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THE ELECTRONIC CONFIGURATIONS AND ENERGIES IN SOME THERMODYNAMICALLY CORRELATED LAVES COMPOUNDS

by

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ABSTRACT

The known electronic configurations of simple elements in Laves compounds are correlated with those of the more complex systems to determine their electronic configurations and gaseous state promotion energies.

I. INTRODUCTION

The formation of intermetallic compounds is usually accompanied by a size change of the atoms involved in going from their pure solid state to the alloy form. In AB_2 type Laves compounds the structural features permit unambiguous determination of interatomic distance in the compound. The radius ratio R_A/R_B in these compounds is very close to 1.225. A linear correlation of R_A/R_B with the heat of formation, ΔH_f^0 was found to occur between metals of equal valence.^{1,2} Some compounds such as UAl_2 and $PuAl_2$ with radius ratios of 1.077 and 1.064 seem to lie below the limit where this type of compound should be stable.

Zachariasen³ has correlated the unalloyed metallic radius with the number of bonding electrons in a given element as a means of deducing the metallic valence for the element. In this paper, use will be made of these radii to show the relationship between heat of formation, ΔH_f^0 , and cohesive energy, E_{coh} . It will be shown that this relationship can be used to determine electronic configurations and gaseous state promotion energies.

II. CORRELATION OF ΔH_f^0 vs R_A/R_B FOR COMPOUNDS THAT HAVE UNALLOYED METALS OF UNEQUAL VALENCE

Experimental evidence⁴ indicates that metals capable of valence change increase valence when alloyed with metals of higher valence and decrease it when alloyed with a metal of lower valence. The compounds UAl_2 , $PuAl_2$, $CeAl_2$, $YbAl_2$ and $NaCd_2$ are examples of Laves compounds which have unequal valence before alloy formation. The metals U, Pu, Ce and perhaps Yb are believed to be able to change valence by promoting f electrons. We will consider all non-f electrons as valence electrons. Since Al is unlikely to differ from a valence of 3 we will assume that U, Pu and Ce achieve a valence of 3 when alloyed with Al. The radius ratios for these compounds with valence 3 are given in Table I. It will be noted in Figure 1 that the $\Delta H_{f_{298}}^0$ values plotted as a function of R_A/R_B all lie below the line which correlates the rare earth-aluminum compounds. It will also be noted that the difference is exactly equal to the heat of fusion, ΔH_m , of the A metal in each case. A test of plotting $YbAl_2$ with Yb as divalent or as trivalent leaves no doubt that the perfect fit requires Yb to be divalent. Other evidence⁵ indicates that it is either divalent or mostly divalent at 298 K. In the compound $NaCd_2$ neither metal is likely to have more than one valence. It can be seen from Figure 1 that the $\Delta H_{f_{298}}^0$ value for this compound differs from the line correlating the alkali earth-magnesium compounds by exactly the heat of fusion of Na.

The rare earth-aluminum compounds whose metals have equal valence at room temperature have $\Delta H_{f_{298}}^0$ value given by

$$-\Delta H_{f_{298}}^2 = 560.37 - 389.15 R_A/R_B \text{ kJ/g-atom.} \quad (1)$$

All other compounds in this group are given by

$$-\Delta H_{f_{298}}^0 = -\Delta H_{f_{298}}^2 + \Delta H_f^3, \quad (2)$$

where ΔH_f^3 is the heat of fusion of the A metals, Ce, Pu, U and Yb.

The line correlating the alkali metal-magnesium compounds is given by

$$-\Delta H_{f_{298}}^2 = 97.48 - 67.91 R_A/R_B \text{ kJ/g-atom} \quad (3)$$

TABLE I
COMPARISON OF CALCULATED AND EXPERIMENTAL HEATS OF FORMATION

Compound	Valence of A	R_A/R_B	ΔH_m of A kJ/g-at.	$-\Delta H_{f298}^0$ kJ/g-atom		Ref.
				Calc.	Exptl.	
CeAl ₂	3	1.287	5.18	54.4	54.4	12
LaAl ₂	3	1.311	-	50.2	50.2	13
PrAl ₂	3	1.277	-	63.4	62.8	14
PuAl ₂	3	1.306	3.93	48.2	47.4	15
UAl ₂	3	1.327	12.95	31.1	31.1	16
YbAl ₂	2	1.355	7.66	25.4	25.7	17
CaCd ₂	2	1.260	-	36.1	41.1	18
MgZn ₂	2	1.149	-	17.6	17.9	11
PuFe ₂	6	1.198	-	16.6	16.6	1
PuOs ₂	6	1.132	-	5.2	4.9	1
PuRu ₂	6	1.143	-	7.1	7.4	1
UFe ₂	6	1.208	-	18.3	20.6	2
BaMg ₂	2	1.396	-	2.7	2.1	19
CaMg ₂	2	1.233	-	13.7	13.4	19
NaCd ₂	1	1.219	2.6	11.0	11.3	10
SrMg ₂	2	1.343	-	6.3	7.1	19

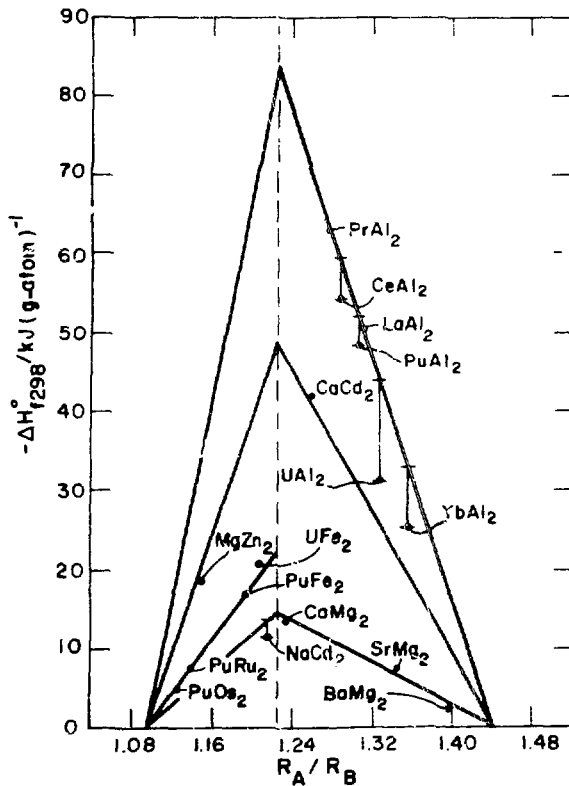


Fig. 1. Heat of formation vs geometry factor for some AB₂ Laves compounds.

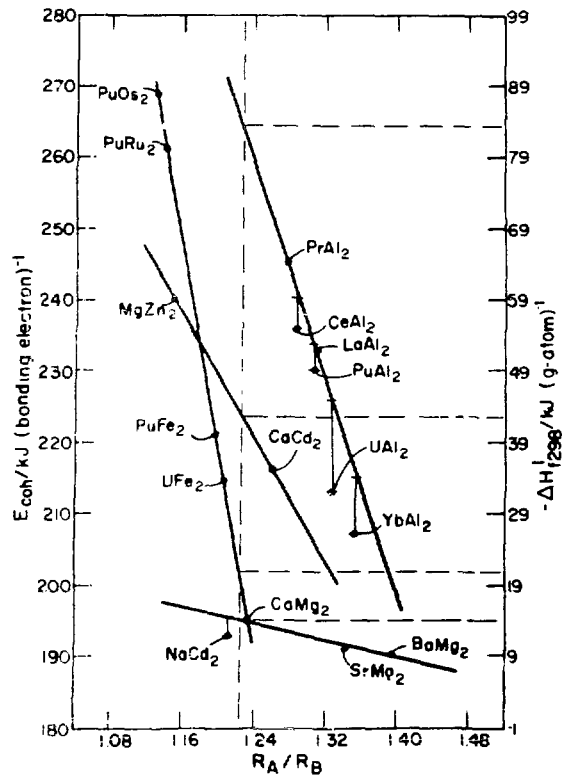


Fig. 2. Cohesive energy vs geometry factor for some AB₂ Laves compounds.

Since a break occurs in the correlation line at $R_A/R_B = 1.225$ we will refer to the ΔH value at this point as $\Delta H_{f,298}^1$. The correlation line for CaMg_2 , BaMg_2 has a $\Delta H_{f,298}^1$ value of -14.3 kJ/g-atom. The corresponding line connecting this point and $\Delta H_{f,298} = 0$ at $R_A/R_B = 1.1$ is given by

$$-\Delta H_{f,298}^2 = -120.32 + 109.89 R_A/R_B \text{ kJ/g-atom} \quad (4)$$

The $\Delta H_{f,298}^0$ for NaCd_2 is given by Eq. 2 with ΔH_f^3 the heat of fusion of Na.

The heat of formation may be viewed as consisting of three parts. The first term ΔH_f^1 resulting from chemical properties of the two metals is increased to ΔH_f^2 to meet structural size requirements. A third term ΔH_f^3 is related to an electronic configurational change required to accommodate unequal valences.

III. DETERMINATION OF ΔH_f^1 FROM COHESIVE ENERGIES

The cohesive energy, E_{coh} , will be defined here as the energy required to atomize a neutral element and promote it to a particular electronic configuration in the gaseous state. Brewer has tabulated cohesive energies for a large number of elements and electronic configurations⁶ and lists promotion energies for actinides and lanthanides.⁷ All E_{coh} values not calculated from correlated ΔH_f^1 values in the present paper will be taken from these two references. Heats of fusion were taken from Hultgren et al.^{8,9} The total cohesive energy will be calculated by the relation.

$$E_{\text{coh}}^t = \Delta H_{v,0} + E_p \quad (5)$$

where $\Delta H_{v,0}$ is the heat of vaporization of the element at 0 K and E_p is the promotion energy from the gaseous ground state to the electronic configuration of interest. E_{coh} will be the symbol for the cohesive energy per bonding electron, determined by dividing the total cohesive energy, E_{coh}^t , by the number of bonding electrons. The cohesive energy per bonding electron of the compound will be calculated for the AB_2 laves compound from

$$E_{\text{coh}}(\text{AB}_2) = 1/3 E_{\text{coh}}(\text{A}) + 2/3 E_{\text{coh}}(\text{B}) \quad (6)$$

A. Cohesive Energies for Correlated Group I Compounds

The cohesive energies for the compounds BaMg_2 , CaMg_2 , NaCd_2 and SrMg_2 are given in Table II. There seem to be little choice of electronic configuration for the first and third groups of correlated compounds. The least squares line which fits the compounds BaMg_2 , SrMg_2 and CaMg_2 is

$$E_{\text{coh}} = 232.2 - 30.32 R_A/R_B \text{ kJ/electron} \quad . \quad (7)$$

The value for NaCd_2 differs from this line as seen in Figure 2 by ΔH_f^3 (Na), the heat of fusion of Na. We see that if the ΔH_f^1 values are proportional to E_{coh}^1 then

$$-\Delta H_f^1 = E_{\text{coh}}^1 - 180.7 \text{ kJ/g-atom} \quad , \quad (8)$$

where $E_{\text{coh}}^1 = E_{\text{coh}}$ at $R_A/R_B = 1.225$.

B. Cohesive Energies for Correlated Group II Compounds

In order for cohesive energies of the compounds PuOs_2 , PuRu_2 , PuFe_2 and UFe_2 as well as the value of $\Delta H_{f_{298}}^1$ to be on the same line, the cohesive energy of Pu must be 451 kJ/electron. When compared to the possible electronic configurations and their promotion energies for Pu, it seems likely that the $5f^26d^47s7p$ configuration which allows electrons to be shared with the $3d^64s4p$ configuration of iron at the d, s and p levels is the correct one. Each metal is hexavalent. The line describing the cohesive energies for these compounds is

$$E_{\text{coh}} = 1082. - 718.4 R_A/R_B \text{ kJ/electron} \quad . \quad (9)$$

At $R_A/R_B = 1.225$, $E_{\text{coh}}^1 = 202 \text{ kJ/electron}$.

From Eq. 8, $\Delta H_{f_{298}}^1 = -21.3 \text{ kJ/g-atom}$.

The heats of formation for this group are given by

$$-\Delta H_{f_{298}}^0 = -190.5 + 172.9 R_A/R_B \text{ kJ/g-atom} \quad . \quad (10)$$

TABLE II
ELECTRONIC CONFIGURATION AND COHESIVE ENERGIES IN THE GASEOUS
VALENCE STATE AT 0 K FOR CORRELATED GROUP I

Element or Compound	Electronic Configuration in the Compound	Energy Per Bonding Electron kJ	
		Ret. 6	Calc.
BaMg ₂	-	190.0	190.0
Ba	5s6p	163.0	-
Mg	3s3p	203.0	-
CaMg ₂	-	195.0	195.0
Ca	4s4p	178.0	-
NaCd ₂	-	193.0	193.0
Na	3	108.0	-
Cd	5s5p	236.0	-
SrMg ₂	-	191.0	191.0
Sr	5s5p	167.0	-

TABLE III
ELECTRONIC CONFIGURATION AND COHESIVE ENERGIES IN THE GASEOUS
VALENCE STATE AT 0 K FOR CORRELATED GROUP II AND III

Element or Compound	Electronic Configuration in the Compound at 298.15 K	Energy Per Bonding Electron kJ	
		Ret. 6	Calc.
PuFe ₂	-	-	221.0
Pu	5f ⁷ 6d ⁴ 7s7p	-	451.0
Fe	3d ⁶ 4s4p	107.0	-
PuOs ₂	-	-	269.0
Os	5d ⁶ 6s6p	178.0	-
PuRu ₂	-	-	261.0
Ru	4d ⁶ 5s5p	-	167.0
UFe ₂	-	-	215.0
U	6d ⁴ 7s7p	-	431.0
Fe	3d ⁶ 4s4p	107.0	-
CaCd ₂	-	217.0	217.0
Ca	4s4p	178.0	-
Cd	5s5p	236.0	-
MgZn ₂	-	240.0	240.0
Mg	3s3p	203.0	-
Zn	4s4p	258.0	-

C. Cohesive Energies for Correlated Group III Compounds

The two compounds CaCd_2 and MgZn_2 in this group have known cohesive energies and electronic configurations. The line joining the E_{coh} values in Table III is

$$E_{\text{coh}} = 480.7 - 209.6 R_A/R_B \text{ kJ/electron} \quad (11)$$

and $E_{\text{coh}}^1 = 223.9$ which from Equation 8 gives $-\Delta H_f^1 = 43.2$. When a line is drawn between this value and $\Delta H_f^1 = 0$ at $R_A/R_B = 1.1$ the result is described by

$$-\Delta H_f^0 = -379.9 + 345.36 R_A/R_B \text{ kJ/g-atom} \quad (12)$$

from which ΔH_f^0 for CaCd_2 can be calculated. The line between this point and $\Delta H_f^0 = 0$ at $R_A/R_B = 1.44$ is

$$-\Delta H_f^0 = 289.13 - 200 R_A/R_B \text{ kJ/g-atom} \quad (13)$$

from which ΔH_f^0 for CaCd_2 can be calculated.

D. Cohesive Energies for Correlated Group IV Compounds

Promotion energies⁷ for the trivalent Ce, and Pu, and cohesive energies⁶ for Yb and Al are given by Brewer.

As was the case with the compound NaCd_2 the cohesive energy per electron for these metals alloyed with Al must be increased by ΔH_f^3 to be on the line joining LaAl_2 and PrAl_2 . The line is given by

$$E_{\text{coh}} = 741.1 - 389.1 R_A/R_B \text{ kJ/electron} \quad (14)$$

The cohesive energies of this group of compounds couple with the size adjustment energies ΔH_f^2 to form a line terminating at $E_{\text{coh}}^1 = 264.5$ giving $-\Delta H_f^1 = 83.8$ and passing through a point where $\Delta H_f^1 = 0$ at $R_A/R_B = 1.44$ which is identical to the ΔH_f^0 vs R_A/R_B line for this group.

The cohesive energies and electronic configurations are given in Table IV.

TABLE IV
ELECTRONIC CONFIGURATION AND COHESIVE ENERGIES IN THE GASEOUS
VALENCE STATE AT 0 K FOR CORRELATED GROUP IV

Element or Compound	Electronic Configuration in the Compound at 298.15 K	Energy Per Bonding Electron kJ	
		Refs. 6,7	Calc.
CeAl ₂		235.0	235.0
Ce	4f6s6p ²	258.0	258.0
Al	3s3p ²	224.0	-
LaAl ₂	-	-	231.0
La	6s6p ²	-	246.0
PrAl ₂		-	244.0
Pr	4f ² 6s6p ²	-	285.0
PuAl ₂		228.0	229.0
Pu	5f ⁵ 7s7p ²	235.0	239.0
UAl ₂	-	-	212.0
U	5f ³ 7s7p ²	-	188.0
YbAl ₂		210.0	206.0
Yb	4f ¹⁴ 6s7p	181.0	171.0

IV. SUMMARY

The purpose of this paper has been to show by example the energy relationships involved in change of valence, and the proportionality of cohesive energy per electron in the gaseous state to heats of formation, or transition at constant temperature in the solid state. The heats of formation calculated from these relationships are compared to experimental values in Table I. There is very good agreement in all cases with the exception of CaCd₂ for which the selected value is too negative and should be redetermined. The latest value for the $\Delta H_{f,298}^0$ selected for MgZn₂ by Hultgren et al.,¹⁰ -10.9 kJ/g atom, is too positive. The value in Table I is from the work of Biltz.¹¹

It has been noted in Figure 2 that the cohesive energy of the compounds as a function of R_A/R_B forms straight lines all of which have negative slopes. This is undoubtedly the prime factor in causing the $\Delta H_{f,298}^0$ vs $R_A/R_B = 1.225$ to be asymmetric around $R_A/R_B = 1.225$.

The total cohesive energy arrived at for U in the case of UAl₂ is very close to the heat of vaporization if it is assumed that there are only three electrons involved in bonding. Brewer⁶ has treated f electron bonding separately from d, p and s bonding. It appears from this work that in the case of U in UAl₂ all electrons should be treated equally. Assigning a value of 6 bonding electrons, each having 188 kJ cohesive energy we find that the promotion energy

for the $5f^3 7s 7p^2$ configuration is $49.5 \times 10^3 \text{ cm}^{-1}$. Brewer⁷ gives $41 \times 10^3 \text{ cm}^{-1}$ for the $f^4 p^2$ configuration. The $f^3 sp^2$ configuration is not given. There appears to be little f electron bonding in PuAl_2 .

It is too soon to make an attempt to explain from first principles why cohesive energy per electron in the gas phase is proportional to heats of transition or formation per g-atom in the solid phase, or why energy exactly equivalent to the heat of fusion of one g-atom of A is involved in the change of valence of A in one g-atom of AB_2 .

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