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Structural information from Miedema's theory for the heat of formation of intermetallic phases

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We show in this paper that, notwithstanding the isotropic nature of Miedema's semiempirical theory for the heat of formation ΔH of intermetallic phases, and contrary to the present view in literature, the parameters Φ^* and n_{WS} used to predict the signs of ΔH can contribute to our understanding of structural phenomena quantitatively. On a $(\Delta\Phi^*,(\Delta n_{\mathrm{WS}})^{1/3})$ map considerable resolution is obtained among the binary systems in which different structure types occur, showing the importance of the energy of formation of an intermetallic compound in deciding the crystal structure that it adopts. The points corresponding to the systems in which the Laves phases ($MgCu_2$, $MgZn_2$, and $MgNi_2$ types), the $SiCr_3$-type phases, the $TiAl_3$-type phases, etc., occur, show linear relationships on the $(\Delta\Phi^*,(\Delta n_{\mathrm{WS}})^{1/3})$ map, whereas the binary systems with $MoSi_2$-type phases are resolved into two lines corresponding to the two groups of $MoSi_2$-type phases with different c/a ratios and near-neighbor coordinations. The above observations enable us to explain many structural trends that can be noticed from the phase diagrams: for instance, the almost total exclusion of the $SiCr_3$-type phases from the 250 binary systems in which Laves phases occur and that of Laves phases from the 87 binary systems with $SiCr_3$-type phases.

I. INTRODUCTION

Since an *ab initio* quantum-mechanical calculation of the crystal structure adopted by intermetallic compounds remains beyond our reach today[1] and since an immense wealth of experimental data exist in the literature in the form of solved structures, it becomes interesting to look for systematics in the available experimental data. Such systematics could form a practical guideline for the production of new members of the same structure type and they could also throw more light on the basic physical processes leading to the occurrence of a particular structure type in a binary system. We examine in this paper the possibility of obtaining structural information on intermetallic compounds using the highly successful thermochemical scheme of Miedema *et al.*[2-4] which predicts the signs of the heat of formation of liquid and solid metallic mixtures with a reliability between 96% to 100%. They have used two variables: Φ^*, which measures the chemical potential (closely related to the experimental work functions or electronegativity), and n_{WS}, which was thought to represent the electron density at the surface of the Wigner-Seitz (WS) cell for each element. A quantum-mechanical interpretation of Miedema's parameters has been proposed by Chelikowsky and Phillips.[1] The equation suggested by Miedema *et al.*[3,4] for the heat of formation of solid alloys formed from elements A and B is

$$\Delta H \sim [-(\Delta\Phi^*)^2+(Q/P)(\Delta n_{\mathrm{WS}})^{2/3}-R/P] \,. \tag{1}$$

Q/P and R/P are constants obtained from the examination of phase-diagram information. $R=0$ for all alloys except for combinations of a d metal with a p element or with divalent Mg or Be. Equation (1) shows that in cases where $R=0$, if $(\Delta\Phi^*)^2/(\Delta n_{\mathrm{WS}})^{2/3}>Q/P$ for a particular binary system, the heat of formation is negative and vice versa. Accordingly, Miedema *et al.* have been able to separate "+" signs (representing element combinations with less that 10% mutual solid solubility) and "−" signs (representing element combinations with more than 10% mutual solid solubility and/or having intermediate phases in the phase diagram) on a map using $|\Delta\Phi^*|$ and $|(\Delta n_{\mathrm{WS}})^{1/3}|$ as coordinates. From the slope of the straight line that separates the two regions, the value of Q/P was obtained as $9.4\ \mathrm{V}^2/(\mathrm{d.u.})^{2/3}$. [See Refs. 2 and 3 for the definition of Miedema's density units (d.u.).] For the combination of transition metals with p elements the boundary that separates the + and − signs was found from phase-diagram data to be a parabola dependent (slightly) on the valency of the p element. It is this observation that necessitated the introduction of the parameter R in Eq. (1) for the transition-metal—p-element combinations.

Miedema *et al.* have treated only the isotropic (structurally averaged) part of ΔH. So at the first look it is not obvious that the theory will yield any structural information at all. Attempts have been made to separate various structure types occurring in equiatomic phases using the coordinates $(|\Delta\Phi^*|, |(\Delta n_{\rm WS})^{1/3}|)$ without success.[5] We intend to show in this paper that useful conclusions regarding the structure of intermetallic phases can be obtained if one uses $(\Delta\Phi^*, (\Delta n_{\rm WS})^{1/3})$ as the coordinates. In the next section we discuss the structure types studied in detail. In addition to those structure types, six other structure types are also treated in this paper.

II. THE STRUCTURE TYPES STUDIED IN DETAIL

(1) The *Laves phases* denote a large group of intermetallic phases AB_2 with one of the following structure types: (a) $\rm MgCu_2$, (b) $\rm MgZn_2$, and (c) $\rm MgNi_2$. The $\rm MgCu_2$ structure is cubic with eight formula units in the elementary cell and belongs to the space group $Fd3m$. $\rm MgZn_2$ is hexagonal with four formula units in the elementary cell and belongs to the space group $P6_3/mmc$. $\rm MgNi_2$ is hexagonal and belongs to the space group $P6_3/mmc$ and has eight formula units in the elementary cell. The above three structure types are closely related and are discussed in detail elsewhere.[6,7]

(2) The cubic *$SiCr_3$ type* ($A15$) belongs to the space group $Pm3n$ and has two formula units in the elementary cell. This structure type has evinced a lot of interest because many of the intermetallic compounds which are superconducting with high T_c crystallize in this structure type. A detailed description of this structure type is also available elsewhere.[8,9]

(3) The *$MoSi_2$ type* is tetragonal and belongs to the space group I/mmm; two formula units are in the elementary cell.[10] The description of this structure is based on the recognition of two "ideal" axial ratios: $3\sqrt{2}/\sqrt{3} = 2.45$ when close-packed layers are stacked in bcc [110] packing, and $3\sqrt{2} = 4.24$ when close-packed layers are packed in close packing. The first group with c/a values ranging from 2.29 to 2.60 can be discussed using $\rm HfAu_2$ as a typical example. The Hf atom lying in the plane $z = \frac{1}{2}$ has ten Au nearest neighbors: eight at equal distances in

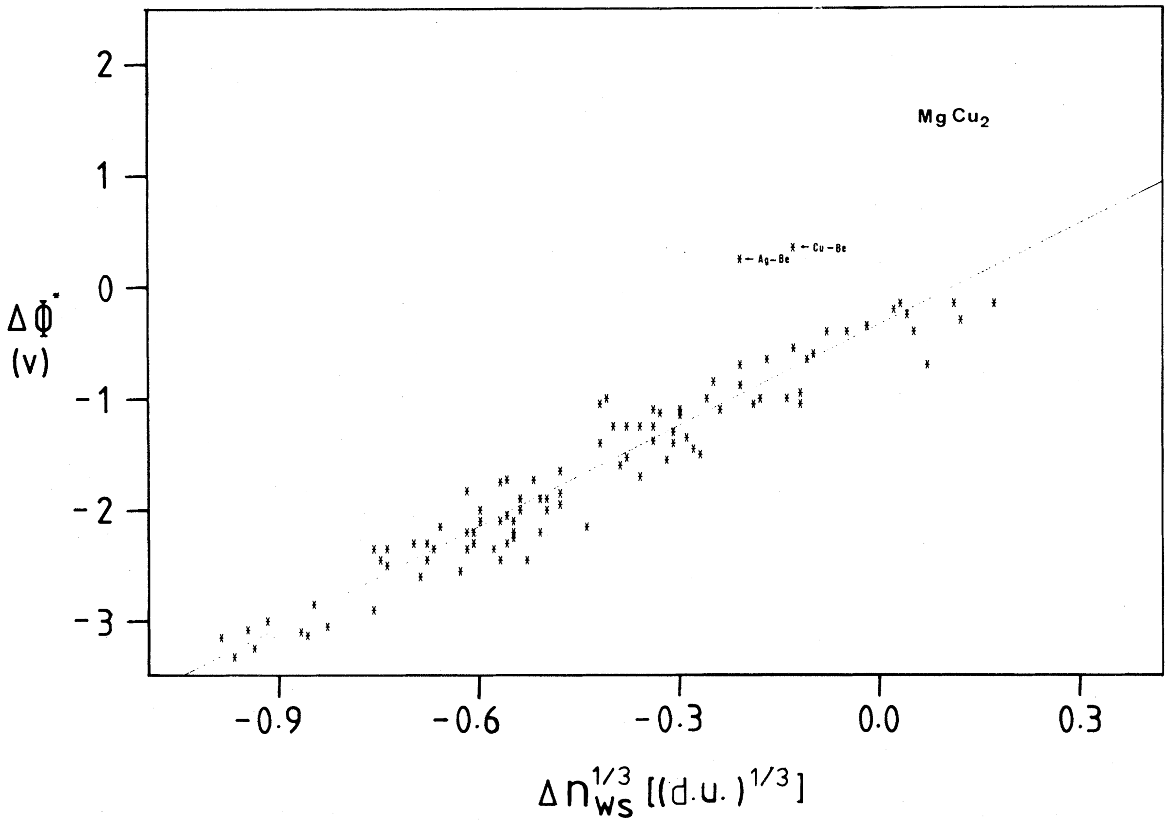

FIG. 1. A plot of $\Phi_A^* - \Phi_B^*$ vs $(n_{\rm WS}^A)^{1/3} - (n_{\rm WS}^B)^{1/3}$ for the binary systems with $\rm MgCu_2$-type phases. A is the minority element.

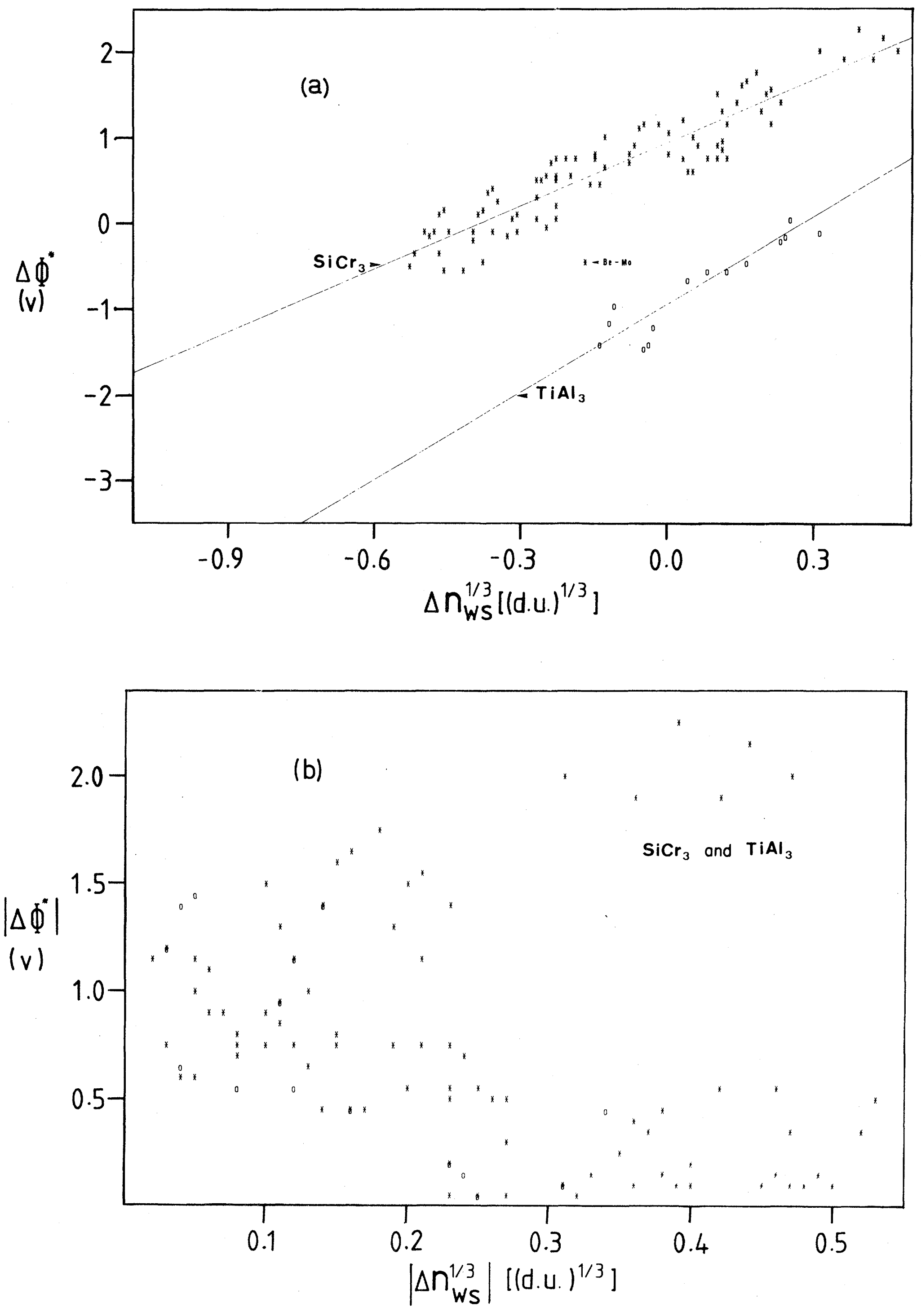

FIG. 2. (a) Plots of $\Phi_A^* - \Phi_B^*$ vs $(n_{\mathrm{WS}}^A)^{1/3} - (n_{\mathrm{WS}}^B)^{1/3}$ for the binary systems with $SiCr_3$-type (crosses) and $TiAl_3$-type (circles) phases. A is the minority element. (b) Binary systems with $SiCr_3$-type (represented by crosses) and $TiAl_3$-type (represented by circles) compounds are depicted on a $(| \Delta\Phi^* |, |(\Delta n_{\mathrm{WS}})^{1/3}|)$ map. The linear dependence between $\Delta\Phi^*$ and $(\Delta n_{\mathrm{WS}})^{1/3}$ observed in (a) and also the resolution of the binary systems with $SiCr_3$-type and $TiAl_3$-type phases are lost in this diagram.

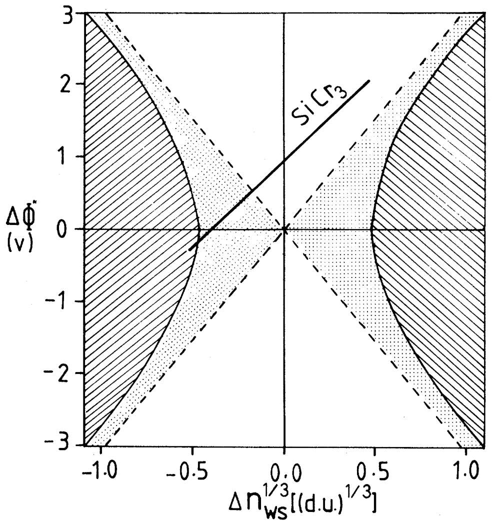

FIG. 3. Line corresponding to the binary systems with SiCr$_3$-type compounds is shown on a $(\Delta\Phi^*,(\Delta n_{WS})^{1/3})$ map. The unshaded region has *t-t* and *t-p* combinations, the dotted region has only *t-p* combinations, and there are no compounds in the region shaded with lines. It is the negative-energy contribution from the R term that enables the *t-p* compounds to occur in the dotted region, though the positive-energy contribution from the $(\Delta n_{WS})^{2/3}$ term is more than the negative-energy contribution from $(\Delta\Phi^*)^2$ term in this region.

the planes $z \sim \frac{1}{3}$ and $\frac{2}{3}$, and two almost at the same distance along the c direction in the planes $z \sim \frac{1}{6}$ and $\frac{5}{6}$. The Au atom has essentially a coordination of the same form, with five atoms of the like kind and five atoms of the unlike kind. In the other group where the axial ratio varies from 3.18 to 4.68, only the atoms lying in the planes $z \sim \frac{1}{3}$ and $\frac{2}{3}$ are equidistant from the central atom. The distance of the two atoms in the c direction is 20–30 % greater, and four more atoms in the a direction are at about 10% greater distance. CuTi$_2$ is a typical member of this group. The compounds AlCr$_2$, MoU$_2$, and AlTc$_2$ have axial ratios that lie midway between the ranges of these two groups and do not fit into the above classification.

(4) The *TiAl$_3$ type* is tetragonal with two formula units in the elementary cell and belongs to the space group $I4/mmm$.[11]

III. OBSERVATIONS AND DISCUSSION

We see from Eq. (1) that in cases where $R=0$,

$$\Delta H<0 \quad \text{if } (\Delta\Phi^*)^2/(\Delta n_{WS})^{2/3}>Q/P\ , \tag{2}$$

i.e.,

$$\Delta H<0 \text{ if } |\Delta\Phi^*|/|(\Delta n_{WS})^{1/3}|>(Q/P)^{1/2}\ . \tag{3}$$

It is reasonable to assume that in cases where one looks for structural information in a binary alloy in which the two types of atoms occupy different and distinct point positions, the actual direction of charge transfer and hence the signs of $\Delta\Phi^*$ and $(\Delta n_{WS})^{1/3}$ are of significance. In fact, inequality (2) offers a more general solution than inequality (3), i.e., ΔH is negative if $-(Q/P)^{1/2}<\Delta\Phi^*/(\Delta n_{WS})^{1/3}<(Q/P)^{1/2}$. $\Delta H=0$ would correspond to $\Delta\Phi^*/(\Delta n_{WS})^{1/3}=\pm(Q/P)^{1/2}$.

In Fig. 1 we show a plot of $\Phi_A^*-\Phi_B^*$ vs $(n_{WS}^A)^{1/3}-(n_{WS}^B)^{1/3}$ for the binary systems in which the Laves phases with the *MgCu$_2$-type* structure occur: A is the minority element. The list of the binary systems with phases isostructural with MgCu$_2$ is from Ref. 11. Out of a total of 173 such binary systems only 126 systems formed by the 62 elements whose Φ^* and $(n_{WS})^{1/3}$ values are avail-

TABLE I. Slopes (m) and intercepts on the $(\Phi_A^*-\Phi_B^*)$ axis (c) of the straight lines obtained in plotting $\Phi_A^*-\Phi_B^*$ vs $(n_{WS}^A)^{1/3}-(n_{WS}^B)^{1/3}$ are listed. A is the minority element. R is the regression factor. The structural data are taken from Ref. 11 except for the SiCr$_3$ structure type, in which case the data are taken from Ref. 13.

Number	Structure type	Pearson symbol	Number of representatives	m $[\text{V}/(\text{d.u.})^{1/3}]$	c (V)	R
1	MgCu$_2$	$cF24$	126	3.02	−0.33	0.95
2	MgZn$_2$	$hP12$	67	3.30	−0.20	0.96
3	MgNi$_2$	$hP24$	10	2.05	−0.58	0.92
4	SiCr$_3$	$cP8$	87	2.44	0.94	0.92
5	TiAl$_3$	$tI8$	14	3.20	−0.94	0.93
6	CeCu$_2$	$oI12$	11	2.02	−0.80	0.96
7	CuTi$_3$	$tP4$	10	3.62	0.12	0.89
8	Ni$_2$Al$_3$	$hP5$	11	2.85	0.03	0.96
9	AsNa$_3$	$hP8$	16	2.34	0.73	0.98
10	TiNi$_3$	$hP16$	10	4.12	−0.64	0.97
11	CoAs$_3$	$cI32$	6	2.51	−0.33	0.89

able[3,12] could be considered. The points lie on a straight line on the $(\Delta\Phi^*,(\Delta n_{\text{WS}})^{1/3})$ map with a regression factor $r=0.95$. The only two exceptions among the 126 binary systems considered are the Cu-Be and Ag-Be systems, and these exceptions will be discussed later.

67 binary systems having $MgZn_2$-type phases and 10 binary systems with $MgNi_2$-type phases form straight lines on the $(\Delta\Phi^*,(\Delta n_{\text{WS}})^{1/3})$ map with $r=0.96$ and 0.92, respectively.

Figure 2(a) shows plots of $\Delta\Phi^*$ vs $(\Delta n_{\text{WS}})^{1/3}$ for 87 binary systems with *$SiCr_3$-type* compounds and for 14 binary systems with *$TiAl_3$-type* compounds. They form two separate straight lines with $r=0.92$ and 0.93, respectively. Figure 2(b) illustrates that the binary systems with $SiCr_3$- and $TiAl_3$-type phases get mixed up in a $(|\Delta\Phi^*|,|(\Delta n_{\text{WS}})^{1/3}|)$ map. In Figure 3, we show schematically the distribution of points corresponding to the transition-metal—transition-metal (*t-t*) combinations ($R=0$), and the transition-metal—*p*-metal (*t-p*) combinations ($R\neq 0$).

The behavior, on the $(\Delta\Phi^*,(\Delta n_{\text{WS}})^{1/3})$ map, of intermetallic compounds with six more different structure types was studied and they also form straight lines on the map. The results are summarized in Table I. Among the binary systems with the compounds listed as having an $AsNa_3$-type crystal structure in Ref. 11, the system Ir-Si (with the compound $IrSi_3$) was observed to lie far from the straight line. This compound is exceptional, with a value for c/a of 1.52, which is unusual for $AsNa_3$-type compounds whose c/a values lie around 1.8. Hence Pearson has expressed doubts about the correct assignment of the structure type.[11] The value of R quoted in Table I for this structure type is excluding the Ir-Si system. ($R=0.94$, if the Ir-Si system is also included.)

A $(\Delta\Phi^*,(\Delta n_{\text{WS}})^{1/3})$ map for the binary systems with *$MoSi_2$-type* phases [Fig. 4(a)] shows two straight lines with some interesting exceptions. The different behavior of the binary systems with $MoSi_2$-type phases compared to those of the binary systems with Laves phases, $SiCr_3$- and $TiAl_3$-type phases, and also the other structure types listed in Table I, can be understood if one recalls from Sec. II that the intermetallic compounds belonging to this structure type can be classified into two groups with different near-neighbor coordinations based on their c/a ratios. A plot of c/a vs R_A/R_B for the $MoSi_2$-type phases is given in Fig. 4(b). A comparison of Figs. 4(a) and 4(b) clearly shows that the two lines on the $(\Delta\Phi^*,(\Delta n_{\text{WS}})^{1/3})$ map correspond to the two groups of compounds with two different c/a ratios. The phases $AlCr_2$, $AlTc_2$, and MoU_2 which cannot be classified into either of the two groups on the basis of the c/a ratios are exceptions on the $(\Delta\Phi^*,(\Delta n_{\text{WS}})^{1/3})$ map too. The only exceptions to the above-mentioned correlation are the compounds $CdTi_2$ and $AuMn_2$ [Nos. 23 and 28 in Figs. 4(a) and 4(b)]. $CdTi_2$ has an exceptionally high c/a ratio for a $MoSi_2$-type compound and hence its structure has been considered doubtful in Ref. 11. We cannot offer an explanation for the exceptional behavior of $AuMn_2$ at present. The geometry of the structure and the assumption of simultaneous contacts between spherical atoms in *A-A* and *A-B* directions would necessitate an ideal radius ratio $R_A/R_B=1$ for the $MoSi_2$-type phases.[10] The following can be seen from Figs. 4(a) and 4(b): The $MoSi_2$-type compounds with high c/a ratios have $R_A/R_B<1$ and positive $\Delta\Phi^*$; the $MoSi_2$-type compounds with low c/a ratios have $R_A/R_B>1$ and negative $\Delta\Phi^*$. Therefore one can conclude that the direction of the difference in chemical potential is such that the transfer of electrons between the atoms would make the R_A/R_B closer to the ideal value; for instance, electrons are transferred from B to A for the higher-(c/a) group.

It is seen from Figs. 1—4(a) and Table I that *it is possible to define a definite region on the $(\Delta\Phi^*,(\Delta n_{\text{WS}})^{1/3})$ map where points corresponding to the binary systems with a particular structure type are situated.* There are three binary systems which are exceptions: The Cu-Be and Ag-Be systems among the 250 binary systems with Laves phases and the Mo-Be system among the 87 binary systems with $SiCr_3$-type phases. These alloy systems of Be are exceptions probably because of the small size of the Be atoms. The above observation enables us to conclude, at least for the structure types that we have considered, that a proper relationship between $\Delta\Phi^*$ and $(\Delta n_{\text{WS}})^{1/3}$ is a *necessary* condition for the occurrence of a particular structure type in a binary system. To elaborate the above condition means that even if two elements satisfy the "geometrical conditions" for the formation of a structure type such as favorable R_A/R_B ratio, etc., the binary system will not have a particular structure type unless it is properly located on the $(\Delta\Phi^*,(\Delta n_{\text{WS}})^{1/3})$ map.

An examination of the phase-diagram data leads to an interesting observation that *certain structure types do not occur together in the same binary system.* For instance, in the 250 binary systems in which Laves phases occur, the $SiCr_3$-type phases do not occur and in 87 binary systems in which $SiCr_3$-type phases occur, the Laves phases do not occur: The only two exceptions are the Mo-Be system and the Ir-Zr system. $BeMo_3$ and $IrZr_3$ are of $SiCr_3$ type, $ZrIr_2$ is of $MgCu_2$ type, and $MoBe_2$ is of $MgZn_2$ type. Savitskii and Gribulya[14] have also made a similar observation which they propose as a

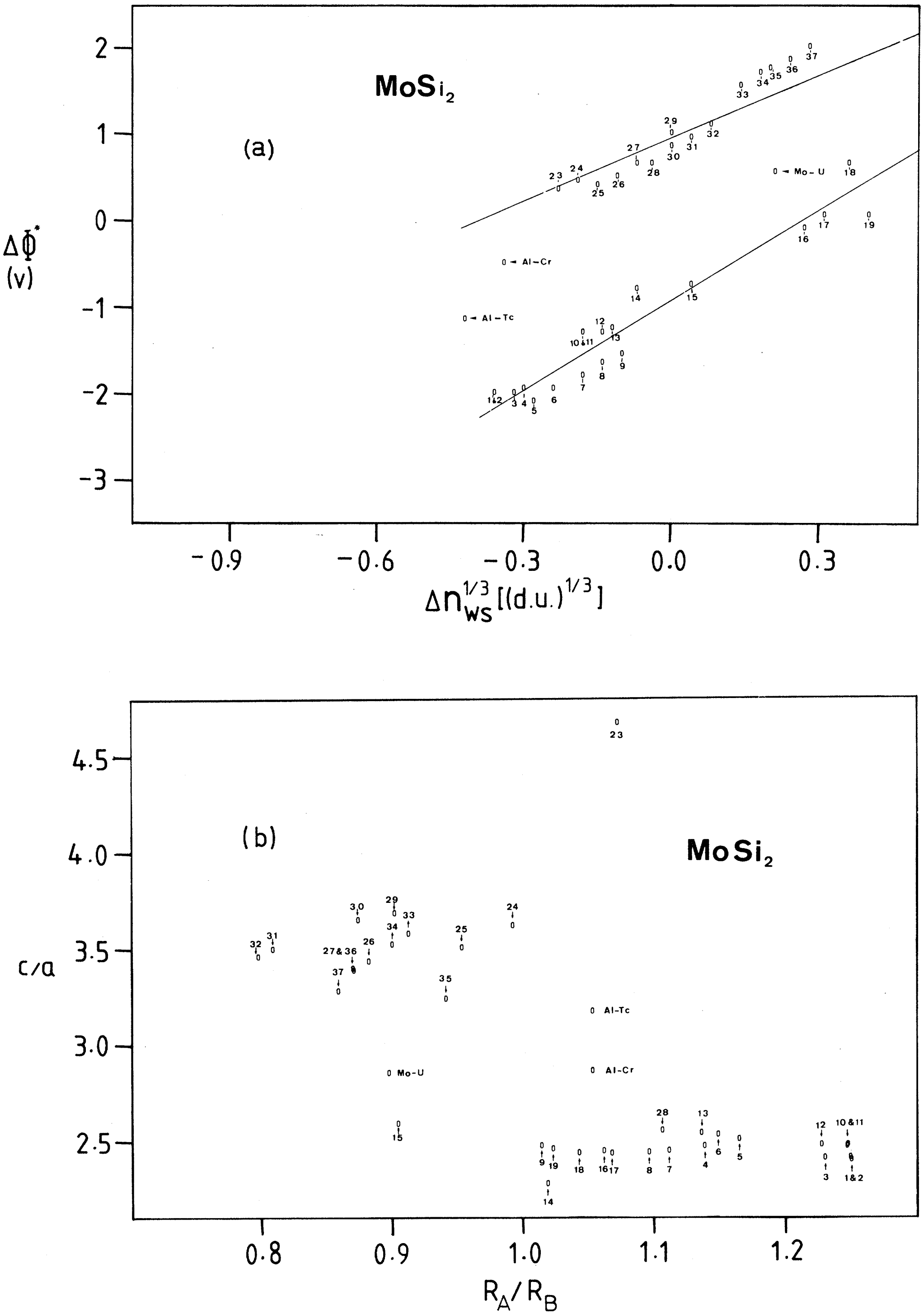

FIG. 4. (a) A plot of $\Phi_A^* - \Phi_B^*$ vs $(n_{\mathrm{WS}}^A)^{1/3} - (n_{\mathrm{WS}}^B)^{1/3}$ for the binary systems in which $\mathrm{MoSi_2}$-type phases occur. The numbers in the figure correspond to the serial numbers used in Table II. Comparison with Fig. 4(b) shows that the two lines in the $(\Delta\Phi^*, (\Delta n_{\mathrm{WS}})^{1/3})$ map correspond to the two groups of compounds with the two different axial ratios. The compounds $\mathrm{MoU_2}$, $\mathrm{AlTc_2}$, and $\mathrm{AlCr_2}$ are exceptions in both Figs. 4(a) and 4(b). (b) A plot of c/a vs R_A/R_B for the $\mathrm{MoSi_2}$-type compounds. The serial numbers of Table II are used for referring to the compounds.

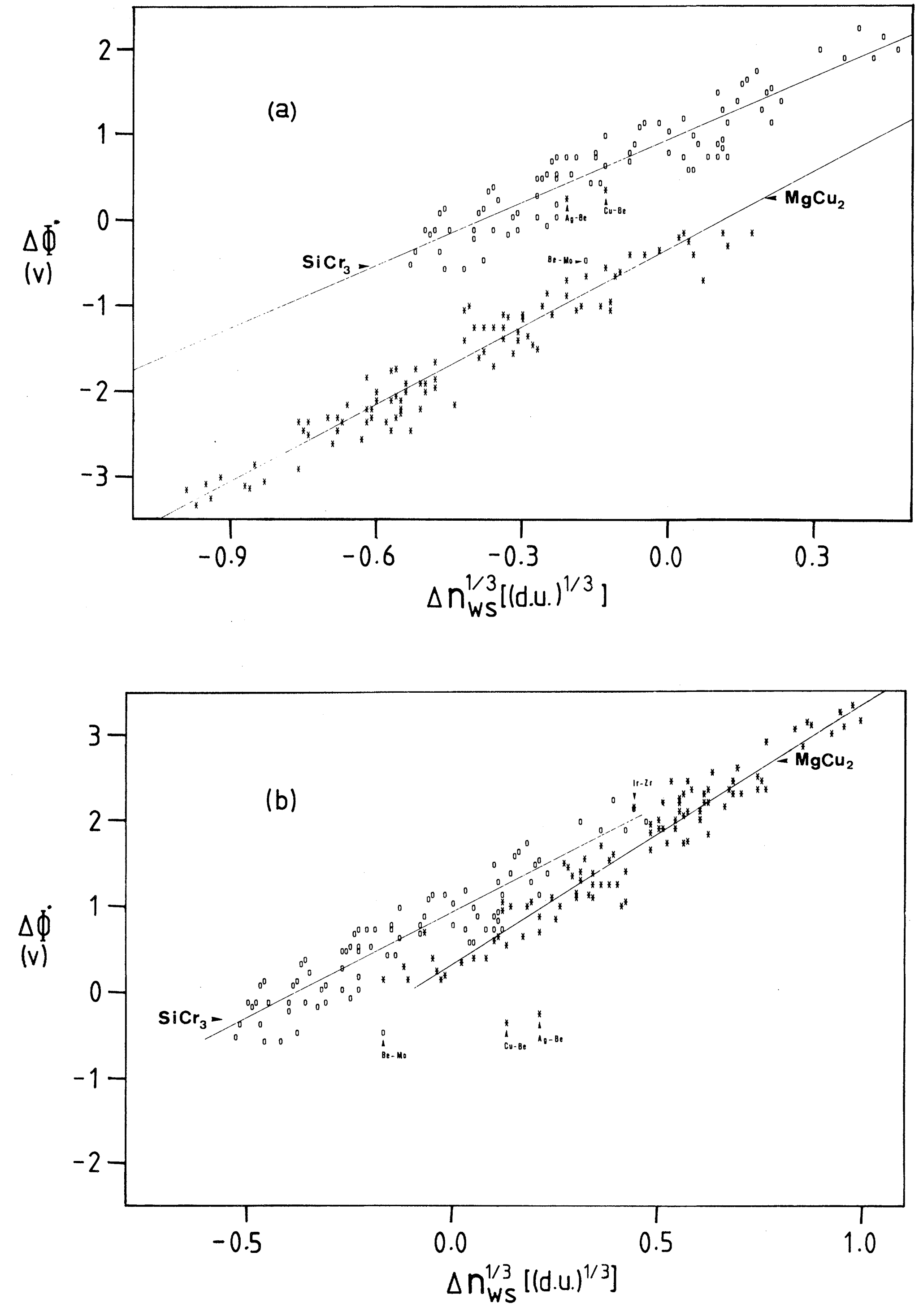

FIG. 5. (a) Plots of $\Phi_A^* - \Phi_B^*$ vs $(n_{\mathrm{WS}}^A)^{1/3} - (n_{\mathrm{WS}}^B)^{1/3}$ for the binary systems with MgCu$_2$-type phases (represented by crosses) and SiCr$_3$-type phases (represented by circles). The good resolution between the two lines on the $(\Delta\Phi^*, (\Delta n_{\mathrm{WS}})^{1/3})$ map explains the absence of a SiCr$_3$-type phase at composition AB_3 in a binary system with a MgCu$_2$-type phase at composition AB_2. (b) Plots of $\Phi_B^* - \Phi_A^*$ vs $(n_{\mathrm{WS}}^B)^{1/3} - (n_{\mathrm{WS}}^A)^{1/3}$ for the binary systems with MgCu$_2$-type phases and $\Phi_A^* - \Phi_B^*$ vs $(n_{\mathrm{WS}}^A)^{1/3} - (n_{\mathrm{WS}}^B)^{1/3}$ for the systems with SiCr$_3$-type phases.

guideline for looking for new representatives of the σ phase. They point out that "in systems with a σ phase there also exist phases of the $SiCr_3$, Laves ($MgZn_2$), and CsCl type which may be called concomitants of the forecast structure." We demonstrate below the utility of the $(\Delta\Phi^*,(\Delta n_{WS})^{1/3})$ maps for predicting the "concomitants" of a particular structure type. Figure 5(a) is a plot of $\Phi_A^* - \Phi_B^*$ vs $(n_{WS}^A)^{1/3} - (n_{WS}^B)^{1/3}$ for the systems with $MgCu_2$-type crystal structure and for those with $SiCr_3$-type structure: A is the minority element. Since the two lines are without overlap we can conclude that if a $MgCu_2$-type compound occurs at composition AB_2 in a binary system, a $SiCr_3$-type compound cannot exist in the system at composition AB_3. In Fig. 5(b) we plot $\Phi_B^* - \Phi_A^*$ vs $(n_{WS}^B)^{1/3} - (n_{WS}^A)^{1/3}$ for the binary systems with $MgCu_2$-type phases along with a plot of $\Phi_A^* - \Phi_B^*$ vs $(n_{WS}^A)^{1/3}(n_{WS}^B)^{1/3}$ for the systems with $SiCr_3$-type compounds. These two lines are nearly resolved. However, the partial overlap suggests that at least in some systems with a $MgCu_2$-type compound at composition AB_2, a compound with $SiCr_3$-type structure can exist with the minority element of the $MgCu_2$-type compound as its majority element. Indeed, the only system which is an exception to the mutual exclusion of $MgCu_2$ phases and $SiCr_3$ phases from the same binary system is in conformity with the above conclusion. $ZrIr_2$ is $MgCu_2$ type whereas $IrZr_3$ has a $SiCr_3$-type structure. The mutual exclusion of the other Laves phases ($MgZn_2$ and $MgNi_2$) and $SiCr_3$-type phases from the same binary system can also be similarly explained.

Figure 2(a) shows that a plot of $\Phi_A^* - \Phi_B^*$ vs $(n_{WS}^A)^{1/3} - (n_{WS}^B)^{1/3}$ resolves the binary systems with the AB_3 phases with $SiCr_3$- and $TiAl_3$-type structures. This figure would enable us to say whether a $SiCr_3$- or $TiAl_3$-type compound could exist in a certain binary system with a particular element as the minority element. Nevertheless a plot of $\Phi_B^* - \Phi_A^*$ vs $(n_{WS}^B)^{1/3} - (n_{WS}^A)^{1/3}$ for the binary systems with $TiAl_3$ phases on the same map would show that $SiCr_3$-type phases and $TiAl_3$-type phases could coexist in the same binary system at 1:3 and 3:1 compositions, respectively. $AlNb_3$, AlV_3, $GaNb_3$, and PtV_3 are $SiCr_3$-type compounds whereas $NbAl_3$, VAl_3,

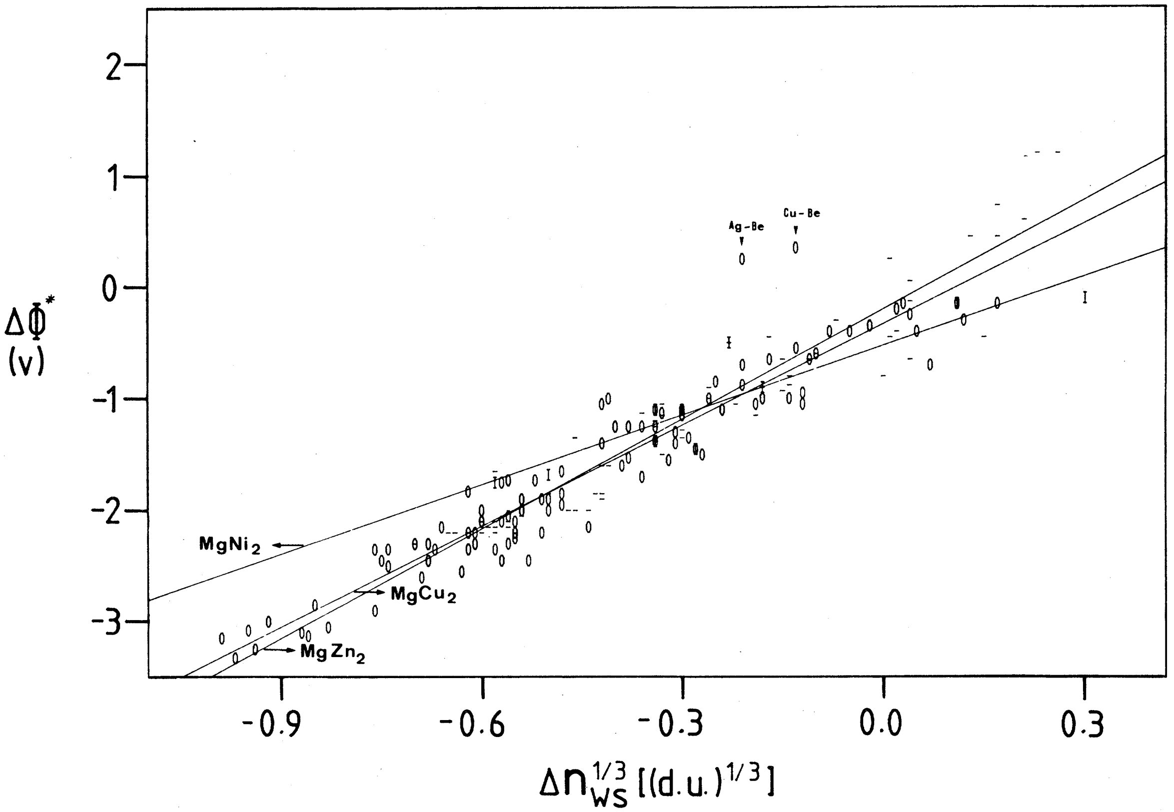

FIG. 6. Plots of $\Phi_A^* - \Phi_B^*$ vs $(n_{WS}^A)^{1/3} - (n_{WS}^B)^{1/3}$ for the binary systems with the Laves phases $MgCu_2$, $MgZn_2$, and $MgNi_2$ types. Systems with $MgCu_2$-type phases are represented by "0," those with $MgZn_2$-type phases with "—" and those with $MgNi_2$-type phases with "I." A combination of two or more symbols represents a binary system with two or more of the Laves phases occurring at different temperatures.

$NbGa_3$, and VPt_3 are $TiAl_3$-type phases. Another relationship between structure types that coexist in the same binary system is the following. When an intermetallic compound with $SiCr_3$-type structure coexists with a $MoSi_2$-type phase at compositions 1:3 and 2:1, respectively, the $MoSi_2$-type compound belongs to the lower—axial-ratio group. Examples are the $SiCr_3$-type compounds $AuTi_3$, $SiMo_3$, and $GeMo_3$ which coexist with the $MoSi_2$-type compounds Au_2Ti, Si_2Mo, and Ge_2Mo of the lower—axial-ratio group. But, if the $MoSi_2$-type compounds exist at the composition 1:2 they belong to the larger—axial-ratio group. $AgZr_3$ and $AuZr_3$ which are $SiCr_3$ type coexist with the $MoSi_2$-type phases $AgZr_2$ and $AuZr_2$ which belong to the group of compounds with larger c/a values. The resolution of the binary systems with $MoSi_2$-type phases into two groups based on their c/a values on the $(\Delta\Phi^*,(\Delta n_{\mathrm{WS}})^{1/3})$ map in Fig. 4(a) enables us to explain the above behavior. A plot of $(\Phi_A^* - \Phi_B^*)$ vs $(n_{\mathrm{WS}}^A)^{1/3} - (n_{\mathrm{WS}}^B)^{1/3}$ for the $SiCr_3$-type phases on Fig. 4(a) would coincide with the upper line corresponding to the binary systems with larger—axial-ratio compounds, showing that, in the same binary system, if the $SiCr_3$- and $MoSi_2$-type compounds have the same minority element, the $MoSi_2$-type compound will belong to the larger—axial-ratio group. A plot of $(\Phi_B^* - \Phi_A^*)$ vs $(n_{\mathrm{WS}}^B)^{1/3} - (n_{\mathrm{WS}}^A)^{1/3}$ for the $SiCr_3$-type compounds will coincide with the lower line corresponding to the lower—axial-ratio group compounds showing that, when $SiCr_3$- and $MoSi_2$-type compounds exist with different minority elements in the same binary system, the $MoSi_2$-type compounds will belong to the lower—axial-ratio group, e.g., $AuTi_3$ ($SiCr_3$ type) and Au_2Ti ($MoSi_2$ type).

The $MgCu_2$-, the $MgZn_2$-, and the $MgNi_2$-type compounds are closely related structurally and Laves has suggested that the major factor controlling the formation of these phases is the relative size of the A and B atoms.[15] On the basis of a hard-sphere-packing model, ideal space filling is achieved when the ratio of the atomic radii $R_A/R_B = 1.225$. It has been convincingly demonstrated by the work on ternary alloy systems that the occurrence of one or the other Laves phases, once the geometrical conditions are fulfilled, is determined by Brillouin-zone effects.[6] Figure 6 shows that these closely related structure types occur in binary systems lying close together on the $(\Delta\Phi^*,(\Delta n_{\mathrm{WS}})^{1/3})$ map.

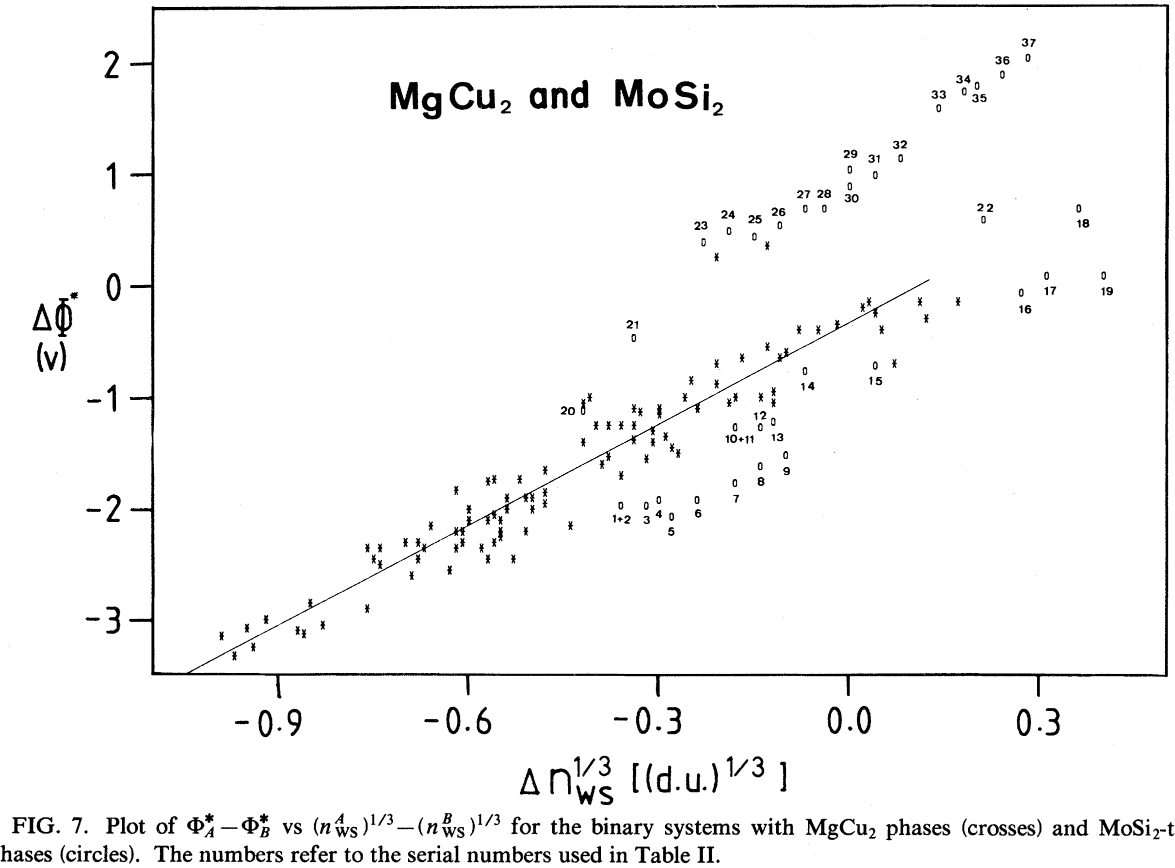

FIG. 7. Plot of $\Phi_A^* - \Phi_B^*$ vs $(n_{\mathrm{WS}}^A)^{1/3} - (n_{\mathrm{WS}}^B)^{1/3}$ for the binary systems with $MgCu_2$ phases (crosses) and $MoSi_2$-type phases (circles). The numbers refer to the serial numbers used in Table II.

In Fig. 7 the binary systems having 1:2 phases with $MgCu_2$- and $MoSi_2$-type crystal structures are shown on the same $(\Delta\Phi^*,(\Delta n_{WS})^{1/3})$ map. The binary systems with the $MoSi_2$ phases of the larger c/a values are well separated from those with the $MgCu_2$-type phases. The resolution of the binary systems with $MoSi_2$-type phases of smaller c/a values is not very good: Nevertheless we can explain at least partially a "curious anomaly" noted by Nevitt.[10] He has pointed out that though many combinations of the elements of the Cu group with *A* components (i.e., minority elements) from the long periods have nearly the proper radius ratio (1.225) for crystallizing in one of the Laves phases, they crystallize with $MoSi_2$-type structure. Table II lists the $MoSi_2$-type compounds with their radius ratios. The combinations YAu_2, $GdAu_2$, $DyAu_2$, $ScAu_2$, $ZrPd_2$, and $HfPd_2$ (Nos. 1–6 and 8 in the figure) have radius ratios which are favorable for the formation of Laves phases, but are not located in the region where systems with $MgCu_2$ phases are located on the $(\Delta\Phi^*,(\Delta n_{WS})^{1/3})$ map. The combinations YAg_2, $GdAg_2$, $DyAg_2$, and $ScAg_2$ (Nos. 10–13), also with favorable radius ratios for the formation of Laves phases, do not crystallize with the $MgCu_2$-type structure probably for the same reason; however, they are not very well resolved from the systems with $MgCu_2$-type phases. One can also demonstrate the same for the other Laves phases ($MgZn_2$ and $MgNi_2$ types).

Though the difference in equilibrium energies of a particular intermetallic compound in closely related structures is known to be small, it becomes evident on inspection of structural data compilations[11,16–18] that some structural information can be grossly deduced from the Periodic Table. For instance, a relationship between the position of elements in the Periodic Table and their equipoint occupation in a structure can be noticed.[13] Pearson[19] has pointed out that this is possible because in structures which are quite different from one another, the near-neighbor coordinations that determine a large part of the enthalphy are different. However, there has been no quantitative way of understanding structure types on the basis of the energy of formation of the binary systems in which they exist. The $(\Delta\Phi^*,(\Delta n_{WS})^{1/3})$ maps give us a means of doing the same. For instance, we can see from Figs. 5(a) and 5(b), respectively, that the resolution of the binary systems with $MgCu_2$ and $SiCr_3$ structure types on the $(\Delta\Phi^*,(\Delta n_{WS})^{1/3})$ map results from (i) the specific direction of the chemical potential difference $(\Delta\Phi^*)$ and electron density difference $[(\Delta n_{WS})^{1/3}]$ between particular point positions of a structure type, and (ii) the fact that the magnitude of the chemical potential differences ($|\Delta\Phi^*|$) in binary systems with a $SiCr_3$-type compound is generally greater than that of a system with a $MgCu_2$-type phase at a given $|(\Delta n_{WS})^{1/3}|$ value. This shows that the energy of formation of a binary system with a $SiCr_3$-type compound is greater than that of a system with a $MgCu_2$-type compound.

IV. CONCLUSIONS

It has been shown in this paper that, at least for the structure types we have considered, the structure of an intermetallic compound depends on the energy of formation of the binary system in which it occurs, and that one can separate those structure types that occur in systems with considerably different energy of formation, and hence with very dif-

TABLE II. Ratios of the radii of the minority element to those of the majority element in $MoSi_2$-type phases are listed. The serial numbers used here are the same as the one referring to the compounds in Figs. 4(a), 4(b), and 7. The table shows that some $MoSi_2$-type phases have nearly the ideal radius ratio (1.225) for crystallizing in one of the Laves phases. Figure 7 and the text explain as to why they do not crystallize as a Laves phase.

Number	Compound	R_A/R_B	Number	Compound	R_A/R_B	Number	Compound	R_A/R_B
1	YAu_2	1.25	14	$CuZr_2$	1.02	26	$ZnHf_2$	0.88
2	$GdAu_2$	1.25	15	$MnAu_2$	0.87	27	$ZnZr_2$	0.87
3	$DyAu_2$	1.23	16	$MoSi_2$	1.06	28	$AuMn_2$	1.11
4	$ScAu_2$	1.14	17	WSi_2	1.07	29	$AgZr_2$	0.90
5	$ZrPd_2$	1.16	18	$ReSi_2$	1.04	30	$CuTi_2$	0.87
6	$HfPd_2$	1.15	19	$MoGe_2$	1.02	31	$CuHf_2$	0.81
7	$ZrAu_2$	1.07	20	$AlTc_2$	1.05	32	$CuZr_2$	0.80
8	$HfAu_2$	1.10	21	$AlCr_2$	1.05	33	$AuHf_2$	0.91
9	$TiAu_2$	1.01	22	MoU_2	0.90	34	$AuZr_2$	0.90
10	YAg_2	1.25	23	$CdTi_2$	1.07	35	$PdTi_2$	0.94
11	$GdAg_2$	1.25	24	$CdHf_2$	0.99	36	$PdHf_2$	0.87
12	$DyAg_2$	1.23	25	$ZnTi_2$	0.95	37	$PdZr_2$	0.86
13	$ScAg_2$	1.14						

ferent average energy in the near-neighbor bonds, on a $(\Delta\Phi^*,(\Delta n_{\mathrm{WS}})^{1/3})$ map. Differentiating closely related structure types lying close together on the $(\Delta\Phi^*,(\Delta n_{\mathrm{WS}})^{1/3})$ map might require the consideration of effects such as Fermi-surface effects which are weaker in comparison with the isotropic volume-dependent forces contributing to the energy of formation of a solid and described by Miedema's theory for the heat of formation of intermetallic phases. The reason for the occurrence of two groups of compounds with different axial ratios in the $MoSi_2$ structure type is found to be the difference in the direction of $\Delta\Phi^*$ between the point positions in these two groups. The $(\Delta\Phi^*,(\Delta n_{\mathrm{WS}})^{1/3})$ maps have been demonstrated to be quite effective in explaining in a quantitative fashion the structural trends exhibited in the phase diagrams and in accounting for structures which are concomitant with a particular structure type.

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