Structure stability maps for intermetallic $AB_5$ compounds

L. Guénee, K. Yvon*

Laboratoire de Cristallographie, Université de Genève, 24 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

Received 26 August 2002; accepted 1 September 2002

Abstract

The structural stability of $AB_5$ compounds ($A=$ lanthanide, alkaline earth, transition element; $B=$ d- and/or p-block element) has been modelled in terms of atomic properties and represented in the form of structure stability maps. The results on some 520 known binary and ternary representatives show that the various structure types form rather well-defined stability domains in three-dimensional space spanned by valence electron concentration, $VEC$, electronegativity difference, $\Delta X$, and radius ratio, $R_A/R_B$. Emphasis is placed on $AB_5$ hexagonal CaCu type compounds that occur within the intervals $5.5 < VEC < 9.5$, $-0.3 < \Delta X < 0.1$ and $1.3 < R_A/R_B < 1.5$. The maps are of interest for the search of new hydrogen storage materials, in particular those containing light and inexpensive 3d transition metals (Fe, Mn, etc.).

Keywords: Intermetallic compounds; Crystal structure; Valence electron concentration; Atom size; Electronegativity; Metal hydrides

1. Introduction

Intermetallic compounds of composition $AB_5$ ($A=$ lanthanide, alkaline earth, transition element; $B=$ d- and/or p-block element), in particular those crystallizing with the hexagonal CaCu$_5$ type structure and their ternary derivatives, are of interest for various technological applications such as permanent magnets and hydrogen storage. They crystallize with at least 20 different structure types. In order to find new $AB_5$ compounds it was of interest to model their structural stability in terms of atomic properties. Modeling of various structures based on purely geometrical grounds has been made some time ago by dimensional analysis of measured cell parameters, interatomic distances and tabulated sets of atomic radii (see, for example, Ref. [1]). Recently, the stability regime of the CaCu$_5$ structure has been re-investigated by this method for some 50 known binary representatives containing rare-earth (R) and transition elements [2]. The analysis was based on measured structure parameters which means that its predictive power could not be easily tested. In this work, an analysis is made based on atomic properties along the lines of Ref. [3] and others. Both binary and ternary compositions are included, covering a total of 520 compounds that crystallize with some 15 structure types. It will be shown that the various structures occupy well defined stability domains in three-dimensional space spanned by valence electron concentration (VEC), electronegativity difference ($\Delta X$) and radius ratio ($R_A/R_B$). The predictive power of the analysis was tested on a few examples. Special attention was payed to CaCu$_5$ type compounds because of their importance in the energy sector.

2. Model

The structural stability of binary $AB_5$ and ternary $A(B,B')_5$ compounds ($A=$ rare earth, alkaline earth, Zr, Hf, Th; $B=$ transition elements and/or p-block element such as Al, Ga, Sn, In, Si, Ge) was modelled in terms of three parameters:

2.1. Geometric factor

The influence of atomic size was described by the radius ratio $R_A/R_B$ as calculated from a tabulated set of atom radii [4]. For ternary compositions $AB_5-B'_5$, an average radius for the B component was calculated according to the relation $R_{BB'}=\frac{(5-x)R_B+xR_{B'}}{5}$. 

---

*Corresponding author. Tel.: +41-22-702-6231; fax: +41-22-702-6864.
E-mail address: klaus.yvon@cryst.unige.ch (K. Yvon).
2.2. Electronegativity

Its influence was described by the electronegativity difference $\Delta \chi = 2/6(\chi_A - \chi_B)$ as calculated from values reported by [5]. For ternary compositions $AB_2-B'_2$ an average value for the $B$ component was calculated according to the relation $\chi_{BB'} = [(1-x)\chi_B + x\chi_{B'}]/5$.

2.3. Valence electron concentration (VEC)

For binary $AB_2$ compounds its value was calculated as $\text{VEC} = (\text{VEC}_A + 5\text{VEC}_B)/6$ and for ternary $AB_2-B'_2$ compounds as $\text{VEC} = (\text{VEC}_A + (5-x)\text{VEC}_B + x\text{VEC}_{B'})/6$ ($\text{VEC}_A, \text{VEC}_B$, number of valence electrons of A and B atoms). Full valences were used, such as $\text{VEC}(\text{Cu}) = 11, \text{VEC}(\text{Th}) = 4, \text{VEC}(\text{R}) = 3$ (except for Ce$^{IV}$, Eu$^{II}$ and Yb$^{II}$).

2.4. Structure data

The compositions and structures of $AB_2$ compounds were retrieved from the following sources: Pearson’s Handbook of Crystallographic Data for Intermetallic Phases [6], Atlas of Crystal Structure Types for Intermetallic Phases [7], Binary Alloy Phase Diagrams [8], Handbook of Ternary Alloy Phase Diagrams [9], and Red Books [10]. The structure types covered, and their symmetry and number of representatives are summarised in Table 1. Those containing boron and silicon are included in the maps but not discussed in detail because of their specific crystal chemistry. On the other hand, structure types having few representatives such as LuMn$_2$, ErZn$_2$, MgZn$_2$, MnCu$_2$In, LaAl$_5$Co, YAl$_5$Ni, ScNi$_5$Si$_3$, and LiMg$_2$Zn$_3$ are not included in Table 1. For each compound appropriate data points with appropriate symbols that refer to the various structure types. For cleanness, the maps of binary and ternary compounds are presented separately. That for the binary compounds was drawn as a function of $R_A/R_B$, $\Delta \chi$ and VEC were calculated (for a detailed list see Ref. [11]) and used to construct structural stability maps (called ‘maps’ thereafter). For cleanness, the maps of binary and ternary compounds are presented separately. That for the binary compounds was drawn as a function of $R_A/R_B$, $\Delta \chi$ and VEC were calculated (for a detailed list see Ref. [11]) and used to construct structural stability maps (called ‘maps’ thereafter).
3. Results

3.1. Domains of stability

As expected AB$_3$ compounds crystallising with the same structure are concentrated in the maps in domains of structural stability (called ‘domains’ hereafter). The domains are relatively well defined for commonly occurring structure types such as CaCu$_2$ (194 members), AuBe$_2$ (74) and YNi$_2$Al$_3$ (50) (see closed lines in Figs. 1–6) but less well defined for uncommon structure types such as LaRu$_x$Si$_2$ (3) that overlaps with the structurally related CeCo$_x$B$_3$ (32) and ErRh$_x$Si$_2$ (9) domains (see Figs. 5 and 6), and PrNi$_x$Al$_3$ (10) that overlaps with YNi$_x$Al$_3$ (Fig. 6). As expected, some overlap also exists between the structurally related YNi$_x$Al$_3$, CaCu$_2$, and CeCo$_x$B$_3$ (30) domains (Figs. 4 and 5), and the CaCu$_2$ domain is not well defined (La$_x$Mg$_{1-x}$)Ni$_y$ for low VEC values for which it overlaps with the YNi$_x$Al$_3$ and PrNi$_x$Al$_3$ domains (Figs. 5 and 6). For binary compositions AB$_3$ the major domains are CaCu$_2$ and AuBe$_2$ type (Fig. 1). Both extend over relatively wide VEC intervals (CaCu$_2$: 7.3<VEC<10.3; AuBe$_2$: 3<VEC<9.8, VEC values not indicated in Fig. 1 but listed in Ref. [11]) which suggests that electron concentration is not of major importance for structural stability. On the other hand, the geometric factor appears to be important because big radii ratios favour CaCu$_2$ type ($R_A/R_B$>1.4) and small ratios AuBe$_2$ type structures ($R_A/R_B$<1.3). For intermediate ratios the domains overlap (see ‘mixed’ region in Fig. 1). This is due to the fact that AuBe$_2$ type structures tend to form at low and CaCu$_2$-type structures at high temperature. Electronegativity appears to be less important for structural stability because the $\Delta \chi$ ranges are relatively wide and do not much differ between structure types (CaCu$_2$: $-0.3<\Delta \chi<0.1$; AuBe$_2$: $-0.2<\Delta \chi<0.2$).

For ternary compositions AB$_{x-y}$B$_y$ (Figs. 2–6) at least 15 (for complete list see Ref. [11]) different structure...
domains occur of which the CaCu₅ type is the most important. Compared to the binary compounds the latter extends over a wider VEC range (5.5<VEC<9.5) and towards lower VEC values (see for example NdNi₅Al₃; VEC=6.5, (1) in Fig. 5). Yet valence appears to play an important role because the domain size and shape changes considerably as a function of VEC. As VEC decreases the number of different structure types generally increases. At high VEC (8<VEC<10) four domains appear (CaCu₅, AuBe₅, Nd₃Ni₅B₂, CeCo₁₁B₄) while at low VEC seven (5<VEC<6) and eight (6<VEC<7) domains appear. At high VEC values (9<VEC<10) AuBe₅ type structures prevail while at low values (5<VEC<6) PrNi₅Al₅, CeCo₅B₂ and YNi₅Al₅ type structures prevail. VEC values below 7 appear to preclude the formation of AuBe₅ type structures and values below 8 preclude Nd₃Ni₅B₂ and CeCo₁₁B₄ type structures. As to the geometric factor low $R_A/R_{BB'}$ values favour the AuBe₅ type (1.1<$R_A/R_{BB'}$<1.3) and high values the CaCu₅ type (1.3<$R_A/R_{BB'}$<1.5). The highest $R_A/R_{BB'}$ values occur with CeCo₁₁B₄, CaRh₂B₂, Ce₂Co₄B₃ and CeCo₁₅B₄ type structures (1.5<$R_A/R_{BB'}$<1.6). Electronegativity is important because the domains limits depend strongly on $\Delta E$. As to the YNi₅Al₅ type structures they appear to be governed mainly by the VEC. They are situated in a relatively narrow interval of 5.5<VEC<7 and are at the border of the CaCu₅ domain at high and of the PrNi₅Al₅ domain at low VEC values. The geometric factor appears to be less important in view of the relatively wide range of 1.28<$R_A/R_{BB'}$<1.45. BaZn₅ type structures appear only at relatively big $R_A/R_{BB'}$ values (Fig. 6).

In summary, the model allows one to rationalize the structural stability of 480 known AB₅ and A(B'B')₅ compounds. Only six compounds appear to be less well situated. Among these three CaCu₅-type compounds (ANi₅Mn₅, A=La, Nd, Pr; VEC=7.83; see (1), (2) and (3) in Fig. 4) are slightly outside their domain in the 8<VEC<9 map (they would be inside their domain in the 8<VEC<9.5 map), while the two AuBe₅ type compounds (YNi₅Mn₅, YNi₅Mn; I and 2 in Fig. 3) and a recently reported MgCu₂Sn type compound (YNi₅Mg [12], (14) in Fig. 4) are in the CaCu₅ domain (for a possible explanation see below). Thus more than 98% of the compounds is correctly reproduced by the maps. The validity of these maps can be demonstrated by the following examples.

3.2. Selected examples

3.2.1. Binary CaCu₅ type structures

In the presence of trivalent A components such as rare earths, B components having less than nine valence electrons (Ti, V, Cr, Mn, Fe) and more than 11 valence electrons (Zn) do not form CaCu₅ type structures under normal synthesis conditions because their VEC is presumably too low (VEC=7.17) and to high (VEC=10.5), respectively. However, this structure forms with tetravalent A components such as Th, as shown by ThFe₅ (1) in Fig. 1, VEC=7.33 which is the only known iron-based member of that type. The influence of atom valence and size on the stability domain of CaCu₅ type structures can be seen on the maps for R elements that are not necessarily trivalent such as Ce, Yb and Eu. Ytterbium in YbCu₅, for example, is divalent in the (low-pressure) CaCu₅ type polymorph (2) in Fig. 1. $R_A/R_{BB'}$=1.518 and trivalent in the high-pressure AuBe₅ type polymorph (3) in Fig. 1, $R_A/R_{BB'}$=1.362, in agreement with literature. As to cerium, it is known to be trivalent in the CaCu₅ type compound CeCu₅ (4) in Fig. 1 but higher-valent in the structural analogues CeNi₅ (6) in Fig. 1 and CeCo₅ (7) in Fig. 1. These findings are consistent with the maps in which CeCu₅ would be situated in the AuBe₅ domain (5) in Fig. 1 if its Ce valency was >3. Yet, no such compound has been reported so far.

3.2.2. CaCu₅ versus AuBe₅ type structures

At high VEC values (8<VEC<10) the limits between CaCu₅ and AuBe₅ domains shift to higher $R_A/R_{BB'}$ values as the VEC is increased (see maps 8<VEC<9 and 9<VEC<10). Thus AuBe₅ type compounds are expected to be stabilised by substituting B atoms of either higher valence and similar atom size, or of similar valence and bigger atom size. This is confirmed by the solubility of Ag, Au and Al in ACu₅ and ANi₅ (A=rare earth). Substitution of Cu and Ni in CaCu₅ type NdCu₅ and DyNi₅ (9) and (10) in Fig. 1) by bigger Ag and Au decreases $R_A/R_{BB'}$ and stabilises the AuBe₅ type compounds NdCu₅Ag and DyNi₅Au ((1) and (2) in Fig. 2), while substitution by lower valent Al maintains the CaCu₅ type structure in NdCu₅Al ((3) in Fig. 3, VEC=8.33) and DyNi₅Al ((4) in Fig. 4, VEC=7.67) in spite of their smaller $R_A/R_{BB'}$.

3.2.3. Solid solutions ACo₅₋ₓNiₓ and ACu₅₋ₓNiₓ (A=rare earths)

According to the maps both series are expected to crystallise with the structure types of the corresponding binary compounds ACo₅ and ANi₅ (CaCu₅ type, see for example (12)-LuNi₅ in Fig. 1) and ACu₅, (CaCu₅ type for A=La ((13) in Fig. 1)–Sm (14), AuBe₅ type for A=Er (15)Lu (16), mixed for A=Gd–Ho). Literature data in fact confirm that ACo₅₋ₓNiₓ forms a continuous solid solution (0≤x≤1) with CaCu₅ type structure, as does ACu₅₋ₓNiₓ (A=Gd–Sm,Y). For heavy (small) rare earths and copper-rich compositions the latter series crystallizes with AuBe₅ type structures ((4)-GdCu₅Ni in Fig. 2) and for Ni-rich compositions with CaCu₅ type structures ((3)-GdNi₅Cu in Fig. 2).

3.2.4. Solubility of Mn in CeNi₅

Literature data show that the CeNi₅₋ₓMnₓ series crystallizes with CaCu₅ type structure for $x=0.7$ and $2.4≤x≤2.7$ and AuBe₅ type structure for $0.9≤x≤2.1$. For $x=3$ an undetermined hexagonal structure occurs. Inspection of the
maps suggest that these structural changes are accompanied by a valence change of cerium from Ce\textsuperscript{IV} in Ni-rich compositions to Ce\textsuperscript{III} in Mn-rich compositions as shown by CeNi\textsubscript{4.3}Mn\textsubscript{0.7}, (4) in Fig. 3) and CeNi\textsubscript{3}Mn\textsubscript{1-}, CeNi\textsubscript{2.5}Mn\textsubscript{1.5}, and CeNi\textsubscript{2}Mn\textsubscript{2} (6), (7) and (8) in Fig. 4) that are at the limit of the CaCu\textsubscript{3} domain. A trivalent valence state of cerium in the latter is consistent with the existence of ANi\textsubscript{2}Mn\textsubscript{1-} analogues with trivalent A components such as $R$=La, Nd, Gd ((9), (10) and (11) in Fig. 4).

### 3.3.2.5. Solubility limits of LaNi\textsubscript{5-}xB\textsubscript{y} (B’=Mn, Al, Cu, Co, Fe)

These CaCu\textsubscript{3} type systems are of particular interest for applications as rechargeable metal hydride electrodes. For the manganous series the maps reproduce well the observed solubility limit at $x \approx 2.1$ (see (8)-LaNi\textsubscript{5} in Fig. 1 and (5)-LaNi\textsubscript{5}Mn\textsubscript{1-} and (6)-LaNi\textsubscript{5}Mn\textsubscript{1-} in Fig. 3). Although LaNi\textsubscript{5}Mn\textsubscript{1-}, (1) in Fig. 4, VEC=7.83) is situated slightly outside the CaCu\textsubscript{3} domain on the 7<=VEC<8 map, it is inside the domain on the 8<=VEC<9 map (6) in Fig. 3). At higher Mn contents the compositions 2<x<=2.5 (7<= VEC<8) and 4<=x<=5 (6<=VEC<7) are clearly outside the CaCu\textsubscript{3} domain, in agreement with literature. For the Al series the reported limit of solid solution (x=1) is close to that suggested by the maps (x~1.5) (VEC=7.667, inside the CaCu\textsubscript{3} domain in the 7<VEC<8 map, outside in the 6<VEC<7 map). For the Cu series the maps suggest a complete solid solution (0<x<1), in accordance with literature. For the Fe series the maps suggest a solubility limit of 1<x~2 (7)-LaNi\textsubscript{5}Fe, (8)-LaNi\textsubscript{5}Fe\textsubscript{2} in Fig. 3), again in accordance with literature. The hypothetical compound LaNi\textsubscript{5}Fe\textsubscript{3} is outside the CaCu\textsubscript{3} domain ((15) in Fig. 4) while the hypothetical compound LaNiFe\textsubscript{2} ((13) in Fig. 4) is close to its border.

### 3.3.6. CaCu\textsubscript{3} versus YNi\textsubscript{Al} \textsubscript{2} type structures

Aluminium- and gallium-rich compounds AB\textsubscript{5-}xB\textsubscript{y} with x>2.5 crystallise mainly with YNi\textsubscript{Al} \textsubscript{2} type structures. Clearly, their domain of existence superposes in part with the CaCu\textsubscript{3} domain (Figs. 5 and 6). This is due to the fact that some compounds adopt both structures, i.e., CaCu\textsubscript{3} type for as cast, and YNi\textsubscript{Al} \textsubscript{2} type for annealed conditions (see (2)-DyNi\textsubscript{2}Ga\textsubscript{2} and (3)-GdNi\textsubscript{2}Ga\textsubscript{2} in Fig. 5). A similar dimorphism occurs also with the recently reported GdNi\textsubscript{3}Sn\textsubscript{2} (13) ($R_A/R_B=1.320$, VEC=6.833, $\Delta\chi=-0.236$, (4) in Fig. 5).

### 3.3. Attempts to synthesize new AB\textsubscript{4} compounds

In order to test the usefulness of the maps a few compositions were selected for which compound formation was either not reported or the structure not known. Note that the compositions selected on the maps refer to structural rather than thermodynamic stability. In order to avoid formation of ‘pseudo-ternary’ solid solutions only those compositions were tested that involve systems not known to form binary AB\textsubscript{3} compounds.

#### 3.3.1. CeFe\textsubscript{5}

Iron-based compounds AFe\textsubscript{4} are expected to crystallize with CaCu\textsubscript{3} type structures only if the A component is tetravalent. According to the maps Ce\textsuperscript{IV} would be a candidate capable of stabilising that structure (VEC=7.33) ((11) in Fig. 1). However, attempts to form CeFe\textsubscript{5} at high pressure (25 kbar) and temperature (950 °C) failed.

#### 3.3.2. LaNi\textsubscript{5}Mg and NdNi\textsubscript{3}Mg

According to the maps these hypothetical compounds should crystallize with CaCu\textsubscript{3} type structures provided Mg is counted as a B element ((12)-LaNi\textsubscript{5}Mg and (16)-NdNi\textsubscript{3}Mg in Fig. 4). Compounds of that composition were indeed synthesised, but found to crystallize with the MgCu\textsubscript{2}Sn type structure, an ordered ternary derivative of AuBe\textsubscript{5}. In this context it is worth recalling that the AuBe\textsubscript{5} structure is closely related to the MgCu\textsubscript{2} type structure in which magnesium can be considered as an A type rather than a B type component. This suggests that Mg containing compounds having MgCu\textsubscript{2}Sn type structures should be classified as AB\textsubscript{2} rather than AB\textsubscript{3} compounds which would explain their unexpected position in the AB\textsubscript{3} series La Mg Ni crystallizes with a disordered cubic MgCu\textsubscript{2} (C15) type structure at low Mg contents (0<x<0.67) and with the MgNi\textsubscript{3} (C36) type structure at higher Mg contents (x>0.67). As to the ordered compounds RNi\textsubscript{2}Mg (R=La, Nd) they were found to absorb hydrogen reversibly in a useful range to compositions of up to RNi\textsubscript{2}MgH\textsubscript{4} [14].

#### 3.3.3. LaNi\textsubscript{5}Mn\textsubscript{3}

This hypothetical compound ($R_A/R_B=1.466$, VEC=7.33) is slightly outside the CaCu\textsubscript{3} type domain ((9) in Fig. 4) and inside the YNi\textsubscript{Al} \textsubscript{2} domain. Attempts to synthesize this compound were successful and its structure was found [15] to be of YNi\textsubscript{Al} \textsubscript{2} type. It is the first manganous member of this type. So far, only aluminium, gallium and tin members were known, and they were relatively poor hydrogen absorbers. Interestingly, LaNi\textsubscript{3}Mn\textsubscript{3} displays excellent hydrogen storage properties and forms a reversible hydride of composition LaNi\textsubscript{3}Mn\textsubscript{3}H\textsubscript{4.6} [15].

#### 3.3.4. YCu\textsubscript{4}Al\textsubscript{2}

This new compound [16] was reported after the present study was completed. It crystallizes with the CaCu\textsubscript{3} type structure and thus fits well onto the maps (5) in Fig. 4).

### 4. Conclusions

The structural stability of AB\textsubscript{4} compounds has been modeled successfully based on atomic properties. Maps as
a function of $R_A/R_B$, $\Delta \chi$ and VEC reproduce well the stability domains of 15 structure types covering some 470 compounds. The maps have predictive power in the sense that they are capable of foreseeing structures of compounds that are thermodynamically stable. The successful synthesis of some new AB$_3$ compounds at ‘predicted’ compositions underlines the usefulness of the structure modeling approach for the search of new hydrogen storage materials.

Acknowledgements

This work has been supported by the Swiss National Science Foundation and the Swiss Federal Office of Energy.

References