

Properties of valuable new intermetallics: Brewer–Engel model applied to the bonding of transition metal dialuminides

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Abstract

The Brewer–Engel Theory is a model capable of predicting novel materials, used in the past in particular for quite stable intermetallics based on the reaction of metals with non-bonding d electron pairs combined with metals with empty d orbitals. In this paper are shown the calculation procedures for bonding energies of 1:2 transition metal aluminide compounds characterized by MgCu₂ crystal structures. The model utilizes parameters that include crystal field effect, Hume-Rothery Rules, and a modified Born–Haber cycle to characterize covalent and ionic bonding contribution of alloys. Interactions between transition metals exhibit enhanced d-bonding, whereas interactions between transition metals and non-transition metals exhibit reduced d-bonding. From the bonding energies, the percentage ionicity factor is determined which is an indication of the stability of the intermetallic compound.

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1. Introduction

The Brewer–Engel Theory, initially created by Neils Engel and later expanded by Leo Brewer, correctly predicts since the early 1960s the effect of pressure upon the relative stabilities of different crystalline structures of the transition metals [1–5]. Many objections are still raised for the use of the Brewer–Engel chemical bonding model that the authors wish to address in this paper. The Brewer–Engel Model uses various criteria to accurately characterize bonding that include Lewis Acid–Base reactions, Hume–Rothery Rules, modified Born–Haber Cycle, Crystal Field Effect, Regular Solution Theory, and the bonding that characterizes local areas of Mendeleev’s Table. Hume–Rothery Crystal Structure Rules correlate s and p electrons with the long-range order effects that fix the crystal structure. A Modified Born–Haber Cycle can be utilized to anticipate periodic trends of both covalent and ionic character [6,7]. Crystal Field Effect is used to explain the fact that all d orbitals are unable to demonstrate equal bonding capability

because some orbitals will be more contracted, so that more extended orbitals provide stronger bonding. Regular Solution Theory is based on the fact that atoms or molecules interact with different bonding strengths: phase boundary can be calculated from Regular Solution Theory [8].

Characterisation of the Brewer–Engel Model begins with Neils Engel, Leo Brewer and Hume–Rothery. Leo Brewer began by using for metals the bonding models of G. N. Lewis and Linus Pauling, the type of bonding models that chemists use for other materials, like those in organic chemistry. There is a change in crystal structure from one metal to its neighbour when dealing with non-transition metals. Hume–Rothery related the total number of valence electrons, that is 1s to sp^{0.5} is body-centered cubic (bcc), sp^{0.7} to sp^{1.1} is hexagonal closed-packed (hcp), sp^{1.5} to sp² is cubic closed packed (ccp), and sp³ is diamond: but Hume–Rothery did not know how to handle the transition metals. Neils Engel determined that the d electrons are somewhat localized and do not affect the long-range order in the way that s and p electrons affect long-range order, and further that the crystal structure should be related to the number of s,p electrons, and not the total number of valence electrons. As electrons are added to the transition metals, it is found that the number of d electrons increases, but the

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number of s and p electrons does not change appreciably for the first half of the transition series. For ionic substances the Born–Haber Cycle is used to evaluate the energy required to take the elements to the gaseous ion that corresponds to the ions in the solid. The bonding energy is calculated as ionic substances condense to the solid. The same process is carried out for the metals, that is the electronic configuration of the neutral atoms that corresponds to the metal are used in configurations associated with a given crystal structure. This Modified Born–Haber Cycle can be extended to combinations of the metals including those that interact as acids and bases.

To improve prediction of bonding trends for metals the Brewer–Engel Theory takes advantage of the values, such as enthalpy of formation data, that vary smoothly and values that are primary factors to determine variation across Mendeleev’s Table. Brewer–Engel Theory allows us to account for major bonding factors in terms of functions that vary smoothly with atomic number.

In the search for new stable intermetallics, it is not always practicable and often difficult to use thermodynamic measurements such as calorimetry and galvanic cells alone to find the many possible novel phases. Thermodynamic measurements will be essential after predictive models such as the Brewer–Engel Theory have indicated phases that should be developed and investigated.

We here apply the Brewer–Engel Theory to the calculation of percentage ionicity for 1:2 MgCu₂ intermetallics of transition metals with aluminum.

2. Overview for bonding energy calculations

2.1. Using Born–Haber type cycle to calculate thermodynamic properties

The Born–Haber type cycle of calculations has been used to trace the energy levels of the species, and to find the relationship of thermodynamic values between states. Acid-base reactions have two types of chemical bonding interactions, covalent and ionic bonding. Covalent bonding energy is equal to the summation of the number of s-, p-, d-, and f-electrons that participate in bonding times the bonding energy per s-, p-, d-, and f-electron. The bonding energies of the pure elements are used, and correspond to the use of the average for bonding of overlapping orbitals of two elements. Any deviation from the average is included in a back-bonding correction. Covalent bonding energy for a transition metal aluminide is represented by the expression:

$$\begin{aligned} \Delta; E_{\text{covalent}}/R = & N_{s,A}E_{s,A}/R + N_{p,A}E_{p,A}/R \\ & + N_{d,A}E_{d,A}/R + N_{f,A}E_{f,A}/R \\ & + N_{s,B}E_{s,B}/R + N_{p,B}E_{p,B}/R \end{aligned} \quad (1)$$

where R is the gas constant, A is a transition metal, and B is aluminum. For the lanthanides the 4f-electron bonding energy term was ignored in the expression above because the 4f-orbitals contract so rapidly with increased nuclear charge that bonding overlap is negligible. For the actinides, the 5f-orbitals do not contract as rapidly with increased nuclear charge, and the 5f-electron bonding term is included in Eq. (1) for actinides up to Bk.

Ionic bonding energy is calculated assuming 100% charge transfer and neglecting repulsion through the relation:

$$\Delta; E_{\text{ionic}}/R = NMz_Az_Be^2/R4\pi\epsilon_0r_{AB} \quad (2)$$

where N is Avogadro’s number, M is the Madelung constant, z_A and z_B are, respectively, charges on the base and acid metals, e is electronic charge, ϵ_0 is vacuum permittivity, and r_{AB} is the shortest interatomic distance between A and B in a given crystal structure. The Madelung constant can be estimated from the average coordination number of A and B and the average interatomic distance between A and B [see Eq. (6)]. This estimate for Madelung constants for crystal structures like MgCu₂, with three-dimensional lattices and well-defined coordination numbers, has an error of 1.4% compared to Madelung constants determined by series convergence. When the lattice constant is available, the interatomic distance can be derived from simple geometry of the MgCu₂ crystal [9]. When the lattice constant is not available, the interatomic distance can be estimated from the radii of the individual elements of A and B .

The total bonding energy for a 1:2 AB₂ intermetallic can be expressed by Eq. (3):

$$\begin{aligned} \Delta; E_{\text{total}}/R = & \Delta; H_{\text{subl},A}/R + 2(\Delta; H_{\text{subl},B}/R) \\ & + \Delta; EA_A/R + \Delta; PE_A/R + \Delta; IE/R \\ & - \Delta; H_{f,AB_2}/R \end{aligned} \quad (3)$$

where ΔH_{subl} is the enthalpy of sublimation for elements, ΔEA is electron affinity, ΔPE is promotion energy, ΔIE is atomic ionization energy, and $\Delta H_{f,AB_2}$ is enthalpy of formation from the elements. The electron affinity of the transition metals is generally small, and available in literature. When the charge n is greater than unity, ΔEA is taken as n times the value of the electron affinity per unit charge. Both 1:1 CsCl [10] and 1:2 MgCu₂ aluminide systems share one pair of s-electrons and one p-electron for bonding (see Section 2.2), so that n is equal to 1.5. ΔPE_A is the promotion energy from the ground state of the -1.5 charge state of the negative ions of the transition metals to the excited states of the

–1.5 charge state of the negative ions of the transition metals. Promotion energies of the negative ions of transition metals to the excited state are not available in literature but are believed to be relatively small. With fairly weak interaction, the energy of promoting one electron from the ground state to a higher excited state will be small. For the crystal structure MgCu_2 , the arbitrary value for $\Delta PE_A/R$ is taken as 3 ± 2 kK for all compounds for the energy of the ground states to the excited states of the negative ions. Adjustments for these assumed values are included in a back-bonding correction factor, called the percentage ionicity. As for the evaluation of the ionization energy of Al, it is based on the following approximation:

$$\Delta; IE_B^{+1.5} = \Delta; IE_B^+ + \Delta; IE_B^{+0.5}$$

where ΔIE_B^+ is the first ionization energy of Al and $\Delta IE_B^{+0.5}$ is the ionization energy of the extra 0.5 electrons of Al, estimated to be one-half the amount of the second ionization energy of Al because the ionization energy for 1.5 electrons is not available. In order to calculate the ionization energy for the 1.5 electrons, an assumption is made that the energy state of $\text{Al}^{+1.5}$ ($s^{1.5}$) is equal to the energy state of $\text{Al}^{+1.5}$ ($sp^{0.5}$). The ionization energy for Al to the Al^+ ground state is 5.984 eV, which corresponds to 69.44 kK [11]. The ionization energy for Al to Al^{+2} ground state is 218.44 kK [11]. Therefore:

$$\text{Al}(s^2p) \rightarrow \text{Al}^+(s^2) \quad \Delta; IE^+/R = 69.44 \text{ kK}$$

$$\text{Al}(s^2) \rightarrow \text{Al}^{+1.5}(s^{1.5}) \quad \Delta; IE^{+0.5} = 109.22 \text{ kK}$$

$$\text{Al}(s^2p) \rightarrow \text{Al}^{+1.5}(s^{1.5}) \quad \Delta; IE + 1.5/R = 178.66 \text{ kK}$$

Thus, 178.66 kK is used to represent the ionization energy of $\text{Al}^{+1.5}$ ($sp^{0.5}$).

2.2. Calculation of the percentage ionicity for 1:2 MgCu_2 dialuminides

The percentage ionicity determines the stability of intermetallic compounds. The worth of the Brewer–Engel Theory approach is the ability to predict thermodynamic values for acid-base intermetallic compounds when no data is available. For the 1:2 MgCu_2 intermetallic compounds the Brewer–Engel Theory is applied to reactions between transition metals and non-transition metals with degraded d-electron bonding, that is 1:2 AB_2 transition metal aluminides that have MgCu_2 -type crystal structure, where A is the transition metal and B is aluminum [9].

Calculations for 1:1 [10] and 1:2 transition metal aluminides are similar because to a first-order approximation charge transfer for the 1:2 intermetallic compounds occurs between the transition metal and one Al atom, while the other Al atom remains neutral. Ionic bonding involves two steps, the transfer of 1.5 charges of s- and p-electrons from Al to the transition metal, and back-bonding of a fraction of the electrons from the transition metal to Al. Should one B atom remain neutral, the covalent bonding energy is the same for 1:1 AB and 1:2 AB_2 transition metal aluminides where A is the same because the B atom does not participate in electron orbital overlap. The back-bonding term is incorporated as percentage ionicity and used to correct the oversimplification due to the first-order approximation. The percentage ionicity indicates the stability of the intermetallics and generally varies smoothly across Mendeleev's table. This periodic trend allows us to use the Brewer–Engel Theory to predict thermodynamic values for acid-base intermetallic compounds.

2.3. Example of calculation

For the sake of example the bonding energy calculations for ScAl_2 is illustrated. The gaseous ground state electron configuration for Al is $3s^2p$ and for Sc is $3d^4s$. The addition of Al causes depromotion of the s-electron of Sc to yield a $3d^3$ electron configuration. The Al s^2 electron pair bonds with the vacant s-orbital of Sc, and the p-electron is shared. Three Sc d electrons are available for bonding. Eq. (4) illustrates that the covalent bonding energy is equal to:

$$\begin{aligned} \Delta; E_{\text{covalent}}/R &= N_{s,\text{Sc}}E_{s,\text{Sc}}/R + N_{p,\text{Sc}}E_{p,\text{Sc}}/R \\ &+ N_{d,\text{Sc}}E_{d,\text{Sc}}/R \\ &+ N_{s,\text{Al}}E_{s,\text{Al}}/R \\ &+ N_{p,\text{Al}}E_{p,\text{Al}}/R \end{aligned} \quad (4)$$

$$1(25.5) + 0.5(25.5) + 3(11.5) + 1(27.1) + 0.5(27.1) \text{ kK} = 113.4 \text{ kK}$$

For the 1:2 AB_2 MgCu_2 crystal structure, the average coordination number is:

$$\begin{aligned} \langle \text{CN} \rangle &= 2x/(x+y) \cdot \text{CN}(A) = [2^*1/(1+2)] \cdot 12 \\ &= 8 \end{aligned} \quad (5)$$

Therefore, the Madelung constant for the MgCu_2 crystals from Eq. (6) is:

$$\begin{aligned} M &= r_{\text{AB}}/r_{\text{avg}}(x+y)[\langle \text{CN} \rangle/(1+\langle \text{CN} \rangle)] \\ &= 1(1+2)[8/(1+8)] \pm 1.4\% = 2.67 \pm 0.04 \end{aligned} \quad (6)$$

Furthermore:

$$r_{AB} = 11^{1/2}a/8 = 11^{1/2}(0.7580)/8 \text{ nm}$$

$$= 0.3143 \times 10^{-9} \text{ m} \quad (7)$$

From Eq. (2), the value of the ionic bonding energy for 100% charge transfer is then:

$$\Delta; E_{\text{ionic}}/R(\text{for } 100\% \text{ charge transfer})$$

$$= NMz_A z_B e^2 / R4\pi\epsilon_0 r_{AB}$$

$$= (6.022 \times 10^{23} / \text{mol})(2.67 \pm 0.04)(1.5)^2(4.803$$

$$\times 10^{-10} \text{ esu})^2 (1C/2.998$$

$$\times 10^9 \text{ esu})^2 / (8.3144 \text{ J/K} \cdot \text{mol}(4\pi)(8.854188$$

$$\times 10^{-12} \text{ C}^2/\text{J} \cdot \text{m})(0.3143 \times 10^{-9} \text{ m}) \quad (8)$$

$$= 319.40 \pm 4.47 \text{ kK}$$

From Eq. (3), and taking the relevant data from Table 1, we obtain:

$$E_{\text{total}}/R = \Delta; H_{\text{subl.Sc}}/R + 2(\Delta; H_{\text{subl.Al}}/R)$$

$$+ EA_{\text{Sc-1.5}}/R + \Delta; PE_{\text{Sc}}/R$$

$$+ \Delta; IE_{\text{Al+1.5}}/R - \Delta; H_{\text{f.ScAl2}}/R$$

$$= (45.5 \pm 0.5) + (79.3 \pm 0.6) + (-3.27)$$

$$+ (3 \pm 2) + (178.66) - (-17.2 \pm 0.4) \text{ kK} \quad (9)$$

$$= 320.29 \pm 2.18 \text{ kK}$$

By subtracting Eq. (9) and (4) we calculate the ionic contribution to the bond as:

$$E_{\text{ionic}}/R = \Delta; E_{\text{total}}/R - \Delta; E_{\text{covalent}}/R$$

$$= (320.29 \pm 2.18) - 113.4 \text{ kK}$$

$$= 206.89 \pm 2.18 \text{ kK} \quad (10)$$

and then,

$$\% \text{ Ionicity} = \Delta; E_{\text{ionic}}/R$$

$$\div \Delta; E_{\text{ionic}}/R (100\% \text{ charge transfer})$$

$$= 65 \pm 1\%$$

and

$$\text{electrons transferred} = 1.5 (\% \text{ Ionicity})$$

$$= 1.5 (0.6477 \pm 0.0114) = 0.97$$

Thus, with back-bonding, the approximate electron configuration for ScAl₂ is AlSc^{-0.97}(d^{3s^{0.65}p^{0.32}}) Al^{+0.97}(s^{1.35}p^{0.68}).

3. Results

In Tables 1 and 2 are reported, respectively, the thermodynamic and structural data used for calculating

bonding energies for the 1:2 AB₂ transition metal aluminides, and the results of the calculations.

Referring to Table 1, column 1 represents the 1:2 transition metal compounds with the non-transition Al metal. Column 2 contains the enthalpy of sublimation for the transition metals, divided by R ($\Delta H_{\text{subl,A}}/R$) [12,13]. The enthalpy of sublimation for Al is $39.65 \pm 3 \text{ kK}$ [12]. Column 3 contains the electron affinity for the transition metals, divided by R ($\Delta EA_A/R$) [14–16]. Column 4 contains the standard enthalpy of formation for the intermetallic, divided by R ($\Delta H_{\text{f,AB2}}/R$) [17–25]. The enthalpies enclosed in parentheses are predicted values. For PmAl₂, the enthalpy of formation was predicted by a graphical interpolation of the experimental values for the 1:2 AB₂ lanthanide aluminides. For FeAl₂, ZrAl₂, and HfAl₂, the enthalpies of formation were estimated to be $3 \pm 2 \text{ kK}$ less negative than the experimental values obtained from the actual non-MgCu₂ type crystal structures because they are more thermodynamically favourable. Thus, the MgCu₂ phase is expected to be metastable for these intermetallics. Intermetallics for which no stable MgCu₂ phase are reported are also presumed to be metastable, except for PmAl₂ which is expected to be a stable phase because the rest of the AB₂ lanthanide aluminides have a stable MgCu₂ phase. Predicted metastable MgCu₂ phases for the intermetallics are indicated in italics. The rest of the enthalpies enclosed in parentheses are predicted from the modified Born–Haber cycle calculations as explained in ensuing text. Column five contains the available lattice constants for the intermetallics [26]. Column 6 contains the interatomic distance of the compounds, r_{AB} . When the lattice constant is given, the interatomic distance is calculated using Eq. (7). When the lattice constant is unavailable the interatomic distance is taken from literature estimates. These estimates are based on the summation of radii of the transition metal and aluminum [27,28], multiplied by a scaling factor for the effect of contraction due to bonding. A comparison of the interatomic distance for the 1:1 and 1:2 intermetallics for which the lattice constant is known, shows that the interatomic distance for the 1:1 and 1:2 AB₂ compounds for identical A and B elements is nearly the same. The additional error for assuming the same values is 2%. The error in the original estimate for the 1:1 intermetallic was 3%. Thus, the total uncertainty is 4%: the interatomic distance for the 1:2 AB₂ intermetallics in column six marked in parentheses are the same as those for the corresponding 1:1 AB intermetallics, with an uncertainty of 4%.

Referring to Table 2, column 1 contains the 1:2 transition metal compounds with the non-transition Al metal. Column 2 contains the covalent energy as obtained from Eq. (1). The bonding values per s-, p-, d-, f- electrons for the transition metals were obtained from Ref. [7]. The bonding value per s- and p-electrons for Al

Table 1
Thermodynamic and structural parameters of the 1:2 MgCu₂ intermetallics of transition metals with aluminum

AB ₂	$\Delta H_{\text{subl,A}}/R$ (kK)	$\Delta EA_{\text{A}}/R^{\text{a}}$ (to A ^{-1.5} _{gs}) (kK)	$\Delta H_{\text{f,AB}_2}/R$ (kK)	Lattice constant (a) (nm)	r_{AB} Interatomic distance (nm)
ScAl ₂	45.4±0.5	-3.27	-17.2±0.4	0.7580	0.3143
TiAl ₂	56.8±0.1 ^b	-1.38	(-15±20) ^{b,c}	(0.672)	(0.2786±0.0111)
VAl ₂	61.8±0.1	-9.14	(0±21)	(0.642)	(0.2662±0.0106)
CrAl ₂	47.8±0.5	-11.59	(-32±21)	(0.630)	(0.2613±0.0105)
MnAl ₂	33.97±0.2	0	(-29±21)	(0.632)	(0.2620±0.0150)
FeAl ₂	50.5±0.2	-2.84	(-6.4±2)	(0.607)	(0.2518±0.0101)
CoAl ₂	51.2±0.3	-11.51	(-27±22)	(0.598)	(0.2478±0.0099)
NiAl ₂	51.5±0.2	-20.12	(-29±23)	(0.601)	(0.2494±0.0100)
YAl ₂	50.8	-5.34	-18.2±0.4	0.7855	0.3257
ZrAl ₂	72.7±0.5	-7.42	(-15.8±2)	(0.704)	(0.2918±0.0117)
LaAl ₂	51.9±0.5	8.7	-19.6±0.4	0.814	0.3375
CeAl ₂	49.9±0.3	8.7	-18.8±0.4	0.8060	0.3341
PrAl ₂	42.8±0.3	0	-19.5±0.4	0.800	0.3317
NbAl ₂	39.4±0.3	-5.2	-19.30.4	0.800	0.3317
PmAl ₂	(37) ^c ±1.5	-5.2	(-19.5±0.7)	(0.752)	(0.3119±0.0125)
SmAl ₂	24.9±0.3	5.2	-19.6±0.4	0.7942	0.3293
EuAl ₂	21.34±0.1	-5.2	-13.0±0-.4	0.8128	0.3370
GdAl ₂	47.9±0.3	8.7	-19.2±0.4	0.7900	0.3275
TbAl ₂	46.7±0.3	8.7	-18.9±0.4	0.787	0.3263
DyAl ₂	35.02±0.5	-5.2	-19.0±0.4	0.7840	0.3250
HoAl ₂	36.18±0.1	-5.2	-18.9±0.4	0.78173	0.3241
ErAl ₂	37.9±0.2	-5.2	-18.2±0.4	0.779	0.3230
TmAl ₂	27.9±0.5	5.2	-18.4±0.4	0.7780	0.3225
YbAl ₂	18.6±0.2	-5.2	-13.8±0.4	0.7781	0.3267
LuAl ₂	51.43±0.1	8.7	18.98±1.08	0.7742	0.3210
HfAl ₂	74.7±0.5	0	(-12.82)	(0.699)	(0.2898±0.0116)
TaAl ₂	94.1±0.3	-5.61	(-220)	(0.674)	(0.2794±0.0112)
WAl ₂	103.4±1	-14.19	(-16±21)	(0.659)	(0.2734±0.0109)
ReAl ₂	93.3±0.8	-2.61	(25±22)	(0.601)	(0.2494±0.0100)
OsAl ₂	94.9±0.5	-19.1	(-13.2±2)	(0.623)	(0.2602±0.0104)
IrAl ₂	80.7±0.8	-27.24	(-19±22)	(0.623)	(0.2585±0.0103)
AcAl ₂	49±1.5	5.2	(-34±19)	(0.730)	(0.30280.0121)
ThAl ₂	71.8±0.7	8.7	(-6±16)	0.7970	0.3304
PaAl ₂	66.3±3	5.2	(-19±20)	(0.721)	(0.2953±0.0118)
UAl ₂	63.6±0.2	5.2	-11.2±1.2	0.778	0.3225
NpAl ₂	55.9±1	5.2	(-4±16)	0.7808	0.3237
PuAl ₂	41.5±0.3	-5.2	-17.08±0.36	0.7838	0.3249
AmAl ₂	34.21	-5.2	(-9±16)	0.7861	0.3259
CmAl ₂	46.6±0.5	5.2	(-41±20)	(0.698)	(0.2894±0.0116)
BkAl ₂	37.3±0.8	-5.2	(-66±20)	(0.690)	(0.2860±0.0114)
CfAl ₂	23.6±1	-5.2	(-9±18)	(0.758)	(0.3143±0.0126)
EsAl ₂	16±1	-5.2	(-16±18)	(0.754)	(0.3130±0.0125)
FmAl ₂	(17)±2.5	-1.7	(-5±18)	(0.752)	(0.3117±0.0125)
MdAl ₂	(14)±2.5	17.4	(7±18)	(0.749)	(0.3104±0.0124)

^a The $\Delta EA_{\text{A}}/R$ values are 1.5 times the value per unit charge.

^b The values in italics are for predicted metastable MgCu₂ phases.

^c The numbers in parentheses are predicted values.

(27.1 kK) is obtained from the summation of the ground state solid, Al_(s), to the ground state gas, Al_(g) s²p (39.65 kK), and the promotion energy to the valence state gas, Al_(g) sp² (41.754 kK) [9], divided by three electrons. The covalent energies for SmAl₂ and YbAl₂ are predicted based on an average value of bonding for the s- and p-electrons between their divalent and trivalent states. Column 3 contains the ionic energy for 100% charge transfer as obtained by Eq.(2). Column 4 contains the total energy obtained from Eq. (3). Column 5 contains the ionic energy as obtained from Eqs. (2)

and (10). Column 6 contains the percentage ionicity factor derived as the adjusted ionic energy [Eq. (10)] divided by the ionic energy for 100% charge transfer [Eq. (2)]. The values range from 51 to 77%. The percentage ionicities for 1:2 MgCu₂ transition metal aluminides are somewhat lower than those for the corresponding 1:1 CsCl transition metal aluminide compounds, that range from 57 to 87%. Column 7 contains the number of electrons transferred, defined as 1.5 times the percentage ionicity for the aluminide compounds. As the back-bonding correction includes

Table 2

Calculation of the percentage ionicity for the 1:2 MgCu₂ intermetallics of transition metals with aluminum^a

AB ₂	$\Delta E_{\text{covalent}}/R$ (kK)	$\Delta E_{\text{ionic}}/R$ (100% charge transfer) (kK)	$\Delta E_{\text{total}}/R$ (kK)	$\Delta E_{\text{ionic}}/R$ (kK)	Ionicity (%)	Electrons transferred
ScAl ₂	113.4	319±4	320±2	207±	65±1	0.97±0.02
TiAl ₂	108.4 ^b	(360±15) ^{b,c}	(332±20)	(223±20)	(62±5)	(0.93±0.08)
VAl ₂	91.0	(377±16)	(313±21)	(221±21)	(59±5)	(0.89±0.08)
CrAl ₂	109.8	(384±16)	(329±21)	(219±21)	(57±5)	(0.86±0.08)
MnAl ₂	116.9	(383±16)	(324±21)	(207±21)	(54±5)	(0.81±0.08)
FeAl ₂	110.4	(399±17)	(315±3)	(205±3)	(51±2)	(0.77±0.03)
CoAl ₂	104.9	(405±17)	(328±22)	(223±22)	(55±5)	(0.83±0.08)
NiAl ₂	83.6	(402±17)	(321±22)	(227±22)	(59±5)	(0.89±0.08)
YAl ₂	130.4	308±4	325±2	194±2	63±1	0.95±0.02
ZrAl ₂	141.4	(344±15)	(342±3)	(201±3)	(58±3)	(0.88±0.04)
LaAl ₂	113.4	297±4	341±2	228±2	77±1	1.15±0.02
CeAl ₂	110.6	300±4	338±2	228±2	76±1	1.14±0.02
PrAl ₂	104.7	303±4	323±2	219±2	72±1	1.08±0.02
NdAl ₂	103.9	303±4	314±2	211±2	70±1	1.04±0.02
PmAl ₂	104.0	(322±14) ^c	(312±3)	(208±3)	(65±3)	(0.97±0.04)
SmAl ₂	(102.4)	305±4	311±2	(208±3)	(68±2)	(1.02±0.02)
EuAl ₂	100.74	298±4	290±2	189±5	64±2	0.95±0.03
GdAl ₂	120.8	306±4	337±2	216±2	70±1	1.06±0.02
TbAl ₂	110.5	308±4	335±2	225±2	73±1	1.10±0.02
DyAl ₂	112.8	309±4	310±2	197±2	64±1	0.96±0.02
HoAl ₂	113.1	310±4	311±2	198±2	64±1	0.96±0.02
ErAl ₂	113.4	311±4	312±2	199±2	64±1	0.96±0.02
TmAl ₂	111.5	311±4	312±2	201±2	65±1	0.97±0.02
YbAl ₂	(125±6)	307±4	288±2	(163±6)	(53±2)	(0.80±0.04)
LuAl ₂	137.3	313±4	340±2	203±2	65±1	0.97±0.02
HfAl ₂	155.8	(346±15)	(348±3)	(193±3)	(56±3)	(0.8±0.04)
TaAl ₂	146.3	(359±15)	(351±20)	(205±20)	(57±5)	(0.86±0.08)
WAl ₂	157.2	(367±16)	(366±20)	(209±20)	(57±5)	(0.86±0.08)
ReAl ₂	147.3	(402±17)	(377±22)	(229±22)	(57±5)	(0.86±0.08)
OsAl ₂	131.2	(396±16)	(350±13)	(219±3)	(57±3)	(0.85±0.04)
IrAl ₂	118.8	(388±16)	(333±22)	(221±22)	(57±5)	(0.86±0.08)
AcAl ₂	126.9	(331±14)	(349±19)	(222±19)	(67±5)	(1.01±0.08)
ThAl ₂	147.3	304±4	(348±15)	(200±15)	(66±5)	(0.99±0.08)
PaAl ₂	141.0	(340±14)	(352±19)	(211±19)	(62±5)	(0.93±0.08)
UAl ₂	153.6	311±4	341±2	187±2	60±1	0.90±0.02
NpAl ₂	155.6	310±4	(326±16)	(171±16)	(55±5)	(0.83±0.08)
PuAl ₂	134.4	309±4	314±2	180±2	58±1	0.87±0.02
AmAl ₂	132.6	308±4	(299±16)	(166±16)	(54±5)	(0.81±0.08)
CmAl ₂	145.7	(347±15)	(354±19)	(208±19)	(60±5)	(0.90±0.08)
BkAl ₂	137.9	(351±15)	(359±20)	(221±20)	(63±5)	(0.95±0.08)
CfAl ₂	116.2	(319±14)	(289±18)	(172±18)	(54±5)	(0.81±0.08)
EsAl ₂	114.9	(321±14)	(288±18)	(173±18)	(54±5)	(0.81±0.08)
FmAl ₂	107.7	(322±14)	(282±18)	(174±18)	(54±5)	(0.81±0.08)
MdAl ₂	107.7	(323±14)	(286±18)	(178±18)	(55±5)	(0.83±0.08)

^a Table calculated by S. Hahn.^b The values in italics are for predicted metastable MgCu₂ phases.^c The numbers in parentheses are predicted values.

correction for use of the average bonding energy, as well as other corrections, the percentage ionicity and the number of electrons transferred are not quite accurate, but yield approximate values.

When an experimental value for the enthalpy of formation of a compound is not available, a predicted value for percentage ionicity was assumed from which ΔE_{ionic} , ΔE_{total} , and ultimately $\Delta H_{\text{f,AB}_2}$ can be calculated using the modified Born–Haber cycle equations. Predicted values are enclosed in parentheses in Table 2.

The percentage ionicity is expected to vary smoothly across Mendeleev's Table. This means that for TiAl₂, VAl₂, CrAl₂, and MnAl₂, and for CoAl₂ and NiAl₂, the percentage ionicity is linearly interpolated to the nearest integer from the percentage ionicity values of the two respective adjacent compounds in Table 2. Compounds are listed in order of the elements in Mendeleev's Table. NbAl₂, MoAl₂, TcAl₂, RuAl₂, RhAl₂, and PdAl₂ are omitted from the table: the percentage ionicity is difficult to predict because experimental enthalpies of

formation data are not available in the literature for these intermetallics. For PtAl_2 , with the filled d-orbital of Pt, the percentage ionicity is too difficult to predict, and exhibits a significant jump in the smooth trend in the ionicity for the AB 1:1 transition metal aluminide compounds. As a first approximation, the percentage ionicity values for the actinide aluminide compounds is estimated to be 10% lower than for the corresponding lanthanide aluminide compounds with increased uncertainties of 5%, provided that the calculated results for the percentage ionicity for UAl_2 is 10% less than for NdAl_2 , and for PuAl it is 10% lower than for SmAl_2 .

4. Conclusions

The Brewer–Engel Theory can be used to yield accurate predictions for thermodynamic properties of generalized acid-base interactions in intermetallics. Following previous work on 1:1 CsCl type structures of transition metals with Al and Mg [10] in this paper we extended this approach in particular to the calculation of percentage ionicity for transition metals dialuminides. The stability of 1:2 MgCu_2 type intermetallics of transition metals with Al is due to a high degree of charge transfer. Similar calculations will be performed and presented separately for a variety of crystal structures. In addition we plan to conduct experimental work, e.g. using high-temperature galvanic cell technique, to characterize thermodynamically some extraordinarily stable alloys containing lanthanides and actinides predicted through the use of the Brewer–Engel model. To this end a collaboration with Los Alamos National Laboratory (Lashley and colleagues [29–32]) is also planned in order to complement galvanic cell measurements with specific-heat determinations on these alloys.

Intermetallic systems designer for various specific applications may be predicted using the model. A suggested application is the removal of radioactive elements from nuclear power plants by addition of an element that can form a quite stable intermetallic phase with the elements to be removed. Another application is the use of stable intermetallic phases, engineered with desired stoichiometries, as catalysts containing a variety of elements that would play special roles in the field of catalysis or in the field of magnetic materials applications.

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