its critical pressure. From simple thermodynamic consideration of a regular solution it is possible to obtain some information about the rocksalt phase of this alloy. Furthermore, by introducing an ansatz establishing a linear relationship between the enthalpy parameter of the two phases in II-VI ternary compounds, we can make interesting predictions about the behavior of the critical pressure with a concentration for other solid solutions of this family.

II. EXPERIMENTAL PROCEDURE

The solid solutions $Zn_x Cd_{1-x} S$ were grown by the chemical transport method using iodine as the transporter. The monocrystals obtained from the correct stochiometric ratio of CdS (99.9% pure) and ZnS (99.99% pure) powder were about 1×4 mm^3 in size. A more precise determination of the concentration x was obtained from x-ray diffraction using Vegard's rule, which is known to describe the variation of the lattice parameter as a function of concentration for these crystals.[7]

Seven samples have been studied. The crystals were of a wurtzite structure, except for ZnS which grew in the zinc-blende phase. Each crystal was polished mechanically down to 30 μm with the c axis perpendicular to the plane, then cut into small pieces to fit the high-pressure chamber of a Mao-Bell-type diamond-anvil cell. The usual 4:1 methanol-ethanol mixture was used to maintain hydrostatic pressure inside the cell, while the pressure itself was measured from the ruby luminescence technique.

The determination of the critical pressure P_t at which the phase transition appears has been done visually under a microscope. In their normal phase, the samples appear to range in color from clear red to complete transparency, while in the additional phase the II-VI semiconductors are characterized by a small band gap and the crystals become opaque as they transform to this denser state. The pressure P_t was set at the value corresponding with the occurrence of this opaque phase (as the pressure was increased). One has to be careful in measuring this pressure due to the nonhomogeneity of the hydrostaticity in a 4:1 methanol-to-ethanol ratio high-pressure chamber for

pressure above 100 kbar. Indeed, Piermarini, Block, and Barne,[8] have shown that though the pressure is locally hydrostatic, a significant variation of its value can occur throughout the high-pressure chamber. This effect was easily observed as a large crystal sample of ZnS filling most of the high-pressure chamber showed opaque and transparent regions simultaneously for average pressure around its critical value.

We minimized this problem by arranging three small-size crystals (diameter < 60 μm) around one ruby chip. If all the crystals did not show an opaque phase at the same recorded pressure (which was the case only for $P > 100$ kbar), the critical pressure was evaluated as the average of the different critical pressure P_i at which each crystal became opaque. Therefore the precision on the value of P_t will be less for higher values of P_t. Different runs were made on different sets of crystals of identical concentration.

III. RESULTS

Table I gives the critical pressure obtained for the seven $Zn_x Cd_{1-x}S$ crystals studied here. Though several measurements of P_t for the end compounds (CdS and ZnS) exist, this work presents the critical pressure for those mixed crystals. Our findings for CdS and ZnS agree well with other measurements.[9,10] The crystal phases involved in these transitions are known from x-ray measurements; for CdS, the phase transition occurring at 25 kbar takes the crystal from a wurtzite phase to a rock-salt (NaCl) phase,[11] while for ZnS, the 150-kbar critical pressure brings the crystal from its zinc-blende phase to a rocksalt phase.[10] Thought it has not been measured specifically, we speculate that for the solid solution of $Zn_x Cd_{1-x}S$, the transition is from a wurtzite to a rocksalt phase.

Typical of these first-order phase transitions in the presence of a strong hysteresis as one diminishes the pressure from above the transition. We observed a return to the initial phase at a pressure 10 to 30 kbar less than the initial P_t. After returning to the original phase the sample had numerous dark streaks, but by reincreasing the pressure, values of P_t within the experimental uncertainty were obtained.

The variation of the critical pressure with zinc concentration x in $Zn_x Cd_{1-s}S$ is clearly not linear (See Fig. 1)

TABLE I. Experimental results for the critical pressure (P_t) inducing a structural phase transition in the solid solution $Zn_x Cd_{1-x}S$.

	Concentration x	P_t (kbar)
CdS	0.00	25±2
	0.16	44±2
	0.33	71±2
	0.58	107±2
	0.75	122±3
	0.87	131±5
ZnS	1.00	150±5
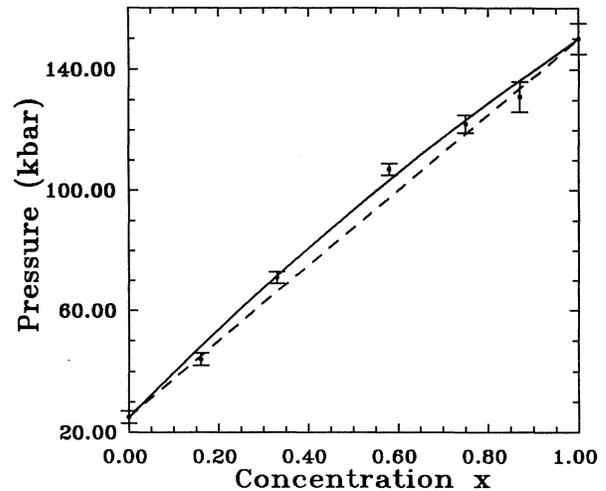
FIG. 1. Variation of the critical pressure inducing a structural phase transformation as a function of the zinc concentration in $Zn_x Cd_{1-x}S$. The solid curve represents a least-squares fit.

and is better described by a quadratic expression. A least-squares fit yields

$$P_t(x) = 24.0 + 152.5x - 27.0x^2 \, ,$$

where P_t given in kbar.

IV. DISCUSSION AND ANALYSIS

Liu, Spain, and Skelton[3] have shown that simple thermodynamic considerations can lead to information on the high pressure of mixed crystals, but we will show that they can also yield interesting predictions on the behavior of the critical pressure for solid solutions of the II-VI family.

Expanding the Gibbs free energy of a solid along an isotherm T_0 and about the atmospheric pressure P_0, one gets

$$G^i(P,T) \approx G^i(P_0, T_0) + V_0^i(P - P_0)$$
$$- \tfrac{1}{2} V_0^i \kappa_0 (P - P_0)^2 + \cdots \, ,$$

where i represents a certain phase of the crystal and the usual thermodynamic definitions are used [volume $V_0 = (\partial G / \partial P)|_{T_0}$ compressibility $\kappa_0 = -(1/V_0)(\partial^2 G / \partial P^2)|_{T_0}$]. In the range of interest, $P_0/P < 10^{-4}$, the difference in the Gibbs energy between two phases (I and II) at the critical pressure P_t is simply

$$\Delta G = G^I - G^{II} \approx \Delta G_0 + \Delta V_0 P_t - \tfrac{1}{2}\Delta(V_0 \kappa_0)P_t^2 + \cdots \, ,$$

where Δ represents the difference between the two phases involved. At the transition, the difference in the Gibbs energies vanishes and neglecting cubic terms we have

$$\Delta G_0 + \Delta V_0 P_t - \tfrac{1}{2}\Delta(V_0 \kappa_0)P_t^2 = 0 \, . \tag{1}$$

TABLE II. List of parameters used in Eq. (5) to evaluate the concentration dependent of the critical pressure P_t. The volumes are those of the unit cell ($V = a^3/4$).

Crystal	V_0^I (Å^3)	V_0^{II} [a] (Å^3)	κ_0^I [b] (10^{-4} kbar^{-1})	κ_0^{II} (10^{-4} kbar^{-1})	P_t kbar	ΔG_0 kbar Å^3	$\dfrac{V_0 - V_t}{V_0}$
CdS	49.8	41.0	16.1	11.8[c]	25[d]	−210	0.20[e]
CdSe	55.4	44.7	18.9	12.5[f]	30[g]	−299	0.22[e]
CdTe	68.3	53.9	23.8	14.5[h]	33[i]	−429	0.25[e]
ZnS	39.5	33.6	13.0	6.1[c]	150[d]	−538	0.21[j]
ZnSe	45.5	34.9	16.1	7.3[f]	135[k]	−996	0.29[j]
ZnTe	56.6	42.7	19.6	8.5[f]	95[l]	−984	0.30[f]

[a] Obtained from the Murnaghan equation.
[b] Obtained from $\kappa_0 = 1/B_0$ where B_0 is given by Cohen (Ref. 15).
[c] Obtained by $1/\kappa_0 = B_0 = B(P) - B_0'P$ with $B_0' \cong 5$, using $B_{CdS}^m(P \sim 50 \text{ kbar}) \simeq 1053$ kbar and $B_{ZnS}^j(P \sim 225 \text{ kbar}) \simeq 2778$ kbar.
[d] Experimental result obtained in this work.
[e] Reference 16.
[f] No experimental result available; this value was interpolated by the authors from the behavior of compounds in the same family.
[g] Reference 17.
[h] Reference 5.
[i] Reference 3.
[j] Reference 18.
[k] Reference 19.
[l] Reference 20.
[m] Reference 21.

This equation can be used along with experimental data to evaluate the difference (at atmospheric pressure and room temperature) in the Gibbs energy (ΔG_0) for binary compounds. The required experimental data (V_0^I, κ_0^I, V_0^{II}, κ_0^{II}, and P_t) have been measured or can be easily deduced for CdS and ZnS (they are given in Table II).

We can adapt Eq. (1) such as to describe a mixed compound of the form $A_x B_{1-x} C$ in the regular solution model. In the semiconducting phase (I), the Gibbs free energy of a solid solution $A_x B_{1-x} C$ can be written[12]

$$G^I = xG_{AC}^I + (1-x)G_{BC}^I + \delta G_M^I \qquad (2)$$

with x the concentration of element A and δG_M^I the change of the Gibbs energy upon mixing. This crystalline nature phase is adequately described by a regular solution model[13] and we have

$$\delta G_M^I = \Omega^I x(1-x) + RT[x \ln x + (1-x)\ln(1-x)] \ . \qquad (3)$$

The first term on the right-hand side gives the variation of enthalpy upon mixing while the second one gives the variation of entropy. The enthalpy parameter Ω^I for a semiconductor is known to be best described by the Stringfellow formula[14]

$$\Omega^I = 4.375 K (\delta a)^2 / (\bar{a})^{4.5} \ , \qquad (4)$$

where $K = 1.15 \times 10^7$ cal/mol $\text{Å}^{2.5}$, $\delta a = a_0^{AC} - a_0^{BC}$ is the difference in the lattice constant of the end compounds AC and BC, and $\bar{a}$ is their average.

Data on the thermodynamic properties of the high-pressure phase of II-VI compounds is scarce. The assumption can be made that this high-pressure phase is also described by equations similar to (2) and (3), so that

Eq. (1) becomes for a solid solution $A_x B_{1-x} C$

$$x\Delta G_0^{AC} + (1-x)\Delta G_0^{BC} + \Delta \Omega_0 x(1-x)$$
$$+ \Delta V_0 P_t - \tfrac{1}{2}\Delta(V_0 \kappa_0)P_t^2 = 0 \ , \qquad (5)$$

where ΔV_0, $\Delta(V_0 \kappa_0)$, and P_t are functions of the concentration x and where $\Delta \Omega_0 = \Omega_0^I - \Omega_0^{II}$. There is no expression of the type (4) giving the enthalpy parameter for the high-pressure rocksalt phase of the II-VI binary compound. This Ω_0^{II} parameter will have to be obtained from the data of $Zn_x Cd_{1-x}S$, but we will show that if a linear relation is assumed between Ω_0^I and Ω_0^{II}, interesting information can be obtained on the behavior of the critical pressure for the II-VI semiconducting solid solution.

To render Eq. (5) useful in predicting the variation of the critical pressure with concentration, every parameter should be expressed in terms of the known binary compounds' physical properties. The volume and the compressibility at normal conditions for each phase (i.e., $V_0^I, \kappa_0^I, V_0^{II}, \kappa_0^{II}$) are fairly well known (or can be extrapolated) for the binary compounds, but have rarely been measured for a solid solution. A linear interpolation will be used. So for an $A_x B_{1-x} C$ mixed crystal we write (for each phase)

$$V_0(x) = xV_0^{AC} + (1-x)V_0^{BC} \ ,$$
$$\kappa_0(x) = x\kappa_0^{AC} + (1-x)\kappa_0^{BC} \ . \qquad (6)$$

The linear interpolation for the volume differs by less than 0.5% from the expected dependence given by Vegard's rule [which would yield $V(x) = a^3(x)/4$ with $a(x) = xa^{AC} + (1-x)a^{BC}$]. The interpolation used here,
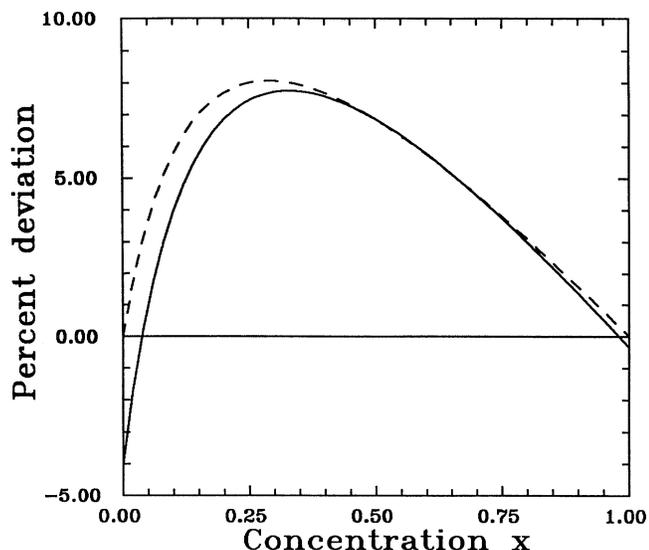
FIG. 2. Comparison between the experimental results (solid curve) and Eq. (5) adjusted to fit the results at $x = 0.5$ (dashed curve). The figure gives the percent deviation from the linear behavior of the transition pressure (% deviation $= 100[P_t(x) - P_t^{\text{linear}}(x)]/P_t^{\text{linear}}(x)$) as a function of zinc concentration in $Zn_xCd_{1-x}S$.

FIG. 3. Prediction of the concentration dependence of the transition pressure in $Zn_xCd_{1-x}Te$ obtained from Eq. (5) and the ansatz of Eq. (7). The experimental results are those of Webb et al. (Ref. 4) and were obtained from electrical resistivity measurements.

for the compressibility, has been shown to hold for some III-V semiconductor alloys.[3]

Table II contains all the parameters necessary for using Eq. (5) for II-VI semiconductors except for Ω_0^{II}. We will now discuss how we obtain this parameter.

The enthalpy parameter for a semiconducting solid solution in its normal tetrahedral phase is given by Eq. (4). For $Zn_xCd_{1-x}S$, this equation yields a value of $\Omega_0^I \approx 4.00$ kcal/mol and for Eq. (5) to yield the interpolated experimental value of $P_t(x = 0.5) \approx 93.5$ kbar, one needs $\Omega_0^{II} \approx 14.08$ kcal/mol. Equation (5) can then be written as

$$P_t(x) = 25 + 149x - 24x^2$$

which compares well with the quadratic expression adjusted to the experimental data (see Fig. 2).

If an empirical expression were known for the evaluation of Ω_0^{II}, one could use Eq. (5) in connection with Eq. (4) to predict the behavior of the critical pressure for the solid solution form of these II-VI compounds. Since for II-VI semiconductors both phases (i.e., normal and high-pressure rocksalt) are cubic face centered, we propose to consider a simple linear relation between the two enthalpy parameters:

$$\Omega_0^I = b\Omega_0^{II} . \tag{7}$$

From our results on the study of $Zn_xCd_{1-x}S$, a value of $b = 3.52$ would seem appropriate. We list in Table III the result yielded by such a form for a few II-VI semiconducting alloys. These alloys are those which have a large difference in the end compounds' critical pressure such that the nonlinear effect can be experimentally observed.

The prediction for $Zn_xCd_{1-x}Te$ can be compared with the result of Webb et al.,[4] who obtained from electrical resistivity measurements the behavior of the critical pres-

TABLE III. Comparison between the prediction of Eq. (5) and the experimental results. The enthalpy parameters were evaluated from Stringellow's formulation formulation for Ω_0^I and by $\Omega_0^{II} = 3.52\Omega_0^I$.

Mixed crystal	Ω_0^I (kcal/mol)	Ω_0^{II} (kcal/mol)	$P_t = a + bx + cx^2$ (kbar)
$Zn_xCd_{1-x}S$	4.00	14.08	$P_t^{\text{theor}} = 25.0 + 149.0x - 24.0x^2$
			$P_t^{\text{expt}} = 24.0 + 152.5x - 27.0x^2$ [a]
$Zn_xCd_{1-x}Se$	2.60	9.15	$P_t^{\text{theor}} = 30.0 + 139.2x - 34.2x^2$
			$P_t^{\text{expt}} = $ (unknown)
$Zn_xCd_{1-x}Te$	1.98	6.97	$P_t^{\text{theor}} = 33.0 + 85.4x - 23.4x^2$
			$P_t^{\text{expt}} = 32.4 + 79.8x - 30.5x^2$ [b]

[a]Results from the present study.
[b]Deduced from the electrical measurements of Webb et al. (Ref. 4). The quadratic expression results from a least-squares fit of their experimental points for $0 \leq x \leq 0.6$.

sure with a concentration for the range $0 \leq x \leq 0.6$. We reproduce in Fig. 3 their results and superpose our prediction based on the empirical relation (7). The agreement is quite satisfactory. For the $Zn_xCd_{1-x}Se$ solid solution, no experimental results have been performed on the concentration dependence of the critical pressure and the expression of Table III consists of a first prediction of this type for this family.

The agreement of our prediction with the experimental results for $Zn_xCd_{1-x}Te$ is encouraging but not sufficient to discriminate between other possible forms for Eq. (7). One should note that though this approach yields interesting results, it is based on equilibrium thermodynamics. We wish to point out that in the case of GaAs (Ref. 22) it is not clear whether or not the experimentally observed transition pressures correspond to equilibrium conditions.

V. CONCLUSION

For the mixed crystals $Zn_xCd_{1-x}S$, we have measured the critical pressure inducing a structural phase transition. While the accepted values for the binary compounds CdS and ZnS are confirmed, the critical pressures for the ternary alloys show an above-the-line variation with concentration for the whole range $0 \leq x \leq 1$. A linear relation has been proposed between the enthalpy parameter for the zinc-blende and the rocksalt phase of the II-VI compounds. This allows us to make predictions on the variation of P_c for the II-VI mixed crystals family.

Though at this stage we have no theoretical justification behind the simple relation between the enthalpy parameters, experimental results on $Zn_xCd_{1-x}Se$ could help to validate this relation and guide theoretical investigations.

[1] For a detailed review, see G. P. Srivastava and D. Weaire, Adv. Phys. 36, 463 (1987).

[2] A. P. Göni, K. Syassen, K. Strössner, and M. Cardona, Phys. Rev. B 39, 3178 (1989).

[3] C. Y. Liu, I. L. Spain, and E. F. Skelton, J. Phys. Chem. Solids 39, 113 (1978).

[4] A. W. Webb, S. B. Qadri, E. R. Carpenter, and E. F. Skelton, J. Appl. Phys. 61, 2492 (1987).

[5] K. Strössner, S. Ves, C. K. Kim, W. Gedhardt, and M. Cardona, Solid State Commun. 58, 563 (1985).

[6] S. B. Qadri, E. F. Skelton, A. W. Webb, E. R. Carpenter, M. W. Schaefer, and J. Furdyna, Phys. Rev. B 35, 6868 (1987).

[7] P. Cherin, E. L. Lind, and E. A. Davis, J. Electrochem. Soc. 117, 233 (1970).

[8] G. J. Piermarini, S. Block, and J. D. Barnett, J. Appl. Phys. 44, 5377 (1973).

[9] B. Batlogg, A. Jayaraman, J. E. Van Cleve, and R. G. Maines, Phys. Rev. B 27, 3920 (1983).

[10] S. C. Yu, I. L. Spain, and E. F. Skelton, Solid State Commun. 25, 49 (1978).

[11] N. B. Owen, P. L. Smith, J. E. Martin, and A. J. Wright, J. Phys. Chem. Solids 24, 1519 (1963).

[12] A. I. Kitaigorodsky, in Mixed Crystals, edited by M. Cardona, P. Fulde, and H. J. Queisser (Springer-Verlag, Berlin, 1984).

[13] E. A. Guggenheim, Roy. Soc. Proc. A148, 304 (1935).

[14] G. B. Stringfellow, J. Phys. Chem. Solids 34, 1749 (1973).

[15] M. L. Cohen, Phys. Rev. B 32, 7988 (1985).

[16] C. F. Cline and D. R. Stephens, J. Appl. Phys. 36, 2869 (1965).

[17] J. A. Majewski and P. Vogl, Phys. Rev. B 35, 9666 (1987).

[18] P. L. Smith and J. E. Martin, Phys. Rev. Lett. 19, 541 (1965).

[19] S. Ves, K. Strössner, N. E. Christensen, C. K. Kim, and M. Cardona, Solid State Commun. 56, 479 (1985).

[20] N. E. Christensen and O. D. Christensen, Phys. Rev. B 33, 4739 (1986).

[21] G. A. Samara and A. A. Giardini, Phys. Rev. A 140, 388 (1965).

[22] J. M. Besson, G. Weill, J. L. Mansot, and J. Gonzalez, High Pressure Research 4, 312 (1990).