YU ISSN 0015—3206
FZKAAA 20 (2) 171 (1988)

STRUCTURAL ENERGETICS OF THE INTERMETALLIC COMPOUNDS $CaMg_2$ AND $CaAl_2$

AHMED M. RADWAN

Theoretical Physics Laboratory, National Research Centre, Cairo, Egypt

Received 18 September 1987

UDC 538.915

Original scientific paper

The structures of the Laves phases $CaMg_2$ and $CaAl_2$ are investigated using the optimised model potential. Charge transfer, which is taken into account in an approximate and simple way, plays an important role in the determination of the stable crystal structures of both $CaMg_2$ and $CaAl_2$.

1. Introduction

The application of pseudo or model potentials in the theory of simple metals was connected with an essential progress in understanding the properties of these metals[1]. Especially it is possible to calculate the observed stable structures by comparing the energy of different structures and looking for the lowest one. These calculations are successful for pure metals[2,3,4].

The question arises, whether it is possible to extend these investigations to intermetallic compounds (IMC), but only few results are available[5,6,7]. It should be borne in mind that there are some additional complications for IMC compared with pure metals. Small reciprocal lattice vectors lower the convergence of the perturbation series. There are stronger deviations of the charge density from a constant value which may not be included in linear screening. This means that charge transfer plays an important role. Furthermore, the situation is complicated by the large differences in the electrostatic energies E_{es} of the structures of the compounds to be compared[8], contrary to the case of simple metals where E_{es} of FCC, BCC and HCP structures is nearly the same. Thus it is of interest to investigate to what extent the pure metal scheme for the calculation of the structural

energy E_{st} in second order perturbation theory is applicable to intermetallic compounds. We have already investigated this question in the case of the Laves phase $MgZn_2$[7] where both Mg and Zn have the same valence 2. But in the present paper we have a further difficulty arising from the fact that in $CaAl_2$, Ca and Al have different chemical valencies, 2 and 3, respectively. This means a further departure from linear screening than in case of $MgZn_2$. The Laves phases are the largest group of IMC and there is some evidence that the structures C14 and C15[9] are electronic phases like HCP and FCC for pure metals. C14 and C15 are close-packed structures of two sorts of spheres with the ideal diameter ratio $\sqrt{3/2}$[9], analogous to HCP and FCC structures for one sort of spheres. The fact that model potential theory is applicable to simple metals only but not to transition metals makes a drastic limitation on its use for IMC. There are only few Laves phases consisting of two simple metals.

2. *Structural energy of compounds and binary alloys*

The structural energy per ion E_{st} is the sum of two terms[1] (at temperature $T = 0$ and a fixed volume)

$$E_{st} = E_{es} + E_{bs}. \tag{1}$$

E_{es} is the electrostatic energy and E_{bs} is the band structure energy, which has to be calculated to second order perturbation using Shaw's optimized model potential[10]. The Laves phases C14 ($MgZn_2$) and C15 ($MgCu_2$) may be considered as a stacking sequence of three different types of layers as described in Ref. 8: Ca planes (α, β, γ), MgI (or AlI) planes (a, b, c) and MgII (or AlII) Kagomé nets (A, B, C). A certain structure is characterized by noting the positions of the Kagomé nets only. For example C14 = β B β a γ C γ a = BC, C15 = α A α c β B β a γ C γ b = ABC. Therefore, in the structural energy of a structure J,

$$E_{st}(J) = \sum_{\mathbf{g}}{}' E_{\mathbf{g}}(j) + Const., \quad E_{\mathbf{g}}(J) = \sum_{M,M'} S^{J}_{M}(\mathbf{g})\, S^{*}_{M'}\, J(\mathbf{g})\, f_{MM'}(\mathbf{g}). \tag{2}$$

The summations are carried out over planes at first and over a special stacking sequence secondly as described in Ref. 8. $S^{J}_{M}(\mathbf{g})$ is the structure factor of atoms of sort M (M = Ca, MgI or AlI, MgII or AlII) and $f_{MM'}(\gamma)$ is given by

$$f_{MM'}(\mathbf{g}) = \frac{2\pi}{V g^2} Z_M Z_{M'} (e^{-g^2/4\lambda} - \overline{F}^{N}_{MM'}(\mathbf{g})). \tag{3}$$

V is the volume per ion, Z_M and $Z_{M'}$ are the effective valencies (or charges) of atoms of type M and M', respectively, λ is the parameter of the Gaussian caps and

$$\overline{F}^{N}_{MM'}(q) = \frac{1}{2}[F^{N}_{MM'}(q) + F^{N}_{M'M}(q)]. \tag{4}$$

$F^N_{MM'}(q)$ is the normalized energy wave number characteristic which is defined analogous to that of simple metals[11] as (in Hartree approximation)

$$F^N_{MM'}(q) = \frac{-q^2 V^2}{4\pi^4 Z_M Z_{M'}} \int_{k<k_F} d^3k \frac{w_n(\mathbf{k}, \mathbf{q}) u^0_{M'}(\mathbf{k}, \mathbf{q})}{k^2 - |\mathbf{k} + \mathbf{q}|^2} \tag{5}$$

Expressions for the screened form factor $w_M(\mathbf{k}, \mathbf{q})$ of atoms of type M and the unscreened one u^0_M, $(\mathbf{k}, \mathbf{q})$ of the M'-atoms are identical with those given by Shaw[10]. Corrections due to exchange and correlation are then added, however, our treatment is somewhat different from that of Shaw[12]. The final formula for $F^N_{MM'}$ is given in Ref. 13. Eq. (2) has then the form:

$$E_\theta(J) = \frac{1}{N^2} \mathrm{Re} \sum_{\mathbf{q}_\perp} \sum_{M=1}^{3} \sum_{M'=M}^{3} \sum_{L=1}^{3} \sum_{L'=k}^{3} (2 - \delta_{MM'} \delta_{LL'}) SM(J, L, \mathbf{g}_\perp) \cdot$$

$$\cdot SM^*(J, L', \mathbf{g}_\perp) W_{MM'LL'}(\mathbf{g}_\perp) \tag{6}$$

where in the summation over L': $k = L$ if $M = M'$ and $k = 1$ otherwise and

$$W_{MM'LL'}(\mathbf{g}_\perp) = \sum_{\mathbf{g}_\parallel} Sl(L, \mathbf{g}_\parallel) S\,l(L', \mathbf{g}_\parallel) S2(M, L, \mathbf{g}_\parallel) S\,2(M', L', \mathbf{g}_\parallel) \cdot$$

$$\cdot f_{MM'}(\sqrt{\mathbf{g}^2_\parallel + \mathbf{g}^2_\perp}). \tag{7}$$

$Sl(L, \gamma_\parallel)$ is the structure factor of the inversion centre of the layer with position L. $S2(M, L, \mathbf{g}_\parallel)$ is the structure factor of the layer in the position L and containing atoms of type M. $SM(J, L, \mathbf{g}_\perp)$ is the structure factor of the sequence of layers with position Δ and atom type M[8]. It should be noticed that both structure factors $Sl(L, \mathbf{g}_\parallel)$ and $S2(M, L, \mathbf{g}_\parallel)$ are independent of the structure under consideration, but $SM(J, L, \mathbf{g}_\perp)$ is a structure dependent one[8].

3. Results and discussion

The experimentally observed structure of $CaMg_2$ is C14 = BC, whereas that of $CaAl_2$ is C15 = ABC. The alloy-values of h_F are: $k_F(CaMg_2) = 0.67763$ and $k_F(CaAl_2) = 0.81649$, corresponding to atomic volumes $V = 190.32$ and 145.06 au, respectively. We have calculated $\bar{F}^N_{MM'}$ for $CaMg_2$ and $ACal_2$ from 0 to $6k_F$ at intervals $TQ = 0.04\,k_F$ using the exchange and correlation function of Singwi et al.[14] and the model potential parameters of Appapillai and Heine[15] for Ca, Mg and Al. However, the use of model potential parameters of pure Ca, Mg and Al in the calculations concerning $CaMg_2$ and $CaAl_2$ is justified only by assuming that the change in the model potential parameters of pure metals upon alloying is very small, like $MgZn_2$ (less than 2%)[16]. Obviously, the effective charges Z_{Ca},

Z_{Mg} and Z_{Al} must be recalculated at $k_F(CaMg_2)$ and $k_F(CaAl_2)$, because the change in the depletion charge on alloying is large[17]. The calculated alloy values are:

$Z_{Ca} = 2.36250$ and $Z_{Mg} = 2.13948$ for $CaMg_2$ and
$Z_{Ca} = 2.52695$ and $Z_{Al} = 3.17708$ for $CaAl_2$.

We have calculated the structural energy E_{st} for all possible but non-equivalent stacking variants consisting of 2, 3 and 6 layers, namely, the four structures:

2 layers: CB = C14
3 layers: ABC = C15
6 layers: BABCAC = 6a
6 layers: ABACAC = 6b

The calculations are carried out using the ideal values of:

1) the axial ratio: $c/a = \sqrt{8/3}$
2) the positions x of MgII (or AlII) in Kagomé planes: $x = 1/6$ and
3) the parameter z giving the heights of the Ca atoms: $z = 1/16$[18].

TABLE 1.

Structure	$E_{es}(CaMg_2)$	$E_{es}(CaAl_2)$
C15	−1.223115	−2.373012
6a	−1.222973	−2.372447
6b	−1.222830	−2.371882
C14	−1.222686	−2.371314

E_{es} (in au; 1au = 27.2 eV) of the different structures of $CaMg_2$ and $CaAl_2$.

The electrostatic energy E_{es} is calculated with $\lambda = 0.5$ and given in Table 1 in au. From Table 1, it is clear that E_{es} favours C15 structure over 6a, 6b and C14 structures. The difference $\Delta E_{es} = |E_{es}(C15) - E_{es}(C14)|$ is quite large, so that for instance to obtain C14 as the most stable structure for $CaMg_2$, this ΔE_{es} must be outbalanced by the difference $\Delta E_{bs} = |E_{bs}(C14) - E_{bs}(C15)|$, i. e. $\Delta E_{bs} > \Delta E_{es}$ which is rather difficult to achieve without taking charge transfer into considera-

TABLE 2.

Structure	$E_{et}(CaMg_2)$	$E_{et}(CaAl_2)$
C15	−1.244494	−2.953745
6a	−1.244482	−2.953729
6b	−1.244451	−2.953585
C14	−1.244402	−2.953313

E_{st} (in au; 1au = 27.2 eV) of the different structures of $CaMg_2$ and $CaAl_2$

tion. The structural energy E_{st} calculated without charge transfer for the different structures under consideration are given in Table 2. A cubic interpolation scheme is used to compute E_{bs} from the tabulated values of the energy wave number characteristic $F^N_{MM'}(q)$. Unlike pure metals[2], it is unpractical to calculate $F^N_{MM'}(q)$ directly at the reciprocal lattice vectors q, because the number of q's in IMC is far greater than in case of pure metals. That is why interpolation has to be used here. From Tables 1 and 2 it is evident that E_{es} dominates the determination of the stable crystal structures of both $CaMg_2$ and $CaAl_2$. Thus, the theoretically predicted most stable structure in both cases is C15, i. e. the one with the lowest E_{es}. For $CaAl_2$ this is a success, because the theory yields already the correct structure C15. However, for $CaMg_2$, the observed structure C14 comes as the most unstable structure according to theoretical results. Although E_{bs} favours C14 for $CaMg_2$, the differences in E_{bs} are smaller than those in E_{es}, which favours C15.

We assume that the disagreement in case of $CaMg_2$ is due to the influence of the strong charge variations in the IMC $CaMg_2$. The deviations from the mean density may not be taken into account by linear screening.

It is well known that the difference in the electronegativity of the two components of a metallic alloy plays an important role in the determination of its stable crystal structure[19,20]. One can, to some extent, conclude the occurence of charge transfer between the two components of an alloy, if they have different electronegativities. This is the case in $CaMg_2$, because Mg has a higher electronegativity[21] (=1.31) than Ca (=1.0). Thus, we believe that a charge transfer takes place from Ca to Mg atoms in $CaMg_2$, not included in linear screening.

We describe the charge transfer in an intermetallic compound AB_2 by a parameter Q defined by $n_B = Q^3 \bar{n}$. n_B is the charge density on atoms of type B and $\bar{n}$ is the charge density of the homogeneous electron gas. For a given Q or n_B the charge density n_A results from the neutrality condition:

$$\bar{n}\,[V_A + 2V_B] = n_A\,V_A + 2n_B\,V_B. \tag{8}$$

Assuming a close packing of rigid spheres in AB_2 we have $V_A = \frac{4}{3}\pi r_A^3$ and $V_B = \frac{4}{3}\pi r_B^3$, where the radii fulfil the relation: $r_A = \sqrt{1.5}\, r_B$[9]. We include higher order effects approximately by screening the A and B cores by n_A and n_B, respectively, instead of $\bar{n}$. Through this process the calculated values of the energy wave number characteristics will change depending on the value of Q. In our simple approximation F^N_{B-B} is spread by a scale factor Q simulating the charge of k_F at B places, while F^N_{A-A} is pressed correspondingly. The $\bar{F}^N_{A-B}$ branch is left unchanged. The results of our calculations of E_{st} including charge transfer are given in Table 3 and Figs. 1 and 2 for $CaMg_2$ and $CaAl_2$. The value $Q = 1.00$ corresponds to calculations without charge transfer. Although, in case of $CaAl_2$ the correct structure C15 is already predicted with $Q = 1$, we wish to study the effect of including charge transfer, because the difference in electronegativity of Al (=1.61) and Ca (=1) is large.

From Table 3 and Fig. 1 we see that the most stable structure of $CaMg_2$ changes according to the amount of charge transfer allowed as follows:

a) In the range $Q^3 = 1$ to 1.024 it is C 15,

b) from $Q^3 = 1.025$ to 1.071 it becomes 6a,
c) around $Q^3 = 1.077$ it changes to 6b,
d) finally starting from $Q^3 = 1.081$ up to $Q^3 = 1.521$ it becomes C14.

TABLE 3.

Q^3	$-E_{st}$			
	C15	6a	6b	C14
$CaMg_2$				
1	1.244494	1.244482	1.244451	1.244402
1.015	1.244956	1.244952	1.244923	1.244867
1.030	1.245408	1.245411	1.245384	1.245326
1.046	1.245851	1.245858	1.245837	1.245790
1.061	1.246284	1.246294	1.246285	1.246259
1.077	1.246707	1.246719	1.246723	1.246718
1.093	1.247121	1.247134	1.247150	1.247169
1.109	1.247523	1.247536	1.247561	1.247597
1.125	1.247919	1.247929	1.247958	1.248005
1.158	1.248680	1.248687	1.248722	1.248784
1.191	1.249394	1.249412	1.249454	1.249520
1.225	1.250021	1.250071	1.250130	1.250199
1.260	1.250686	1.250740	1.250798	1.250859
1.331	1.251912	1.251966	1.252020	1.252075
1.424	1.253358	1.253345	1.253356	1.253390
1.521	1.254724	1.254742	1.254773	1.254818
$CaAl_2$				
1	2.953745	2.953729	2.953585	2.953313
1.015	2.956421	2.956399	2.956237	2.955938
1.030	2.959114	2.959033	2.958825	2.958491
1.046	2.961732	2.961601	2.961358	2.961002
1.061	2.964284	2.964097	2.963817	2.963443
1.093	2.969143	2.968863	2.968536	2.968164
1.125	2.973804	2.973460	2.973104	2.972736
1.158	2.978324	2.978000	2.977639	2.977242
1.191	2.982765	2.982477	2.982099	2.981633
1.208	2.985032	2.984730	2.984332	2.983837
1.225	2.987340	2.987021	2.986609	2.986103
1.242	2.989714	2.989378	2.988962	2.988466
1.260	2.992212	2.991849	2.991430	2.990956
1.331	3.003863	3.003371	3.002943	3.002578
1.424	3.017335	3.018499	3.019463	3.020226
1.521	3.044264	3.045176	3.046113	3.047075

E_{st} (in au; 1au = 27.2 eV) of C15, 6a, 6b and C14 calculated with different charge densities. Q^3 is charge density on Mg ($CaMg_2$) or Al ($CaAl_2$) relative to homogeneous electron gas. $Q^3 = 1$ corresponds to calculations without charge transfer. The most stable structure is underlined for each Q^3 value.

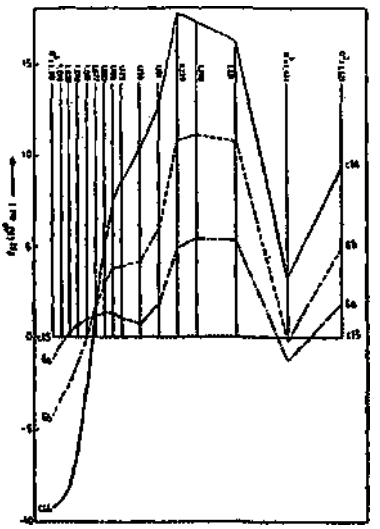

Fig. 1. $CaMg_2$: E_{st} of C14, 6a and 6b relative to C15 calculated with different charge densities on Mg at ideal c/a and x (1au = 27.2 eV). Q^3 is the charge density on Mg relative to homogeneous electron gas. The value 1.00 corresponds to calculations without charge transfer.

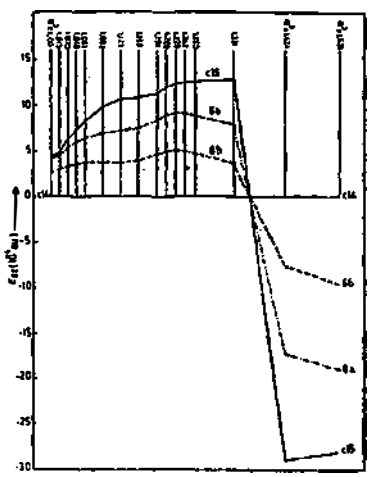

Fig. 2. $CaAl_2$: E_{st} of C15, 6a and 6b relative to C14 calculated with different charge densities on Al at ideal c/a and x (1au = 27.2 eV). Q^3 is the charge density on Al relative to homogeneous electron gas.

This means that the experimentally observed structure of $CaMg_2$ is correctly predicted by the present method starting from a mean charge density on Mg atoms n_{Mg} which is about 8% above that of the homogeneous electron gas $\overline{n}$. This behaviour continues up to $n_{Mg} = 1.52\,\overline{n}$, i. e. n_{Mg} is 52% higher than $\overline{n}$. However, the maximum difference $\Delta E_{st} = |E_{st}(\mathrm{C14}) - E_{st}(\mathrm{C15})|$ is achieved at $Q^3 = 1.225$, then it drops at $Q^3 = 1.424$ and rises again at $Q^3 = 1.521$.

In case of $CaAl_2$ the theory predicts the observed C15 structure in the whole range $Q^3 = 1$ to 1.36, i. e. up to n_{Al} which is 36% above $\overline{n}$. The difference $\Delta E_{st} =$

$= |E_{st}(\mathrm{C15}) - E_{st}(\mathrm{C14})|$ increases in favour of C15 with ascending value of Q^3, reaching its maximum at $Q^3 = 1.331$. However, if more charge transfer is allowed, C14 structure will become the theoretically most stable one in the range $Q^3 = = 1.361$ to 1.521.

We conclude that including charge transfer makes it possible to predict the correct structure for $CaMg_2$. Also C15 remains the most stable structure of $CaAl_2$ over quite a wide range of Q. Thus charge transfer plays an important role in IMC. It may be included approximately by defining new screened pseudoatoms, which result from a screening with individual k_F-values instead of the mean one. With these new screened pseudoatoms second-order perturbation theory leads to the experimentally observed structure. The exact value of Q can be determined by calculating the stacking fault energy of $CaMg_2$ and $CaAl_2$ and comparing it with the experimental values, as we did for $MgZn_2$[7]. Unfortunately, there are, to our knowledge, no such experimental results for $CaMg_2$ and $CaAl_2$.

References

1) V. Heine and D. Weaire, *Solid State Physics* **24**, Academic Press, New York, (1970) 249;
2) A. M. Radwan and A. A. Saleh, Fizika **19** (1987) 17;
3) A. M. Radwan and A. A. Saleh, to be published in Bull. NRC, Egypt (1987);
4) A. M. Radwan, to be published in Cryst. Res. and Technol. **1** (1988);
5) J. E. Inglesfield, J. Phys. C2 (1969) 1285;
6) E. Mrosan, W. John and H. Eschrig, phys. stat. sol. (b) **51** (1972) 793;
7) P. Rennert and A. M. Radwan, phys. stat. sol. (b) **79** (1977) 167;
8) P. Rennert and A. M. Radwan, phys. stat. sol. (b) **77** (1976) 615;
9) G. E. R. Schulze, *Metallphysik*, Akademie-Verlag, Berlin (1967);
10) R. W. Shaw, Phys. Rev. **174** (1968) 769;
11) R. W. Shaw, J. Phys. C2 (1969) 2350;
12) R. W. Shaw, J. Phys. C3 (1970) 1140;
13) A. M. Radwan and P. Rennert, Cryst. Res. & Technol. **10** (1975) 865;
14) K. S. Singwi, A. Sjoelander, M. P. Tosi and R. H. Land, Phys. Rev. B1 (1970) 1044;
15) M. Appapillai and V. Heine, Tech. Rep. No. 5, Solid State Theory Group, Cavendish Laboratory, Cambridge 1972;
16) P. Rennert, G. Lehmann, G. Paasch and M. Taut, phys. stat. sol. **35** (1969) 667;
17) M. Taut and G. Paasch, phys. stat. sol. (b) **51** (1972) 295;
18) B. W. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 2, Pergamon Press, New York (1967);
19) W. H. Hume-Rothery, in: *Phase Stability in Metals and Alloys*, Ed. P. S. Rudman, McGraw Hill, New York, (1967) 3;
20) J. T. Waber, J. K. Gschneider, A. Larson and M. Prince, Trans. MS AIME **227** (1963) 717;
21) A. L. Allred, J. Inorg. Nuclear Chem. **17** (1961) 215.

STRUKTURNE ENERGIJE INTERMETALNIH SPOJEVA $CaMg_2$ I $CaAl_2$

AHMED M. RADWAN

Theoretical Physics Laboratory, National Research Centre, Cairo, Egypt

UDK 538.915

Originalni znanstveni rad

Istraživana je struktura Lavesove faze $CaMg_2$ i $CaAl_2$ koristeći tzv. optimizirani modelni potencijal. Transfer naboja, koji je uzet u obzir na približan i jednostavan način, igra važnu ulogu u određivanju stabilne kristalne strukture $CaMg_2$ i $CaAl_2$.