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CHEMICAL BONDING IN MELTS OF A(IV)B(VI) COMPOUNDS

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ABSTRACT

A discussion of entropies of fusion and calculated entropies of mixing in the liquid state of the compounds GeS, GeSe, GeTe, SnS, SnSe, SnTe, PbS, PbSe and PbTe leads to the conclusion that the tendency to form a covalent semiconducting melt is decreasing in the series germanium, tin, lead compounds, with sulfur, selenium, tellurium compounds respectively, in favour of a more metallic character of the melt. The melting process can be described by a lattice instability model.

INTRODUCTION

In recent investigations of A(III)B(V) and $A(V)_2B(VI)_3$ compounds[1,2] we have tried to evaluate a relation between enthalpies of fusion (ΔH_m), entropies of fusion (ΔS_m) and entropies of mixing in the liquid state ($\Delta S_{mix}(l)$) of semiconducting compounds and the change of bonding on melting. It was shown that by these thermodynamic properties, one could distinguish two classes of semiconducting compounds: (1) semiconducting covalent solids which melt into metallic liquids, and (2) semiconducting covalent solids which melt into semiconducting liquids with mainly covalent bond character.

The first class is characterized by approximately ideal entropies of mixing in the liquid state and enthalpies of fusion, which increase with broadening energy gap of the solid at 300°K. The energy gap is defined as the minimum energy difference between the valence and conduction bands in the band model of semiconductors. For the second class we have measured decreasing enthalpies of fusion with increasing energy gap and we expect that the entropies of mixing should reflect, by their deviation from ideality, the degree of covalent bonding retained in the liquid. To further elaborate this model we have measured the enthalpies of fusion of A(IV)B(VI) compounds[3], where A = Ge, Sn, Pb, and B = S, Se, Te. The interaction of these elements yields a series of compounds including monochalcogenides of the type AB. Important physical properties of these compounds are summarized in Table I. These compounds, normally deviating from stoichiometric composition (Table I, first column), can be divided by their crystal structure into two sub-groups, one with orthorhombic D_{2h}^{16} structure (α-GeTe, α-SnTe, GeS, GeSe, SnS, SnSe), the other with space-group O_h^5 (β-GeTe, β-SnTe, PbS, PbSe, PbTe); both are approximately six-coordinated. A comparison of the interatomic spacings in these compounds with the

TABLE I

PHYSICAL PROPERTIES OF THE COMPOUNDS OF TYPE AB

Composition, c in atomic per cent of A(IV); interatomic spacings, d; electronegativity difference (Allred-Rochow), ΔE_n; enthalpy of formation, ΔH_f^0 (298 °K); energy gap, ΔE; at 300 °K; calculated effective charges e, electrical conductivity of the solid at T_m, σ_s; conductivity change, $\sigma_{ch} = \sigma_s - \sigma_l/\sigma_s$; and melting temperature, T_m; of A(IV)B(VI) compounds[a, c].

Compound	c	d (Å)[b]	ΔE_n	ΔH_f^0 (kcal mol^{-1})	ΔE (eV)	e (e)	σ_s (ohm^{-1} cm^{-1})	σ_{ch} (%)	T_m (°K)
GeS			0.6 (Ref. 5)	−21.4	1.8	0.57			938
GeSe			0.6 (Ref. 5)	−19.7	1.16	0.57			943
GeTe	50.61	3.01 (3.14) (Ref. 5) [2.59] (Ref. 5)	0.4 (Ref. 5)	− 8.0	0.5–1.0	0.38	2.4	8.8	998
SnS	50.000		0.6 (Ref. 5)	−25.1	1.08	0.63			1154
SnSe	50.000		0.6 (Ref. 5)	−21.5	0.9	0.60			1133
SnTe	50.4	3.15 (3.33) (Ref. 5) [2.77] (Ref. 5)	0.4 (Ref. 5)	−14.2	0.26	0.52	1.44	10.8	1079
PbS	50.000	2.97 (3.04) (Ref. 5) [2.50] (Ref. 5)	0.3 (Ref. 5)	−22.5	0.41 (Ref. 6)	0.63 0.71 (Ref. 6)	0.25	−12.0	1392
PbSe	50.005	3.07 (3.18) (Ref. 5) [2.63] (Ref. 5)	0.3 (Ref. 5)	−18.0	0.27 (Ref. 6)	0.58 0.59 (Ref. 6)	0.30	50	1349
PbTe	50.012	3.23 (3.41) (Ref. 5) [2.83] (Ref. 5)	0.1 (Ref. 5)	−10.6	0.31 (Ref. 6)	0.57 0.54 (Ref. 6)	0.42	257	1190

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[a] If no literature reference is given, data were taken from Abrikhosov[4]. [b] Without parentheses, interatomic spacings; between ( ), sum of ionic radii, oxydation state +2, −2; between [ ], sum of covalent radii. [c] Throughout this paper, 1 cal = 4.184 J.

sum of the ionic respectively covalent radii (Table I, second column) suggests a bond with mixed ionic-covalent character. This type of bonding was first explained by Krebs[8] on the representative sample PbS. Krebs assumed a mesomeric system

$$\text{Pb–S Pb–S Pb–S} \leftrightarrow \text{–Pb S–Pb S–Pb S–}$$

by an overlap of the filled *p*-orbitals of the sulfur atom with the vacant *p*-orbitals of the lead atoms along the lattice directions [100], [010] and [001]. This bonding system should partially neutralize the charge of the metal ions. To prove this conclusion we have calculated the effective charges, ε of the cations in these compounds, using a formula given by Gutbier[9] (Table I, sixth column).

$$N_L\left(\frac{\varepsilon e}{z}\right)^2 d^{-1} = \Delta H_f^0 z^{-1} \qquad \text{(AB compounds)}$$

where, N_L, is Avogadro's number; ε, is the effective charge; e, is the charge of the electron; d, is the interatomic distance; z, is the oxidation state of the cation; and ΔH_f^0, is the enthalpy of formation. The computed values are in good agreement with experimental data given by Dalven[6] for the lead compounds. The effective charge is decreasing in the series A(IV)S > A(IV)Se > A(IV)Te and increasing in the series GeB(VI) < SnB(VI) < PbB(VI). The first phenomenon can be explained by decreasing electronegativity of the chalcogen atom, the second by decreasing polarisation of the anion by the cation. The order of magnitude of the effective charges (+0.4 – + 0.7 instead of +2 on the cation) allows the deduction of a covalent bond character of more than 50%, comparable with a covalent bond share of at least 47% in GeTe and SnTe, reported by Rigamonti[10] from Mössbauer studies on GeTe–SnTe alloys.

As another characteristic feature of a mesomeric resonance system, one should expect metallic character of these compounds due to free mobility of electrons in the bonding directions. The observed semiconducting properties can be ascribed to the fact that the mobility of the electrons is hampered by a certain localisation on the atom with higher electronegativity. The free mobility should thus increase with diminishing electronegativity difference of the compound (Table I, third column). This assumption is confirmed by comparing the electrical conductivity (Table I, seventh column) with the electronegativity in the series PbS, PbSe, PbTe. The increase of metallic properties in this series is also manifested by a weakening of the interatomic forces resulting in decreasing enthalpies of formation (Table I, fourth column). The bonding in these compounds is thus changing from a covalent-ionic character in the compounds with higher electronegativity differences (GeS, SnS, GeSe, SnSe) to a more metallic covalent character in GeTe, SnTe, PbS, PbSe and PbTe, as indicated in Table II. It is interesting to note, that the two different structural classes of A(IV)B(VI) compounds are characterized by different electronegativity differences (O_h^5, $\Delta E_n \approx 0.3$; D_{2h}^{16}, $\Delta E_n \approx 0.6$) while the two compounds with intermediate ΔE_n(0.4) are members of both classes.

TABLE II

BOND CHARACTER IN SOLID A(IV)B(VI) COMPOUNDS

ionic-covalent ←

↑	GeS	SnS	PbS	↓
	GeSe	SnSe	PbSe	
	GeTe	SnTe	PbTe	

→ metallic-covalent

TABLE III

SUMMARY OF ENTHALPIES AND ENTROPIES OF FUSION, AND OF MIXING IN THE LIQUID STATE FOR A(IV)B(VI) COMPOUNDS[a]

Compound	ΔH_m *exp.* (*kcal mol*$^{-1}$)	ΔS_m *exp.*	ΔS_{mix} (l) *calc.* (*cal °K*$^{-1}$ *mol*$^{-1}$)	ΔS_{mix}^{exs} (l) *calc.*
GeS	5.4 (Ref. 4)	5.77	[b]	
GeSe	7.8	8.27	−2.0	−4.7
GeTe	9.6	9.7	−3.3	−6.1
SnS	7.55 (Ref. 4)	6.54	[b]	
SnSe	10.2	9.1	−3.6	−6.4
SnTe	10.8	10.0	−0.8	−3.4
PbS	8.7 (Ref. 4)	6.25	[b]	
PbSe	11.8	9.7	+3.2	0.44
PbTe	13.7	11.5	+2.9	0.1

[a] Data for solid germanium, tin, lead, selenium and tellurium used in the calculations of $\Delta C_p/T$ were taken from Ref. 19. Thermal data of the A(IV)B(VI) compounds are given in Ref. 3. Enthalpies of fusion of constituent elements were corrected to the melting temperature of the compounds.
[b] ΔS_{mix} (l) could not be calculated, because S^0 (298 °K) for these compounds is not measured.

RESULTS

A summary of our experimental results, which were described in detail in an earlier publication[3] is given in Table III. In order to calculate the entropies of mixing for the reaction

$$\mathrm{A(IV)(l)+B(VI)(l)} \rightarrow \mathrm{A(IV)B(VI)(l)}$$

we used the thermodynamic cycle

$$\Delta S_{mix}(\mathrm{l}) = \Delta S_m(\mathrm{IV, VI}) - \left[\Delta S_m(\mathrm{IV})+\Delta S_m(\mathrm{VI})-\Delta S_f^0(298\,°\mathrm{K}) + \int_{298}^{T_m} \frac{\Delta C_p}{T}\,\mathrm{d}T\right]$$

where ΔS_m = entropy of fusion, ΔS_f^0(298 °K) = entropy of formation of the solid compound, and $\int_{298}^{T_m} \frac{\Delta C_p}{T} \mathrm{d}T$ = entropy difference between compound and constituent element from 298 °K to melting temperature.

DISCUSSION

In an earlier publication we have shown[2], that on melting of group V chalcogenide compounds the tendency to retain covalent bond character and a coordination similar to that of the solid state is increasing with increasing bond strength, the latter being directly proportional to the energy gap[11]. The increasing bond strength is thus producing a growing similarity between liquid and solid states. The enthalpy of fusion in these compounds is needed for two processes, one due to the destruction of the crystal by introduction of vacancies, the other due to a change from covalent to metallic bonding, *i.e.* transportation of electrons from the valence band into the conduction band. The enthalpies of fusion are accordingly decreasing with increasing energy gap, because the second process is hampered by strong covalent bonds. In a simplified way one could say that the chalcogenide compounds with a low energy gap are melting into a more metallic liquid with random distribution of atoms; the compounds with a high energy gap into a more covalent liquid with association of unlike atoms. In our opinion the same arguments can be applied to evaluate the nature of A(IV)B(VI) melts.

First experimental evidence for this hypothesis is given by plots of the electrical conductivity in the liquid state *vs.* composition in the Sn–Se (Ref. 12), Pb–Se (Ref. 12), Ge–Te (Ref. 13), Sn–Te (Ref. 14), and Pb–Te (Ref. 13) systems, which exhibit pronounced minima at the composition of the solid A(IV)B(VI) compound. Deviation from this composition gives an increase in the conductivity of the melt. This was explained by Dancy[14] as a semiconductive behaviour of the melt. Such an explanation is based on a model of a solid state semiconductor, and implies that the nearest neighbour arrangement of atoms in the solid and the liquid state cannot be basically

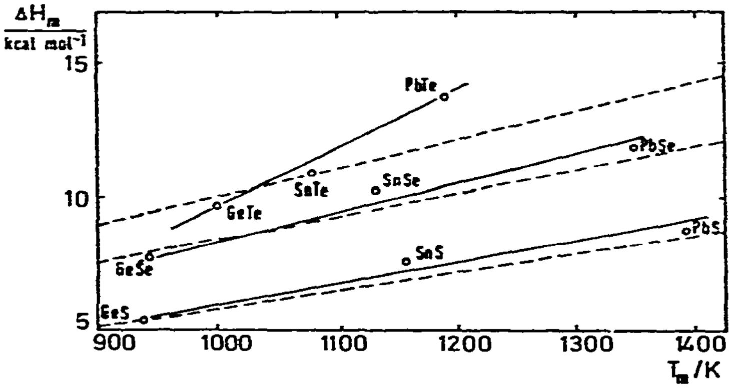


Fig. 1. Enthalpies of fusion of IV/VI compounds *vs.* melting temperature [– – – – – –, constant entropy relation, (6, 7.5 and 10 cal °K⁻¹ mol⁻¹)].

different up to several hundred degrees above the melting temperature. The extent of the difference in bond character of the solid and the liquid state is expressed, in our opinion, by the ratio $\sigma_l - \sigma_s/\sigma_s$ (σ_l = electrical conductivity of the liquid at T_m and σ_s = electrical conductivity of the solid at T_m, see Table I, eighth column). This ratio is increasing in the series S, Se, Te compounds and Ge, Sn, Pb compounds.

In a rather simple view one would expect for crystals of similar structure, which melt into liquids of similar structure, a constant entropy of fusion[15]. A diagram (Fig. 1) demonstrates that ΔH_m is related to T_m. However, a constant entropy as represented by the broken lines is not found, the slight deviations increasing from the sulfides to the tellurides. The conclusions regarding the relationship between bond character in the solids and the melts of A(IV)B(VI) compounds are finally confirmed by considering a plot of enthalpies of fusion *vs.* energy gap for these compounds (Fig. 2). The enthalpies of fusion are decreasing with increasing energy gap as expected from our model. A measure of the degree of ordering in the liquid state is given in Table III by the entropies of mixing $\Delta S_{mix}(l)$. These are increasing in the series Ge, Sn, Pb compounds and for PbSe and PbTe close to the ideal value of 2.76 cal °K^{-1}mol^{-1}:

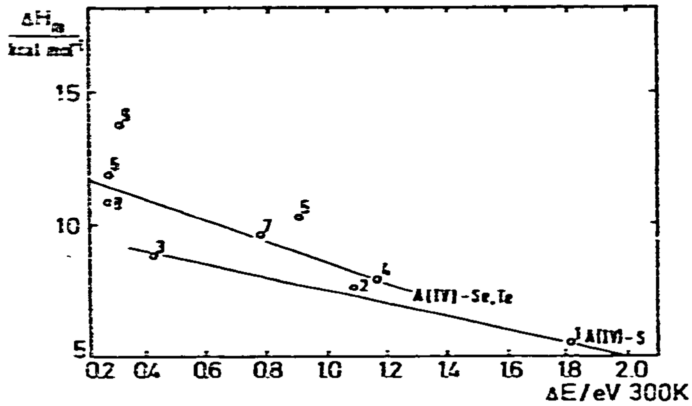


Fig. 2. Enthalpies of fusion of IV/VI compounds *vs.* width of the energy gap at 300°K. (1) GeS, (2) SnS, (3) PbS, (4) GeSe, (5) SnSe, (6) PbSe, (7) GeTe, (8) SnTe, (9) PbTe.

$$\Delta S_{mix}(\text{ideal}) = R\ln 2 \qquad \text{(for AB compounds)}$$

for the entropy of mixing of a binary solution. We can assume that in the case of the lead compounds, which do have a $\Delta S_{mix}(l)$ of approximately 2.7, melting is a drastic change of local order and bonding by a breakdown of covalent bonds and formation of a solution corresponding to the pure molten components, *i.e.* a more metallic solution with nearly random distribution of atoms. This was also observed for A(III)B(V) compounds, of which the change from covalent to metallic bonding was well established by Lichter[16], who found entropies of mixing of the liquid components in the range 2.4–2.7 cal °K^{-1}mol^{-1}, which are, as for PbSe and PbTe, very close to the ideal value. From the experimental data one can deduce that the similarity of bond character in the solid and the liquid state is decreasing in the series Ge, Sn, Pb compounds, with S, Se, Te compounds, respectively, in favour of a more metallic bonding in the liquid state. The conclusion that the similarity of the chemical bonding is decreasing in this order is contradictory to interpretations of composition–electrical conductivity diagrams for liquid mixtures given by Glazov[13], that the tendency for these compounds to "dissociate" on melting is decreasing in the order germanium > tin > lead compounds. We would therefore argue that this statement cannot be made solely from the existence of "singular" points in these conductivity diagrams.

In graphs not given in this paper, the total entropy $S^0(T)$ of solid A(IV)Se and A(IV)Te compounds was plotted against ln W (W = mean gram atomic weight)[17] and a linear relationship was found. This is consistent with melting due to vibrational instability of the crystal lattice. A criterion for the reality of this model is given by the Lindemann constant for a compound, which we have calculated according to the relation

$$C_L^2 = V_m^{2/3}\,\Theta_D^2\,W T_m^{-1}$$

where, C_L = Lindemann constant; V_m = mean gram atomic volume; Θ_D = Debye temperature; and T_m = melting temperature. The values, listed in Table IV, agree to within ±5% in the same structural class. The Lindemann relation between Θ_D and T_m is of the same form as an empirical relation given by Mukherjee[13] between the Debye temperature and the energy, E_v to form a vacancy in close-packed metals in the solid state.

TABLE IV

DATA FOR A(IV)B(VI) COMPOUNDS

Mean gram atomic weight, W; Debye temperature, Θ_D; density, d; and calculated Lindemann constant, C_L.[a]

Compound	*W*	Θ_D *°K*	d *(298°K) (g/cm³)*	C_L	*Structure*
GeS	52.33	292 (Ref. 20)	4.01 (Ref. 7)	162	D_{2h}^{16}
SnS	75.38	270	5.0 (Ref. 7)	171	D_{2h}^{16}
GeSe	75.78	243 (Ref. 20)	5.55 (Ref. 7)	164	D_{2h}^{16}
SnSe	98.8	210	6.20 (Ref. 7)	156	D_{2h}^{16}
PbS	119.62	159 (Ref. 6)	7.5	117	O_h^5
PbSe	143.07	144 (Ref. 6)	8.10	122	O_h^5
SnTe	123.15	140	6.45	126	O_h^5
PbTe	167.40	128 (Ref. 6)	8.16	131	O_h^5

[a] If no literature reference is given, data were taken from Abrikhosov[4].

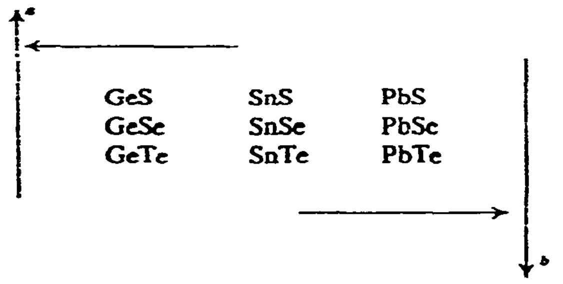
$$\Theta_D = C_M E_v^{1/2}\, V_m^{-1/3}\, W^{-1/2}$$

(C_M = Mukherjee constant). We applied this formula to the compounds investigated and calculated $C_M E_v^{1/2}$. This expression is a constant within the same structural class of these compounds and obviously only dependent on the crystal structure. The deviation from the mean value is ±1.5% for the compounds with a NaCl lattice and ±5% for the compounds with an orthorhombic lattice. The differences in the enthalpies of fusion must accordingly be ascribed to differences in the character of the liquid state.

The connexion between the physical properties of A(IV)B(VI) compounds and the position of the constituent elements in the periodic table is summarized in Table V. The change of bonding on melting is gradually increasing from the GeS corner, which represents the minimum difference between solid and melt, to the PbTe corner, where one finds the maximum increase of metallic bonding on melting.

TABLE V

CHANGE OF PHYSICAL PROPERTIES OF A(IV)B(VI) COMPOUNDS



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[a]Structure of solid compound: D_{2h}^{16}. Similar bond character in solid and liquid state. ΔS_{mix} (l) strongly deviating from ideal. High: Lindemann constant, electronegativity difference, energy gap, density change on melting. Low: Enthalpy and entropy of fusion, change of electrical conductivity on melting. [b]Structure of solid compound: O_h^5. Change to more metallic liquids on melting. ΔS_{mix} (l) nearly ideal. Low: Lindemann constant, electronegativity difference, energy gap, density change on melting. High: Enthalpy and entropy of fusion, change of electrical conductivity on melting.

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