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Structural Stability of Transition-Metal Binary Compounds

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It is shown that the coordinates ΔN and $\bar{N}$, where N is the periodic-table group number, effect a much better crystal-structure separation than do the coordinates of Zunger for 91 transition-metal–transition-metal compounds. It is concluded that there is no evidence from structure maps to support the assumption that s-p electrons control the crystal structure dependent part of the energy of this class of compounds nor is there evidence to deny that d electrons effectuate this control.

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There has been great interest recently in crystal-structure maps. Originally, the coordinates chosen for such maps had an empirical basis,[1,2] but with the work of St. John and Bloch,[3] who based their coordinates on an l-dependent, nonlocal pseudopotential,[4] coordinates based on "first principles" have been used in further developments of crystal-structure maps.[5-11]

The present paper is concerned with structure maps for 91 AB equiatomic binary compounds composed solely of transition elements. The reason for this interest in these particular compounds is the implication in the recent work of Zunger[9] that the s-p electrons are responsible for the crystal structures chosen by transition-metal–transition-metal (TM-TM) compounds. This implication is contrary to the results based on tight binding theory,[12] which lead to the conclusion that the directionality of the d orbitals dictates transition-metal crystal structures. This conflict of viewpoints led us to a review of the data upon which Zunger based his statement: "The success of the present dual coordinates in separating the crystal structures of many TM-TM... compounds... suggests that the structural part of the cohesive energies of compounds may be determined by s-p coordinates... ."

Zunger also stated: "I am unable to separate the closely related NiAs($B8_1$)-MnP($B31$) and the CsCl($B2$)-CuAu($L1_0$) pairs... . Also I find that the seventeen $B20$ (FeSi) compounds [omitted from Fig. 1(b) for clarity] overlap precisely with the $B8_1$, $B2$, and $B33$ domains, respectively. ... A better resolution of the TM-TM compounds may require a specialized scale involving d electrons more directly." It is not possible from the data presented in Zunger's paper to obtain a measure of how well or how poorly, in fact, the Zun-

TABLE I. List of *AB* transition-metal compounds and their stable structures. Phases in parentheses are not included in Fig. 2 but are included in Fig. 1.

BCr, *B*-33	AuCu $L1_0$	γ-CuTi, *B*-11	α-CrFe, $D8_b$	AuCd, *B*-19	CsCl, *B*-2			*A*3	*B*27	$D8_5$
HfNi	AuCu-I	AgZr	CoCr	NbPt	AgLa	(LuPd)	CuY	IrMo	YPt	NiTa
HfPt	CoPt	AuHf	CoV	PtTi	(AgLu)	(LuRh)	FeRh	IrW	YNi	NbNi
LaNi	FePt	AuTi	CrFe	PtV	AgSc	MnV	HfRh	MoRh		
LaPt	FePd	γ-CuTi	FeMo	PdTi	AgY	NiSc	HfRu			
LaRh	IrMn	PdTa	FeTc	MoPt	(AuLu)	OsTi	HfTc			
NiZr	IrNb	AgTi	FeV	MoNi	AuSc	OsV	(IrLu)			
PtZr	MnPt		ReW		AuY	OsZr	IrSc			
	MnRh		NbRe		CoFe	PdSc	TaTc			
	NbRh				CoHf	PtSc	TcTi			
	NiPt				CoSc	ReTi	TcV			
	RhTi				CoTi	RhSc	AuLa			
	AuMn				CoZr	RuSc	RhY			
	FeNi				(CuLu)	RuTi	FeTi			
	MnPd				β-CuPd	RuV				
					CuSc	RuZr				

ger *s*-*p* coordinates separate the crystal structures of TM-TM compounds. Thus, a crystal-structure map showing all 91 TM-TM compounds listed in Table I and based on the Zunger coordinates is given in Fig. 1. (We have used the compounds listed by Watson and Bennett[10] in their Table II, to which we have added the compounds: MoPt, MoNi (*B*19); FeTi (*B*2); YPt, YNi (*B*27); and NiTa, NbNi ($D8_5$). Also, we note that W-B (Ref. 10) listed wrong crystal structures for the stable phase of the following compounds: IrTa, IrMo, IrW, RhMo, and MnPd. The stable crystal structures for these compounds are given in Table I.

It is apparent from examination of Fig. 1 that there exists appreciable overlap and no clear-possible by eliminating the *B*2, *B*27, $D8_5$, and $L1_0$ type phases to effectuate a crystal structure separation of the $D8_b$, *B*19, *B*11, and *B*27 structures with only 3 errors.

One way to evaluate the significance of these results is to determine whether a better separation can be achieved with use of coordinates that are clearly related to the *d* electrons of the transition elements. The recent works of Pettifor; Varma; and Williams, Gelatt, Jr., and Moruzzi[13] suggest that appropriate coordinates may be $\bar{N}$, the average group number of the transition element components and ΔN, the difference in such group numbers. The relation of these coordinates to the *d* electrons is that they provide a measure of the *d*-band center of gravity and width and changes in these quantities in the compounds relative to the components. The coordinate $\bar{N}$ and ΔN might also be related to *s*-*p*-electron properties, but no one to our knowledge has yet established such a relation. Thus, if these coordinates do not separate out crystal structures as well as the Zunger coordinates it is reasonable to conclude that crystal structures of TM-TM compounds are probably not determined by the *d* electrons. On the other hand, if they provide a better separation than that provided by the Zunger co-

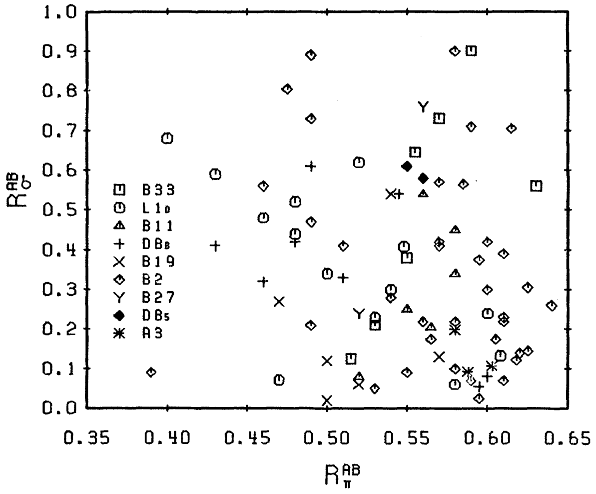

FIG. 1. Crystal-structure map for 91 TM-TM binary alloys (TM represents a transition element) based upon Zunger coordinates.

ordinates then it is reasonable to conclude that there is no reason to deny that *d* electrons control TM-TM crystal structure energy while there is good reason to doubt that *s*-*p* electrons accomplish this control.

Figure 2 shows the ΔN vs $\bar{N}$ plot for the same compounds plotted in Fig. 1. Comparison of Figs. 1 and 2 shows that the separation of crystal structures achieved by ΔN vs $\bar{N}$ is significantly better than that given by the Zunger coordinates R_σ^{AB} and R_π^{AB}. In fact, there are only 2 errors in Fig. 2: CuPd ($B2$) at coordinates (1, 10.5) and AuMn ($L1_0$) at coordinates (4, 8). The two points at coordinates (1, 8.5) are $B2$ phases that are magnetic and are not considered to be errors from the viewpoint of the present analysis.

Thus, the conclusion of this work is that the evidence provided by crystal structure maps does not eliminate the concept that *d* electrons control the structure dependent part of the energy of TM-TM compounds. Further, this evidence provides no basis for the assumption that *s*-*p* electrons materially affect the relative stability of competing crystal structures of TM-TM compounds.

Many of the compounds listed in Table I exhibit polymorphism. For these cases, the difference in free energies of the crystal structures must be very small. Only the known low-temperature polymorph of each compound is listed in Table I.

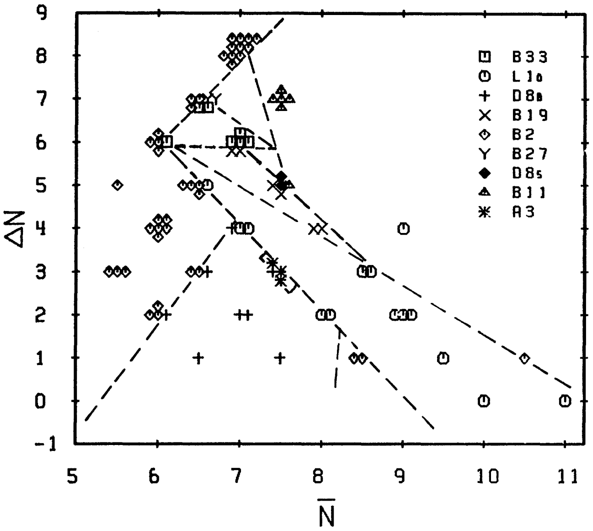

FIG. 2. Crystal structure map for 91 TM-TM binary alloys (TM represents a transition element) based upon Varma–Pettifor coordinates. (Points are slightly displaced from their integer or half-integer positions for the sake of visibility. Several such positions are common to a number of crystal structures.)

The crystal structures corresponding to the polymorphs of a given compound often are widely separated in Fig. 2, e.g., $B2$ and $L1_0$. Considering the small differences in free energy separating the polymorphs, it is remarkable that only two parameters are required to achieve a complete separation of the crystal structures for a given family of AB compounds.

From first principles only two parameters determine the energies of formation of all polymorphs of a binary compound—the atomic numbers of the components. The coordinates of Fig. 2 are linearly related to the latter. These facts, however, do not provide a necessary and sufficient explanation for the results shown in Fig. 2, as can be demonstrated by making a similar plot for the case of *sp*-*sp* compounds.

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