ELECTRONIC STRUCTURE AND CHEMICAL BONDING 
IN LAVES PHASES Al₂Ca, Be₂Ag AND Be₂Ti

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The results of ab-initio calculations of electronic structure of Laves-phase compounds Al₂Ca, Be₂Ag and Be₂Ti are presented. Calculations were carried out in the framework of Density Functional Theory (DFT) and the Full Potential Linearized Augmented Plane Waves + local orbital formalism (FP APW+lo). Total, local and partial densities of electronic states (DOS) were obtained and analysed. These data together with differential electronic density (DED) distribution allow understanding the links of chemical bonding with structural stability of studied compounds.

Keywords: Laves-phases, ab initio calculations, chemical bonding

1. Introduction

Laves phases, with a composition AB₂, are intermetallic compounds generally crystallized into three close-packed structures: cubic (C15-MgCu₂), hexagonal (C14-MgZn₂) and di-hexagonal (C36-MgNi₂) [1, 2].

Last time Laves-phase compounds have been widely investigated due to new perspectives of their applications. For example, CeRu₂ and (Hf, Zr)V₂ compounds are known as super conducting materials [3, 4]. (Tb, Dy)Fe₂ compound reveals a giant magneto-striction [5]. (Ho, Mm)Co₂ compound can be used as hydrogen storage reservoir [6]. Compounds NbCr₂ and HfV₂ attract an interest due to their hardness to high temperatures [7, 8].

Laves-phase crystals are typical size factor compounds with an atomic size ratio \( R_A/R_B \) around 1.225 (where \( R_A \) and \( R_B \) are diameters of A and B atoms, respectively [9]). Their stability depends strongly on electronic structure of constituent atoms. Detailed information regarding the nature of chemical bonds allows understanding physical and chemical properties of Laves phases. In [10] calculations of densities of states and charge density distribution in TiCr₂ were reported. A large covalent component in bonding of small atoms (Cr) was found. In [11] an electronic structure of paramagnetic Laves phases HfV₂ and HfFe₂ was calculated using FP APW + lo formalism. A significant overlap of wave functions for the neighbouring V-V and Fe-Fe atoms shows their mainly covalent bonding. Ab initio calculations of electronic structure of Al₂Ca, Al₄Ca and Mg₂Ca phases [12] showed that among these compounds Al₂Ca phase has the strongest alloying ability and the highest structural stability.

We report results of ab initio calculations of electronic structure of three Laves-phase compounds: Al₂Ca, Be₂Ag and Be₂Ti. Unlike Al₂Ca, in Be₂Ag and Be₂Ti compounds the constituent atoms (Ag and Ti) contain \( d \)-electrons that participate in formation of chemical bonds. It is shown that a structural stability of studied compounds depends on participation of electrons of different symmetry in chemical bonding.

2. Methodology of Calculations

The calculations are carried out in the framework of DFT [13, 14] and FP LAPW + lo formalism [15, 16]. Within this method, the unit cell is divided into two regions in a manner reminiscent of a muffin tin (mt) spheres. The first region consists of non-overlapping spheres (with radii \( R_{mt} \) around each atomic centre. In this region, the Kohn-Sham wave functions are taken as atomic-like functions (Eq. 1), which are solutions for a spherical potential. The second region is the remaining space outside the \( mt \) spheres, so called the interstitial region (IR). In IR electrons are described by plane waves (Eq. 2).

\[
\Phi_{s_k}(\vec{r}) = \sum_{\alpha} A_{s_k,\alpha} u_{\alpha}(\vec{r}; E_{\alpha}) Y_{\alpha}(\hat{r}) + \varphi_{s_k}, \vec{r} \in \text{atomic sphere}, \tag{1}
\]

\[
\Phi_{s_k}(\vec{r}) = \frac{1}{\sqrt{\omega}} e^{i \vec{k} \cdot \vec{r}}, \vec{r} \in \text{interstitial region}. \tag{2}
\]
Here \( A_{lm} \) are coefficients, \( \hat{k} \) is the wave vector inside the first Brillouin zone, \( \hat{k}_n = \hat{k} + \hat{K}_n \) where \( \hat{K}_n \) is a reciprocal lattice vector, \( \omega \) is a normalizing volume per atom, \( u_r(r, E_n) \) is a regular solution of the radial part of Schrödinger equation for energy \( E_n \). \( Y_{lm} \) are spherical harmonic functions, \( l \) and \( m \) are angular momentum quantum numbers. \( \phi_{lo} \) is the wave function of a local orbital. The solution of the Kohn-Sham equations is expended in this combined basis set of functions according to the linear variation method, 
\[
\Psi_l(\hat{r}) = \sum c_n \Phi_{kn}(\hat{r})
\]
where coefficients \( c_n \) are determined by the Rayleigh-Ritz variation principle.

In this work the WIEN2K package [17] was used. The core states are treated in fully relativistic approximation [18] while the valence states are treated in a scalar relativistic approximation [19]. The exchange-correlation potential within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [20] was used. The calculations are performed within the spin-polarization approximation.

To find the equilibrium lattice parameters of studied phases the total energy was optimised by variation of the volume per atom. The accuracy of the total energy self-consistent calculations is \( \sim 10^{-4} \) Ry. In the framework of FP LAPW + lo method the \( mt \) spheres should not overlap. On one hand, the increasing \( R_{mt} \) significantly decreases the computation time. On the other hand, too large \( R_{mt} \) can lead to the overlapping of \( mt \) spheres when the lattice parameter becomes small in the optimisation procedure.

To satisfy these conditions we have chosen \( R_{mt} = 2 \) a.u. for all atoms in all calculations. To achieve the required accuracy in the total energy calculations two additional input parameters in the program should be determined. One of them is the number of \( k \)-points in the first Brillouin zone. It provides the accuracy of the summation over \( k \) in the first Brillouin zone. Another one is the number of plane waves in the expansion of the wave functions in the interstitial region, which is determined by \( K_{\text{max}} \). It was found that for the phase \( Al_2Ca \) a \( k \)-mesh of about 1000 points in the first Brillouin zone makes the total energy independent on the number of \( k \)-points with the required accuracy, while for \( Be_2Ag \) and \( Be_2Ti \) a \( k \)-mesh of 1500 points satisfies this condition (see example on Fig. 1.). The magnitude of \( R_{mt} K_{\text{max}} \) that gives an accuracy of the total energy calculations \( \sim 10^{-4} \) Ry was equal to 8.5 for \( Al_2Ca \) and 9 for \( Be_2Ag \) and \( Be_2Ti \), as justified by results of calculations displayed on Figure 2, where the results for \( Be_2Ag \) are shown as the example.

The energy cut-off, separating core and valence states was equal to \(-6.0 \) Ry. This condition allowed minimizing a leak of the electron core states into interstitial region. Additional details concerning the calculation method can be found in [21].

### 3. Results and Discussion

The equilibrium lattice parameters for studied Laves phases are in good agreement with experimental data published in [22] (Table 1). The calculated band structures for these compounds show that all three phases are conductive materials.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Calculated</th>
<th>Experiment [17]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Al_2Ca )</td>
<td>8.02</td>
<td>8.02</td>
</tr>
<tr>
<td>( Be_2Ag )</td>
<td>6.44</td>
<td>6.43</td>
</tr>
<tr>
<td>( Be_2Ti )</td>
<td>6.29</td>
<td>6.407</td>
</tr>
</tbody>
</table>

The energy cut-off, separating core and valence states was equal to \(-6.0 \) Ry. This condition allowed minimizing a leak of the electron core states into interstitial region. Additional details concerning the calculation method can be found in [21].
To obtain the information about the influence of electronic properties of constitutional atoms on their chemical bonding we calculated total and partial Densities of States (DOS) for all studied phases. We proceed from the fact that electrons with energies in the region of Fermi energy, $E_F$, play the main role in formation of chemical bonds. Comparing the total DOS for Al$_2$Ca (Fig. 3a) and local DOS for Al (Fig. 3b) and Ca (Fig. 3c) we conclude that electrons of Al give the main contribution to conductivity of Al$_2$Ca compound and accordingly cause a metallic bonding.

Figure 3. The total and local DOS (in states/ eV) for Al$_2$Ca: (a) total DOS; (b) DOS for Al atoms; (c) DOS for Ca atoms. The zero on the x axis here and in the following Figs. corresponds to Fermi energy, $E_F$. 

Figure 4. The partial DOS (in states/eV) for Al\textsubscript{2}Ca: (a) s-states of Al atoms; (b) p-states of Al atoms; (c) promoted d-states for electrons of Al atoms

Partial DOS for Al and Ca displayed on Figure 4 show that s- and p-electrons of Al dominate in the energy range $E \leq E_F$. These results indicate that s- and p-electrons of Al determine the bonding
in Al$_2$Ca. From Figure 4c one can see that promoted $d$-electrons of Al also participate in chemical bonding. A hybridisation of $s$- $p$- and promoted $d$-electrons of Al should lead to covalent bonding in Al$_2$Ca but the covalent component is relatively small.

On Figures 5, 6 the results of calculations of DOS for Be$_2$Ag phase are presented. Comparing the total DOS for Be$_2$Ag (Fig. 5a) with local DOS for constitutional atoms Be (Fig. 5b) and Ag (Fig. 5c) in the energy range $E \leq E_F$ it may be seen that Be atoms give a larger contribution to total DOS in comparison with Ag atoms.

*Figure 5. The total and local DOS (spin- up states) (in states/ eV) for Be$_2$Ag: (a) total DOS; (b) DOS for Be atoms; (c) DOS for Ag atoms*
Partial DOS show the formation of the promoted $p$-states for electrons of Be atoms (Fig. 6b). Hybridization is expected in the range 2–8 eV below $E_F$ between $p$-states and $s$-states of Be (Fig. 6a and 6b) and $d$-states of Ag (Fig. 6c). A covalent component should give a visible contribution to chemical bonding. It is larger than in the case of Al$_2$Ca compound. A small value of total DOS at the Fermi level (Fig. 5a) shows a relatively weak metallic component in chemical bonding in the Be$_2$Ag phase as compared with Al$_2$Ca.
Analysis of DOS for Be$_2$Ti compound (Figs. 7 and 8) shows an overlapping of $d$-states of Ti (Figs. 8b and 8c) with promoted $p$-states of Be electrons (Fig. 8a) in the range from $E_F$ to $\sim 3$ eV below Fermi energy.

**Figure 7.** The total and local DOS (spin-up states) (in states/ eV) for Be$_2$Ti: (a) total DOS; (b) DOS for Be atoms; (c) DOS for Ti atoms
Conductivity in Be₂Ti phase should be higher than in Be₂Ag due to larger number of states at Fermi level (Figs. 5a and 7a). This is caused by significant contribution of $d$-electrons of Ti. The splitting of bonding and anti-bonding $d$-states of Ti located in the energy region between $-5$eV and $+5$eV.
is clearly seen. At the same time, in Be\textsubscript{2}Ag d-states of Ag are mainly located below $E_F$. As well as in Be\textsubscript{2}Ag, in Be\textsubscript{2}Ti the promoted p-electrons of Be form hybrid covalent bonds with d-electrons of Ti.

On Figure 9 the calculated Differential Electron Density (DED) in the plane (110) for studied Laves phases is presented.

Figure 9. Mapping of spatial distributions of DED (in e/\textumi\textsuperscript{3}) in the plane (110) for Al\textsubscript{2}Ca (a), Be\textsubscript{2}Ag (b), and Be\textsubscript{2}Ti (c)

DED shows the difference between the self-consistently calculated electron density in the phases and the sum of the atomic electron densities. Peculiarities of spatial DED distribution can be understood on the basis of described DOS analysis. The regions of the relative lack of DED and of the extra electron charge are seen. For example, let us consider the peculiarities of DED behaviour for Al\textsubscript{2}Ca. In region 1 (Fig. 9.a) we obtained the value of DED equal to $+0.1998$ e/\textumi\textsuperscript{3}. The values of DED in this region are mainly caused by the redistribution of the electrons that belong to Al atoms that are placed above and beneath the plane (110). In region 2 the value of DED (+0.0944 e/\textumi\textsuperscript{3}) is mostly caused by atoms surrounding Ca. It is lower in comparison with the value of DED in region 1 that is explained by the degree of overlapping of electronic orbits of constitutional atoms discussed above.

For the phase Be\textsubscript{2}Ag in the plane (110) one can see both the regions of extra DED and the regions with the lack of DED (Fig. 9.b). In region 1 the relative lack in DED ($-0.01$ e/\textumi\textsuperscript{3}) is observed. It is caused by relatively large distances between Be atoms and between Ag and Be atoms in the considered point of this plane. Region 2 in this Figure corresponds to extra DED ($+0.07$ e/\textumi\textsuperscript{3}). It is apparently caused by interaction of Be atom located above this region with surrounding Be atoms in the plane (110).

In the plane (110) of Be\textsubscript{2}Ti phase in the region 1 DED is equal to $-0.005$ e/\textumi\textsuperscript{3}. The lack of DED in this region is caused by the redistribution of the electrons that belong to Be atoms above and beneath this plane. The extra DED, which observed in region 2, is equal to $+0.05$ e/\textumi\textsuperscript{3}. The redistribution of the electrons that belong to Ti atoms surrounding this region (Fig. 9.c) mainly causes this value of DED.
Conclusions

Analysis of total and partial DOS for all studied Laves phases allowed getting information about the nature of chemical bonding in these compounds. Total DOS showed that Al₂Ca is characterized by larger component of metallic bond in comparison with two other compounds. Promoted $d$-electrons of Al participate in covalent bonding which is determined by a superposition of $s$, $p$- and promoted $d$-states of Al electrons. Promoted $d$-electrons of Al play partly a role of conductive electrons and consequently participate in metallic bonding. Electro-negativities of Al and Ca atoms differ significantly (1.5 and 1.0 accordingly). Thus the ionic component in the bonding is significant. As a result this Laves phase compound is characterized by relatively high structural stability [12].

Considering Be₂Ag, it is possible to conclude that this compound is characterized by smallest component of metallic bonding in comparison with two other compounds. The covalent component of chemical bonding in this phase is somewhat larger. Electro-negativities of Be and Ag atoms are close and therefore the ionic component of chemical bonds in Be₂Ag compound is absent. On the phase diagram it exists in a narrow temperature interval and decomposes to other phases outside this interval.

In Be₂Ti phase we found a degree of metallic bonding that is significantly larger than in Be₂Ag and close to metallic bonding in Al₂Ca. The covalent component in the bonding in Be₂Ti is determined by superposition of $p$-states of Be and $d$-states of Ti. Its value is significantly larger than for Al₂Ca and somewhat less than for Be₂Ag. Electro-negativities of Be and Ti atoms are close, and in this case the ionic component in bonding is negligible. We can expect that structural stability of Be₂Ti is somewhat less in comparison with Al₂Ca.

References


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