

# Search for regularities in the melting points of AB compounds

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## Abstract

The melting behaviour of metallic alloys and compounds differs drastically from that of molecular as well as polyanionic and polycationic valence compounds. In correlating melting temperatures with atomic properties, one has to discuss these groups separately. Additional d-electron bonding characteristically changes the trend in the dependence of the melting temperature on the main quantum number of the participating valence electrons. The appropriate atomic parameters which permit an optimal uniform description of the melting temperatures of all AB phases are yet to be found.

## 1. Introduction

Although it is not possible at present to predict the phase diagrams from a knowledge of the elemental constituents, considerable progress toward this goal has been made in the past few years. Miedema's model [1] enables us to predict compound formation (or its absence) with a very satisfactory accuracy. The crystal structure can be predicted with an accuracy of better than 90% having the knowledge of the existence of a specific compound and assuming an already known structure type [2–4]. Recently, Chelikowsky and Anderson [5, 6] examined the melting points of approximately 500 intermetallic AB alloys. They found that the linear average of the constituent melting points is a fairly good approximation for the compound melting point in the case of transition elements, but less so in the case of simple metals. Walzer [7] published a melting point *vs.* radii diagram with a fair separation tendency between compounds and alloys with two transition elements (TT), two simple metals (SS) and a simple metal and a transition metal (ST). The TT group shows the highest, ST intermediate and SS the lowest melting points. Anton *et al.* [8] discussed 300 high  $-T_m$  intermetallic compounds (AB, AB<sub>2</sub>, AB<sub>3</sub>, A<sub>5</sub>B<sub>3</sub> and A<sub>7</sub>B<sub>6</sub>) and classified them according to their crystal structures. Moreover, they discussed a schematic pseudoquaternary crystal structure map.

The aim of this work was to give a complete set of melting points of AB compounds and alloys and to derive from these data the responsible factors governing the melting so that one should be able to predict the

many yet unknown melting temperatures. From a recent work [9] we know that in a first approximation the various element properties can be grouped into six groups of basic properties, here called factors: atomic number, size (pseudopotential radius after Zunger [10]), cohesive energy, electronegativity, valence electron (group number) and angular orbital factors. It turned out to be impossible to fit all AB binaries into the same scheme. The problems may become evident from the following discussion of the AB phases.

## 2. The melting behaviour of AB compounds

It is well known that not even such simple aggregates as the solid elements show a uniform melting behaviour. Arsenic and black phosphorus, for example, undergo sublimation and the liquid state can be forced only by application of high pressure. Non-metallic elements with three-dimensional structures, *e.g.* germanium, suffer a transition to the metallic state on melting. Ordered arrangements of different elements possess a further option: they may become unstable before melting. Furthermore, they may also decompose at lower temperatures. All these possibilities are indicated in Table 1 by different symbols. The predominance of the symbols for congruent melting\* is not so overwhelming as we wished for our deductions on melting temperatures, so

\*The term *congruent melting* indicates melting without decomposition; the term *incongruent melting* is used for both peritectic and peritectoidal decomposition ("n" in our melting point table).





about 1500 K. Thus in the high-temperature modification the rigid Ln–C bonds are broken and the polyanion C<sub>2</sub> can rotate as in a liquid. This behaviour is not general in polycompounds, however.

Most polychalcogenides do not melt congruently. The polyanion (X<sub>n</sub>)<sup>2-</sup> becomes unstable long before the M–X bonds yield. Thus NaSe<sub>3</sub> ≡ Na<sub>2</sub>(Se<sub>6</sub>)<sup>2-</sup> transforms on heating successively to Na<sub>2</sub>Se<sub>4</sub>, Na<sub>2</sub>Se<sub>3</sub>, Na<sub>2</sub>Se<sub>2</sub> and finally to the normal valence compound Na<sub>2</sub>Se which melts congruently at the highest transition temperature occurring in the Na–Se system. As a rule the peritectic temperature is lower the more atoms the anion cluster contains. The polyanionic compounds, as seen above, are not a group with identical melting behaviour. Thus the (non-metallic) alkali polypnictides with helical anion chains all melt congruently whereas the isoelectronic (but metallic) alkaline-earth tetrelides\* with planar zigzag anion chains show both types of melting. The (non-metallic) alkali polytetrelides with tetrahedral cluster anions (e.g. K<sub>4</sub>(Ge<sub>4</sub>)) mainly prefer congruent melting and thus may become liquid semiconductors.

Since there may be a qualitative difference between the melting of metals as compared with non-metals, we present in Table 2 a separation between metallic and non-metallic compounds. We must, however, keep in mind that our characterization refers to the structure given in Table 3. For many compounds only the room-

temperature modification is known, though in certain cases a high temperature transition has been detected but not determined, e.g. for NaSn, ... , CsSn. Above all, for low energy semiconductors the existence of a metallic high temperature modification has to be taken into consideration. We have omitted the whole left part of Table 2 which contains metallic alloys only (in a crude approximation the melting point of an alloy, in contrast to an intermetallic compound, is close to the average of the melting points of the constituents). On the basis of what we learned above, we expect normal melting for the (three-dimensional) normal valence compounds but lower melting points for the polycompounds.

Among the metallic AB compounds there are nearly as many peritectic compounds as congruently melting compounds (not alloys), as can be seen in Table 1. Quite a number of compounds exist at high temperatures only. In most cases they form peritectically and may be obtained at room temperature by quenching after annealing within the existence temperature range. Many of the dissociating compounds may be metastable at room temperature. Prepared at low temperatures and high hydrogen pressure, the transition element monohydrides, for example, lose H on heating to or above room temperature.

In Table 1 the sequence in a row (within the same group) is in some cases c–p (congruent–incongruent), but the reverse is not uncommon either. If we look more closely at such examples, we make the observation that the sequence c–p–(ev.) × (=non-existence) is usually in the direction of decreasing melting point and stability. Examples are

\*We call *tetrelides* compounds with “anions” from column IVb (C, Si, Ge, Sn, Pb), *pnictides* contain anions from column Vb (N, P, As, Sb, Bi), *chalcogenides* contain chalcogen elements (group VIb: O, S, Se, Te) and *halides* contain halogen elements (group VIIb: F, Cl, Br, I).

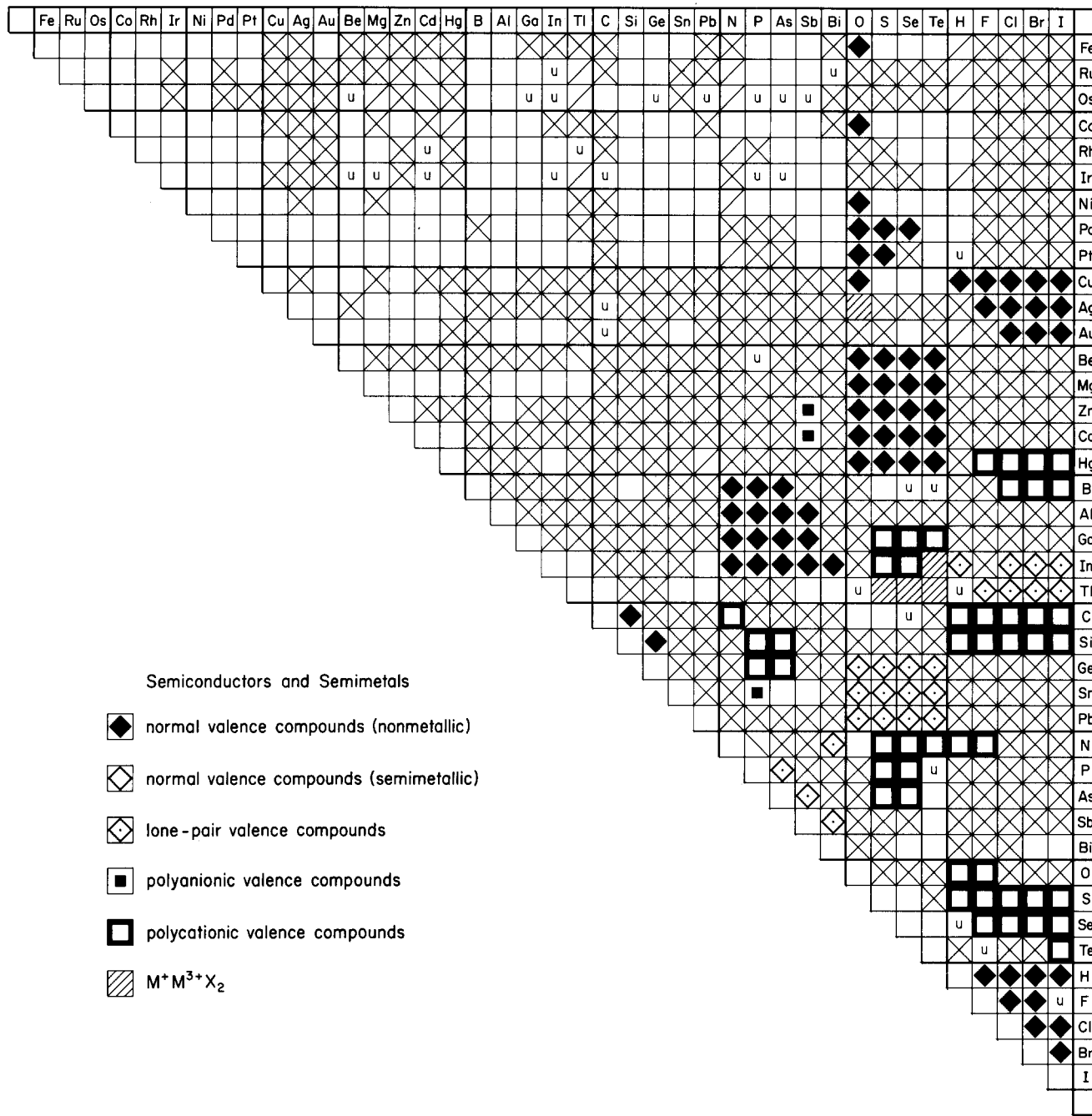
LaTl 1493 K, c	—	LaIn 1398 K, c	—	LaGa 1283 K, c	—	LaAl 1146 K, c	—	LaB ×
LaHg 1333 K, c	—	LaCd 1219 K, c	—	LaZn 1088 K, c	—	LaMg 1018 K, p	—	LaBe ×
LaAu 1598 K, c	—	LaAg 1153 K, c	—	LaCu 798 K, p				
CaHg 1234 K, c CsCl type	—	CaCd 958 K, c CsCl type	—	CaZn 712 K, p CrB type				
PtSi 1502 K, c MnP type	—	PtGe 1343 K, c MnP type	—	PtSn 1578 K, c NiAs type	—	PtPb 1068 K, p NiAs type		

Exceptions are accounted for by changes in the crystal structure.

Although we included the incongruent transition temperatures in our considerations on melting points, we must emphasize that a peritectic decomposition is a phase transition like a structural transition. It is a more drastic change than melting and occurs before the lattice vibrations have reached the critical value. In comparisons we have to keep in mind that the peritectic temperatures are always lower than the corresponding (hypothetical) melting temperatures. This is evident, for example, in the group comprising YbN, YbP, YbAs and YbSb.



TABLE 2. (continued)



LiI    CaTe    ScBi    HfC    TaB    "WBe"    MnAu    FePt    CoIr  
 1+7    2+6    3+5    4+4    5+3    6+2    7+1 (+10)    8+0 (+10)    9+9

or on a parallel line starting 10 groups lower:

CuI            BeTe    AlSb    SiC  
 (10+) 1+7    2+6    3+5    4+4

or parallel, starting one group to the left:

NaSe    SrP    PrGe    HfB    NbCd    "CrAu"    MnPt    FeIr  
 1+6    2+5    3+4    4+3    5+2    6+1(+10)    7+0(+10)    8+9









all we know is the (room temperature) crystal structure of the compound or merely its existence. In these cases we give a lower limit based on estimates mainly derived from annealing temperatures\*.

In Table 3 the lowest melting points are found at the left upper corner, the right lower corner, around alkali-(Hg, Tl) and at HgIn. Whereas the true (alkali) metals and alloys crystallize in the *cI2* W structure, the other low  $T_m$  representatives all adopt rather particular structures.

The highest  $T_m$  values occur along the diagonal

CaO	—	ScN	—	HfC	—	TaB	—	{MnAu	—	RuPt	—	RhIr}
2886 K		2923 K		4223 K		3363 K		1533 K		~2310 K		2543 K
NaCl type		NaCl type		NaCl type		CrB type		CsCl type		Cu type		Cu type

and along the parallel line (with an additional valence electron)

CeS	—	HfN	—	TaC	—	WB	—	{MnHg	—	IrPt}
2723 K		3660 K		4258 K		2938 K				2293 K

A second, short line comprises the more covalent compounds:

MgO	—	BN (AlN)	—	SiC
3125 K, c		~3273 K, c (3073 K, c)		2818 K, p

(c = congruent, p = peritectic) with NaCl, BN (ZnO) and ZnS structure.

Among the metallic elements and their alloys the highest melting temperatures are located within the 5d elements around tungsten:

Hf	—	Ta	—	W	—	Re	—	Os	—	Ir
2504 K		3293 K		3695 K		3459 K		3306 K		2720 K

Within this sequence the crystal structure changes from *cI2* W type (Hf, Ta, W) to *hP2* Mg type (Re, Os) and *cF4* Cu type (Ir, Pt).

The highest element  $T_m$  (W, 3695 K) is surpassed by four carbides, *i.e.* TaC (4258 K), HfC (4223 K), NbC (3873 K) and ZrC (3815 K), whereas the nitride with the highest melting point, HfN (3660 K), does not quite reach the tungsten  $T_m$  value. The shift of the maximum  $T_m$  from group VI for the metals to group V for the carbides and group IV for the nitrides is explained by the Engel-Brewer valence bond theory [14]. The  $T_m$  maxima are associated with the formation of a half-filled d-shell in these rock-salt-type compounds, achieved by donation of one and two electrons from carbon and nitrogen respectively [15]. Unfortunately, the melting points of the rare-earth nitrides, LnN, are poorly known, but those of the actinides (from Th to Pu) as well as those of the Ti group all lie above 3000 K. The same holds for the monocarbides of the Ti group and the group V transition elements. The boride with the highest  $T_m$ , TaB (3363 K), is comparable with ReOs (about 3383 K). It is the only monoboride which melts above 3000 K.

With the exception of boron nitride, BN (coordination number CN=3), all high- $T_m$  compounds crystallize in the most common structure types (Table 4). In these

structures the coordination number CN=4 (ZnO and ZnS type), 6 (6 M-X and ev. 12 M-M; NaCl type) and 8 (8 M-X and ev. 6 M-M; CsCl type), while in the high- $T_m$  elements CN=8 (+6) (W type) and 12 (Mg and Cu types), here of course only with M-M contacts. In Table 4 we listed the high-temperature modifications where known and the room-temperature modification in other cases. Structures which evolve from high-symmetry structures by ordering or distortions (AuCu, MnP, ...) may transform back to the primitive form at high temperature. Thus in the metallic CsCl-type compounds a (yet undetected) partial or complete disordering to the W-type at high temperatures is quite possible.

Since it is easier to get some understanding of the low melting points, we discuss these compounds first. The elements and alloys at the left corner and the elements and compounds at the right corner of Table 3 have one common property: they possess one bonding electron per atom. However, in the alkali alloys this means one electron bonding in 8 (+6) directions, whereas in the halides it means one electron for one single bond, which makes a great difference. The weak fractional bonds in the alkalis are loosened on melting, whereas in the halides melting is determined by the even weaker intermolecular bonds. Since with a few exceptions in the heavy rare earths all elements from Li to Mn and their alloys crystallize below the melting point in the same W-type structure, one can follow

\*In a couple of cases, however, we were shocked by annealing temperatures reported by some authors that were up to 200 K higher than the peritectic temperatures found by other authors.



TABLE 4. (continued)

	Fe	Ru	Os	Co	Rh	Ir	Ni	Pd	Pt	Cu	Ag	Au	Be	Mg	Zn	Cd	Hg	B	Al	Ga	In	Tl	C	Si	Ge	Sn	Pb	N	P	As	Sb	Bi	O	S	Se	Te	H	F	Cl	Br	I	
Li				u						L	L		L	N	N	L		N	N	N	L				L						Q	T				R	R	R	R	R	R	Li
Na																					N	N				P	P		Y	Y	Q	J	T	T		R	R	R	R	R	Na	
K							u														u			K	K	P	P		Y	Y	u		J	J		R	R	R	R	R	K	
Rb												L											u	K	K	P	P		Y	Y			J	J		R	R	R	R	R	Rb	
Cs											L												u	K	K	P	P		u	Y					R	R	L	L	L	Cs		
Ca		u					L			D	D		D	L	L			D	L	L			D	L	L		D	D	D	Q	J	J		R	R	R	R				Ca	
Yb <sup>2+</sup>				u						E	L	L		L	L	L					Q	L	L		D	L	L		Q	Q			R	R	R	R				Yb <sup>2+</sup>		
Eu <sup>2+</sup>		u		u			u	D	u	L	E	E		L	L	L	L				Q	L		D	D	D	Q		J	J		R	R	R	R				Eu <sup>2+</sup>			
Sr				u	u		D	u					L	L	L	L					L		D	D	D	D		J	J		R	R	R	R				Sr				
Ba				u	u		D	u		E	E		L	L	L	L							D	D	D	D		J	J		R	R	R	R				Ba				
Sc		L	u	L	L	L	L	L	L	L	L	L		W	L	L	L		L	D		u	D	D		u	R	R	R	R	R		R	R	A				Sc			
Lu		L	u		L	L	L	L	L	L	L	L			L	L	L	L		D	L		D				R	R	R	R	R		R	R	R				Lu			
Yb <sup>3+</sup>		L			L	L	L	L	L														D				R	R	R	R									Yb <sup>3+</sup>			
Tm		u	u	L	L	L	L	L	L	L	L	L			L	L	L	L		D	L	L	D	D	u	u	R	R	R	R	R		R	R	R				Tm			
Er		u		L	L	L	L	L	L	L	L	L			L	L	L	L		D	L	L	E	D		u	R	R	R	R	R		R	R	R				Er			
Ho		u		L	L	L	L	L	L	L	L	L			L	L	L	L		L	D	L	L	E	D	u	u	R	R	R	R	R		R	R	R				Ho		
Y				L	L	L	L	L	L	L	L	L			L	L	L	L		D	L	L	D	D			R	R	R	R	R		R	R	R				Y			
Dy				L	L	L	L	L	L	L	L	L			L	L	L	L		D	L	L	E	D			R	R	R	R	R		R	R	R				Dy			
Tb		u		L	u	D	E	E	L	L	L	L			L	L	L	L		D	L	L	E	D		u	R	R	R	R	R		R	R	R				Tb			
Gd		u	E	L	u	D	D	E	L	L	L	L			L	L	L	L		L	D	L	L	E	D			R	R	R	R	R		R	R	R				Gd		
Eu <sup>3+</sup>																												R	R											Eu <sup>3+</sup>		
Sm				L	u	D	D	E	L	L	L	L			L	L	L	L		L	D	L	L	E	D		u	R	R	R	R	R		R	R	R				Sm		
Nd		u	u	D	u	D	D	D	E	L	L	L			L	L	L	L		D	L	L	E	D		u	R	R	R	R	R		R	R	R				Nd			
Pr		u		D	u	D	D	D	E	L	L	L			L	L	L	L		D	L	L	E	D			R	R	R	R	R		R	R	R				Pr			
Ce		u	u	D	u	D	D	D	E	L	D				L	L	L	L		D	L	L	E	E	u	u	R	R	R	R	R		R	R	R				Ce			
La		u		D		D	D	D	E	L	D				L	L	L	L		D	L	L	E	E	D			R	R	R	R	R		R	R	R				La		
Am		u	u	u	u	u	u	u	u	u	u	u			u	u	u	u	u	u	u	u	u	E	u	u	u	R	R	R	R	R	R	R	R	R	R				Am	
Pu		L			u	D	E	D	u	u					u	u	u	u	u	u	u	u	u	u	u	u	u	R	R	R	R	R	R	R	R	R	R				Pu	
Np		u	u	u	u	u	u	u	D						u	u	u	u	u	u	u	u	u	u	u	u	u	R	R	R	R	R	R	R	R	R	R				Np	
U				u	D	u	D								u								u	u	u	u	u	R	E	Q	R	R	R	R	R	R	R				U	
Th				D	D	D	E	D	u	D					u	D						u	D				R	E	R	Q	R	R	R	R	L	R	R	L				Th
Ti	L	L	L	L	L	L	L	L	L		L	L			L	Q	Q	Q	u	R	E	E	u	R	T	A	A		R	A	A	A									Ti	
Zr	L	L	L	L	L	D	C	L	L		L	Q	R	D		C	u	R	D	E	u	R	R	T																	Zr	
Hf	L	L	L	L	L	D									u	u	u	u	u	u	u	u	R	E	E	F	u	R	T	T	F										Hf	
V	W	W					C	C			C								D	W						R				u	R	A	G		R	A	A	A				V
Nb		L			Q		C									L			D						R				R							G	u	u			Nb	
Ta		L	u				C								u	u			D						R	u	u	R					R	u	u	u			u	Ta		
Cr	W	M	M	W	M	M	C	C	C					u	u			D				u	F	F			R	G	A	A			A	A	A	A				Cr		
Mo		M	M		M	M	M	M										D					u	H					H	G				A	A	A	A			Mo		
W		M		M	M		C											D					u	H					G	u										W		
Mn	C	M	u	C	L	L	C	L		C	L				W	L	E	Q						F					G	A	A	A	R	R	R	R	A				Mn	
Tc		M		M	M	M	M								u								u	u	u	u	F	u		R	u	u	u		u	u	u		u	Tc		
Re		M	M	M											u				L					u	F		u		u												Re	

(continued)

nically the strengthening influence of an increasing number of bonding valence electrons in these elements and alloys. In the non-transition-element compounds  $T_m$  decreases with increasing size (main quantum number  $n$ ) of the atoms. In the interhalides (Hal)(Hal)', which crystallize in pairs, the dependence of  $T_m$  on size or main quantum number  $n$  is just the reverse.

The melting points rise with larger  $n$ , since the intermolecular bonding increases through the larger extension of the higher  $n$  valence electron wavefunctions.

## 2.2. Polycationic compounds

If we move in Table 3 one square upwards to the chalcogen halides (two and one bonding orbitals), we



molecules. Other representatives form cluster molecules  $N_4S_4$ ,  $N_4Se_4$ ,  $As_4S_4$  and  $As_4Se_4$ , obviously with increasing intercluster bonding: the melting or peritectic temperatures approach 600 K. SbTe, BiSe and BiTe crystallize in layer structures, which accounts for the increased peritectic temperatures.

In the group comprising CH and CHal we find molecules with triple C bonds, *e.g.* the linear molecule acetylene ( $H-C\equiv C-H$ ,  $T_m = 192$  K), and benzene rings with  $1\frac{1}{2}$  bonds ( $C_6H_6$ ,  $T_m = 279$  K). In the corresponding iodides the stability is distinctly higher:  $C_2I_2$  melts congruently at  $T_m = 354$  K whereas  $C_6I_6$  decomposes near 623 K.

The silicon monohalides, SiHal, synthesized from  $CaSi_2$ , still contain the original As-like puckered Si layers, now with halogen ions at the fourth vertex. We expect them to decompose at fairly low temperatures. Analogous Ge compounds are as yet unknown. Hypothetical  $(Ge_4)Hal_4$  may be derived from KGe and form a molecular structure with low melting point.

Among the  $s^2p^3$  elements the second-row element nitrogen is again unique: it forms pair molecules with triple bonds,  $N\equiv N$ . Its melting temperature is as low as 63 K. Phosphorus exists in the molecular form  $P_4$  (tetrahedra) in white P,  $T_m = 317$  K, as well as in a layer-type modification as black P with a higher stability temperature. Arsenic is known in a yellow form,  $As_4$ , which decomposes below room temperature. The normal (semimetallic) modification is the A7-type NaCl-derived layer structure with strong interlayer overlap. It melts only under high As pressure at 1090 K. The interlayer overlap and the melting temperature unexpectedly decrease towards Sb and Bi ( $Sb_{0.9}Bi_{0.1}$  is indeed a semiconductor). The isoelectronic Ge, Sn and Pb chalcogenides show a gradual transition from layered (distorted NaCl) to NaCl structure. In the corresponding In and Tl monohalides with (2)+1:1 valence electrons we observe a similar structural transition from layered to three-dimensional rock salt structure. These compounds are valence compounds in which the layering is a consequence of the  $s^2$  lone pair electrons (note the influence of doubling the number of bonding electrons on going from InBr,  $T_m = 558$  K, to SnSe,  $T_m = 1135$  K). The melting temperatures of the layered representatives are higher than expected, which may be due to a partial bonding by the lone-pair electrons which connects the different layers in some way.

Removal of one cation valence electron leads to two other interesting groups: the "mercurous" halides and the layered Ga and In chalcogenides. The former group consists of linear molecules Hal-Hg-Hg-Hal. In  $Hg_2F_2$  the neighbour distances are  $Hg-F = 2.14$  Å within the molecule and  $Hg-4F = 2.72$  Å to the neighbouring molecules. This relatively short intermolecular distance may account for the fairly high melting point ( $T_m = 843$  K)

of  $Hg_2F_2$ . In this halide series the strengthening effect of the larger anions does not work:  $Hg_2Cl_2$  decomposes peritectically while  $Hg_2Br_2$  and  $Hg_2I_2$  sublime at rather low temperatures. GaS, GaSe, GaTe, InS and InSe all contain cation pairs  $(M-M)X_2$ , but only GaS, GaSe and InSe crystallize in layer structures. The trend in the melting temperatures is plausible in the In series but not in the Ga series. InS and InSe both decompose peritectically whereas InTe melts congruently. The peritectic temperature is lower in the selenide, as we expect on the basis of both the anion effect and the lower dimensionality, while the congruent melting temperature of InTe is highest in the series (as a result of two counteracting effects: lowering due to the heavier anion and rising due to the increased dimensionality). In the gallium monochalcogenide series either layer-type GaSe has a much too high  $T_m$  or three-dimensional GaTe has a too low  $T_m$ . For the different polytypes of GaS and GaSe we should expect a small difference in  $T_m$  as a consequence of the different interlayer M-X and X-X interactions.

The isoelectronic semiconductors SiP, SiAs, GeP and GeAs, all crystallizing in the three-dimensional GaTe structure, show lower peritectic or melting temperatures as a result of the decreased ionicity if we compare GaTe with the corresponding hypothetical "GeSb". Isoelectronic SnP has a completely different character: it is a lone-pair polyphosphide,  $Sn_2^{2+}(P_2)^{4-}$ .

### 2.3. Polyanionic compounds

The polyanionic valence compounds differ from the polycationic compounds discussed above in that they contain cations with empty orbitals. The connection of the anion clusters by the alkali or alkaline-earth ions is therefore non-directional. As a consequence the melting points of  $(Alk)_2^+X_2$  chalcogenides, for example, are roughly twice as high as those of corresponding molecular  $X_2Hal_2$  halides.

We find an ordinary  $T_m$  decrease in the sequence O, S, Se, Te. In the analogous alkaline-earth pnictides CaP, CaAs, EuAs, SrP and SrAs the melting points appear to be unknown, but we expect higher  $T_m$  values owing to the higher cation charges. No analogous tellurides are known. ScSi, for example, is metallic and of the CrB type.

The pseudochalcogens  $Li^+P_2^-$ , ..., CsSb, indeed contain helical chains analogous to the chalcogen elements Se and Te. The additional ionic bonding increases  $T_m$  relative to the "empty" element structures  $\square Se$  and  $\square Te$ . Since in these chain compounds strong covalent bonds act in one direction, the melting temperatures are slightly higher than in the anion pair compounds.

The isoelectronic alkaline earth monosilicides and monogermanides  $M^{2+}Si$  and  $M^{2+}Ge$  crystallize in the CrB type which also contains zigzag anion chains, but

which are planar, not helical. These tetrelides are all metallic, so that the distinct increase in  $T_m$  relative to the alkali pnictide group may in part be due to the conduction electrons, in addition to the stronger  $M^{2+}-X$  bonds.

#### 2.4. Normal valence compounds

There are two isovalent groups: the ionic group based on the large electropositive cations (alkali, alkaline earth, etc.) and the covalent group based on the "cations" with filled  $d^{10}$  subshell. These two groups are hard to compare, since analogous compounds differ in coordination number and size at equal main quantum number  $n$ . The representatives of the former group mainly crystallize in the rock salt structure (CN=6) whereas those of the latter group are found either in the hexagonal ZnO (wurtzite) structure or in the cubic ZnS (sphalerite) structure, both with CN=4 and one valence electron per neighbour. Exceptions are MgO, MgS, MgSe and CdO, which adopt the NaCl structure (Be and Mg are difficult to locate in our tables anyway). Although the number of electrons available for bonding is identical in both groups, the different CN makes a difference in electrostatic energy as a consequence of different distances and effective charges. The difference most preventing a direct comparison of analogous compounds is that in cation size at equal  $n$  as well as that in mass. A further handicap is the influence of the  $d$ -shell in Cu, Ag and Au. The copper monohalides as well as AgI display CN=4 whereas AgF, AgCl and AgBr adopt the NaCl structure with CN=6. AuI, on the other hand, consists of linear  $-I-Au-I-Au-$  zigzag chains. In contrast, the alkali analogues of AuBr and AuI, *i.e.* CsBr and CsI, retain the CsCl structure with CN=8 up to the melting temperature.

In the NaCl-type series RbF ( $T_m=1068$  K), RbCl (1020 K), RbBr (966 K) the melting temperature decreases as expected in ionic compounds. In the corresponding silver compounds AgF (708 K), AgCl (730 K) and AgBr (692 K) the melting point drops less regularly, but the replacement of Rb ( $r^+=1.48$  Å,  $M=85.5$  g mol<sup>-1</sup>) by Ag ( $r^+=1.26$  Å,  $M=107.9$  g mol<sup>-1</sup>) unexpectedly reduces  $T_m$ . Obviously, CN=4 is favoured here, since  $T_m$  rises from AgBr (NaCl, 692 K) to AgI (ZnS, 829 K). A comparison of two CsCl-type compounds, CsBr ( $T_m=909$  K, Cs-Br=3.72 Å) and TlBr ( $T_m=728$  K, Tl-Br=3.44 Å), reveals the influence of the additional  $s^2$  lone electron pair. In the more covalent series BeO (ZnO,  $T_m=2823$  K) – MgO (NaCl, 3125 K) – ZnO (ZnO, 2248 K) – CdO (NaCl, above 1773 K, sublimation temperature 1830 K) CN=6 is favoured.

In the chalcogenide series ZnO, ZnS, ZnSe, ZnTe  $T_m$  decreases in the normal way. In the pnictides {BAS (1343 K, p)} – AlAs (2033 K) – GaAs (1511 K) –

InAs (1215 K) – TlAs (×) as well as in AlN (3073 K) – AlP (2773 K) – AlAs (2033 K) – AlSb (1331 K) – AlBi (×)  $T_m$  decreases with decreasing  $\Delta x$  and increasing M–X distance. Increasing polarity of the bonds raises  $T_m$  in the covalent  $sp^3$  semiconductors Si (1687 K) – AlP (2773 K), SiC (2818 K, p) – AlN (3073 K) and Ge (1212 K,  $a=5.658$  Å) – GaAs (1511 K,  $a=5.654$  Å) – ZnSe (1799 K,  $a=5.669$  Å) – {CuBr (761 K,  $a=5.691$  Å)}. In the last sequence the copper compound deviates strongly (higher stability of CuBr<sub>2</sub>?, but CuI<sub>2</sub> does not exist at all!).

#### 2.5. Metallic alloys and compounds

Metallic elements and compounds crystallize in structures with high CN, so that the number of bonding valence electrons per atom is always smaller. Table 3 clearly shows the rise in  $T_m$  with increasing number of valence electrons when starting from the left corner and following the elements. The maximum number of bonding  $d$ -orbitals is reached at Mo, W and Tc, Re (where the Mg structure becomes stable). Transition element alloys TT' more or less adopt the same structure as the isoelectronic elements and their melting temperatures are fairly high. With increasing difference in the number of  $d$ -electrons of T and T' ordering occurs in the W-type alloys. The CsCl type (possibly disordering to the W type at high temperatures) is found also in rare-earth compounds, together with the orthorhombic CrB and FeB types. In some of the latter cases the CsCl type was identified as the highest temperature modification, but in most cases possible high-temperature modifications are unknown. The CsCl-type structure prevalent in alkaline-earth and rare-earth AB compounds with Mg, Zn, Cd, Hg, In and Tl. With Ga, Si, Ge, ... , however, the CrB and FeB types appear. The melting temperatures are still relatively high in the rare-earth-transition-element compounds LnRh, LnIr, LnPd and LnPt and surprisingly also in the thallium compounds LnTl. They are even higher in LnSi and LnGe, where we gradually approach the non-metallic domain. If in the latter three groups  $d$ -electron bonding contributes to the high bonding strength, it must be due to the rare-earth elements Ln.

The influence of  $d$ -electron bonding is clearly demonstrated in the  $n$  dependence in the case of the elements. While  $T_m$  decreases from K to Rb to Cs and from Ca to Sr to Ba, it drastically increases in the sequences Ti–Zr–Hf to Ni–Pd–Pt. The first irregularity appears in the coinage metal group Cu, Ag, Au, whereas Zn, Cd and Hg behave as elements without  $d$ -bonding. The origin of the rise in  $T_m$  from 3d to 5d elements is the increasing overlap of the  $d$ -electron wavefunctions. The radial extension of the  $d$ -electrons and thus their contribution to the bonding strength increases from 3d to 4d to 5d. Moreover, the size of the transition elements

increases from 3d to 4d but 4d and 5d elements are virtually of the same size. Thus  $T_m$  rises in the sequences

PrNi (1003 K) – PrPd (1448 K)  
– PrPt (2073 K) (CrB type)

ScNi (1548 K) – ScPd (1873 K)  
– ScPt (2523 K) (CsCl type)

TiNi (1583 K) – TiPd (1673 K)  
– TiPt (2103 K) (CsCl type)

It is worthwhile to note the irregularities on going from the Sc group (13 electrons per formula unit) to the Ti group (14 electrons per formula unit), which are certainly related to details of the electron transfer.

The (Ln 5d) size dependence is evident also in the sequence

ScPd	–	TmPd	–	HoPd	–	TbPd
1873 K		1843 K		1753 K		1693 K
	–	SmPd	–	CePd	–	LaPd
		1543 K		1410 K		1353 K

In the series

SrCu	–	SrAg	–	SrAu
859 K, p		953 K		1243 K

we observe the same  $n$  dependence and therefore presume a still effective d-bonding. However, in the sequences

CaZn	–	CaCd	–	CaHg
712 K, p		958 K		1234 K

and

BaZn	–	BaCd	–	BaHg
613 K		861 K		1095 K

we observe a similar rise in  $T_m$  that cannot be accounted for by d-electron contributions.

### 3. Conclusions

During our discussion it became clear that a uniform description of the melting points of all AB compounds

is probably impossible. Molecular, layer-type and three-dimensional compounds have to be treated separately. For melting point predictions concerning new compounds the dimensionality of their structure should be known or guessed. Although our reflections represent only a first step towards solving the melting problem, the tables may demonstrate its complexity as well as the profit of its solution.

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### References

- 1 F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema and A. K. Niessen, in F. R. de Boer and D. G. Pettifor (eds.), *Cohesion and Structure*, Vol. 1, North-Holland, Amsterdam, 1988, pp. 1–101.
- 2 P. Villars, *J. Less-Common Met.*, 92 (1983) 215–238.
- 3 P. Villars, *J. Less-Common Met.*, 99 (1984) 33–43.
- 4 P. Villars, K. Mathis and F. Hulliger, in F. R. de Boer and D. G. Pettifor (eds.), *Cohesion and Structure*, Vol. 2, North-Holland, Amsterdam, 1989, pp. 1–103.
- 5 J. R. Chelikowsky and K. E. Anderson, *J. Phys. Chem. Solids*, 48 (1987) 197–205.
- 6 J. R. Chelikowsky and K. E. Anderson, *Phys. Lett. A*, 114 (1986) 482–484.
- 7 U. Walzer, *Phys. Status Solidi B*, 162 (1990) 75–88; 168 (1991) 397–412.
- 8 D. L. Anton, D. M. Shah, D. N. Duhl and A. F. Giamei, *JOM*, 41 (1989) 12–17.
- 9 P. Villars, in J. H. Westbrook and R. L. Fleischer (eds.), *Intermetallic Compounds*, Wiley, London, 1993, in press.
- 10 A. Zunger, in M. O'Keefe and A. Navrotsky (eds.), *Structure and Bonding in Crystals*, Vol. 1, Academic, New York, 1981, pp. 73–135.
- 11 B. Massalski, H. Okamoto, P. R. Subramanian and L. Kacprzak, *Binary Alloy Phase Diagrams*, Vols. 1–3, ASM International, Materials Park, OH, 2nd edn., 1990.
- 12 P. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, Vols. 1–4, ASM International, Materials Park, OH, 2nd edn., 1991.
- 13 P. Villars, *J. Less-Common Met.*, 109 (1985) 93–115.
- 14 L. Brewer, *Acta Metall.*, 15 (1967) 553–556.
- 15 S. T. Oyama, *J. Solid State Chem.*, 96 (1992) 442–445.