

The electronic structure and mechanical properties of MgCu₂ Laves phase compound

W. Chen*, J. Sun

School of Materials Science and Engineering, Shanghai Jiaotong University, Shanghai, 200030, China

Received 13 November 2005; received in revised form 19 January 2006; accepted 28 February 2006

Abstract

Ab initio calculations have been performed to calculate the density of states (DOS), charge density distribution and enthalpy of formation of MgCu₂ Laves phase compound based on the method of augmented plane waves plus local orbitals (APW + lo) to reveal its electronic structure. The results show a covalent bonding between Cu–Cu and a metallic bonding between Mg–Cu in MgCu₂ that are similar in TiCo₂ and TiCr₂. Hardness and reduced Young's modules of the three compounds are measured by nano-indenter. Differences in the mechanic properties can be explained by the calculated bonding characteristics.

© 2006 Elsevier B.V. All rights reserved.

PACS: 61.50.Lt; 62.20.–x; 71.20.Lp

Keywords: Laves phase; Electronic structure; Mechanical property

1. Introduction

There is an increasing interest in Laves phases as their excellent physical and chemical properties make them available for potential functional as well as structural applications. The major shortcoming of Laves phase compounds is their brittleness at ambient temperatures. This low-temperature brittleness has an adverse impact on the utilization of Laves phase compounds. It is therefore highly desirable to find approaches to increase the low-temperature ductility without compromising many other attractive properties. An investigation of the electronic structure and bonding characteristic of Laves phase compounds can help understand the fundamental mechanism governing the observed mechanical properties.

In this paper, we present the results of an ab initio calculation for C15 Laves phase MgCu₂. The calculation was conducted using the method of augmented plane wave plus local orbitals (APW + lo) with the generalized gradient approximation (GGA). The enthalpy of formation for MgCu₂ was obtained by calculating the total energy. The

calculation results of MgCu₂ including density of states (DOS), charge density distribution map and enthalpy of formation were compared with those for TiCr₂ and TiCo₂ to get a general understanding of the electronic structure and bonding mechanism. We then measured the hardness, reduced Young's modules of the three Laves phase compounds to see the relationship between the electronic structure and the mechanical properties.

2. Methods

2.1. Theoretical calculation

We perform ab initio calculation of the electronic structure and total energy of the MgCu₂ Laves phase using the method of APW + lo, which was implemented in the software package WIEN2K [1]. Core states are treated fully relativistically while semi-core and valence states are treated within a scalar relativistic approximation in the calculation. The APW + lo method converged practically the identical results as the linearized augmented plane wave (LAPW) method, but using smaller basis sets in the APW + lo method leads to significantly reduce the

*Corresponding author. Tel.: +86 21 52412404; fax: +86 21 52413122.
E-mail address: chenw@mail.sic.ac.cn (W. Chen).

computation time by up to an order of magnitude [2]. Potential and charge densities inside the atomic spheres are expanded in lattice harmonics up to $L = 10$ and using GGA to treat exchange and correlation effects within the density functional theory. Muffin-tin radius (R_{mt}) of 2.3 a.u. was chosen for both Mg and Cu atom and a plane wave cutoff ($R_{\text{mt}}K_{\text{max}}$) of 10.0 was used. The calculation was performed with a 3000 \mathbf{k} -point mesh in the irreducible wedge of the Brillouin zone for MgCu_2 structure. When the energy difference was less than 0.1 mRy, convergence was assumed. The Brillouin zone integration was carried out according to a modified tetrahedron method [3].

2.2. Materials preparation and experiment methods

A bulk specimen of MgCu_2 was prepared by melting together Mg and Cu in a magnetic induction furnace with argon filled. Specimen was remelted several times to ensure chemical homogeneity. To remove crystal defects and internal stress, specimen was then annealed for 15 h in a vacuum heat treatment furnace and cooled to room temperature within the furnace. The ingot was then crushed into small fragments. A tiny one was chosen for the mechanical property measurement. MgCu_2 Laves phase was characterized by X-ray diffraction (XRD), which was performed on powdered specimen of a mesh number 300 by $\text{CuK}\alpha$ radiation.

Nano-indenter test was performed to measure the reduced Young's moduli and hardness of the samples. Since Laves phase compounds are brittle at room temperature, mechanical testing method is very limited. Nano-indenter test probes a small polished area and thereby eliminates many of the problems associated with bulk testing. Nano-indenter II measures the force and displacement as an indentation is made, thus a load versus displacement curve is got from the loading and unloading process which can be used to assess mechanical properties of the material. A Berkovich indenter, a three-sided pyramid with an area-to-depth function which is the same as a Vickers indenter, was used in all experiments. Reduced Young's module (E) can be deduced by the following equation [4]:

$$E_r = \frac{\sqrt{\pi} (1 - \nu^2)}{2} \frac{S}{\sqrt{A}},$$

where S is the initial slope of the unloading curve and is defined as the contact stiffness. A is the area of the indentation at peak load. ν is the Poisson's ratio of the specimen, which is assumed 0.36. Linear loading was applied and the maximum load was 300 mN. Loading and unloading rate was 10 mN/s. Hardness can be computed from the test that is defined as the peak load divided by the area of the indentation:

$$H = \frac{P_{\text{max}}}{A}.$$

3. Results and discussion

3.1. Theoretical calculation

Fig. 1 shows the calculated total DOS for MgCu_2 and partial DOS for the Mg and Cu sites. The calculated angular-momentum-decomposed DOS for MgCu_2 are shown in Fig. 2. As a comparison, the total DOS for pure Mg and Cu were also calculated and plotted in Fig. 3. The total DOS of MgCu_2 is formed mainly by the d states as shown in Fig. 1. The dominant contribution to the DOS near Fermi level and at lower energies comes from the d states of Cu. The DOS profile is relatively low and flat at higher energy levels because the outer d orbits of Cu are

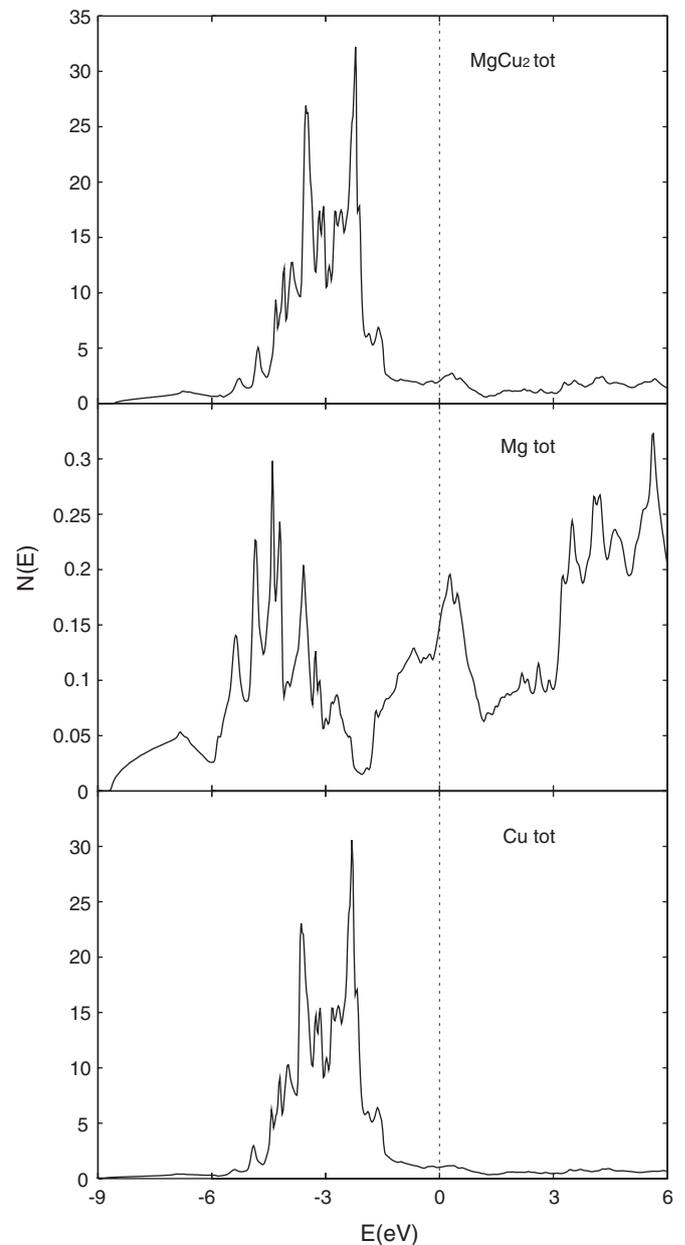


Fig. 1. The calculated total density of states for MgCu_2 and partial density of states for the Mg and Cu sites.

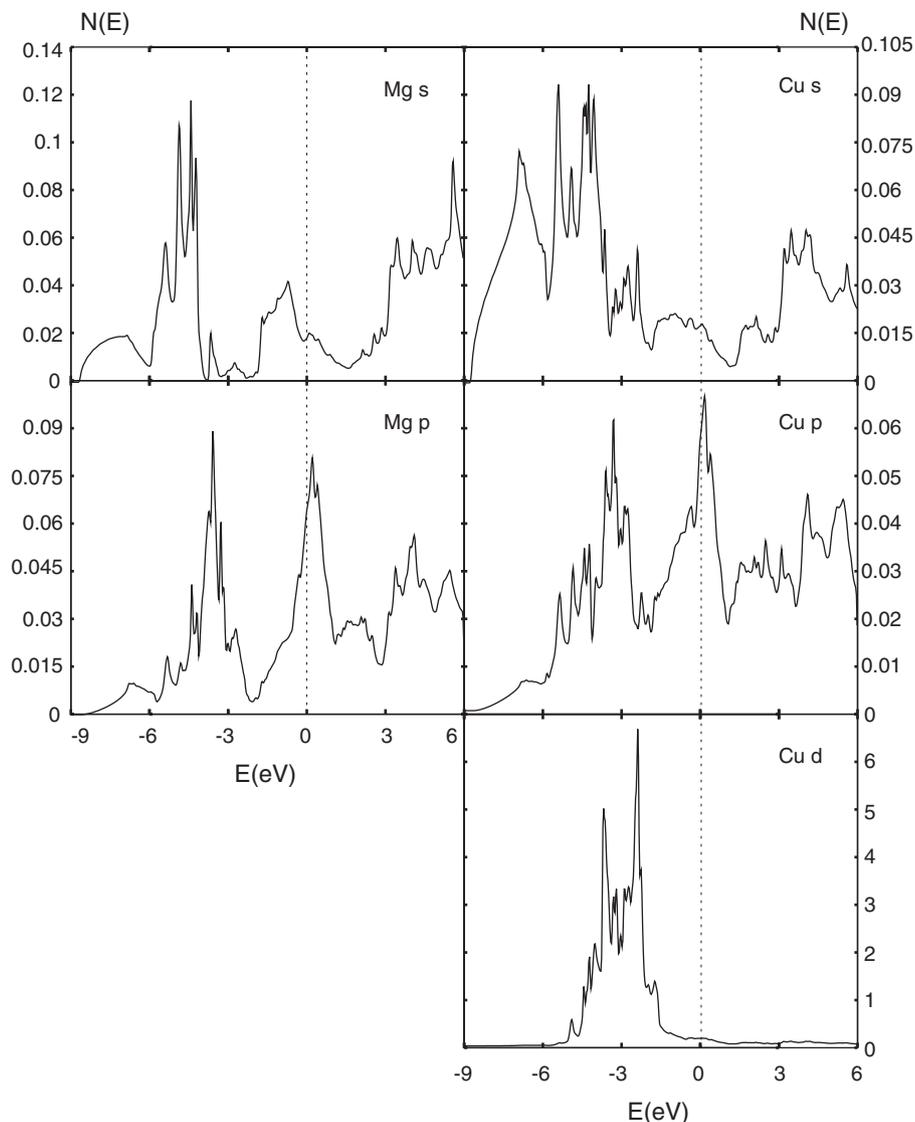


Fig. 2. The calculated angular-momentum-decomposed DOS for MgCu_2 .

fully occupied. The partial DOS for Mg sites exhibits a parabolic shape from -9 to -7 eV, which is more pronounced in the DOS for s states of Mg. The DOS profile for pure Mg is also a parabola under Fermi level. As the DOS of free electron gas is proportional to the square root of the energy, the parabola shape DOS implies the metallic bonding between Mg–Mg in MgCu_2 . Earlier research [5] of DOS for TiCr_2 (TiCo_2) found an overlap of Ti 3d states and Cr (Co) 3d states in the construction of C15 Laves phase compounds TiCr_2 (TiCo_2) s' electronic energy band and it was interpreted as hybridization between the transition metal Ti d and Cr (Co) d states. There is no distinct overlap of Mg and Cu states in the DOS for MgCu_2 , but one can find peak-to-peak correspondence from partial DOS for Cu states. It can be inferred that different kinds of bonding characteristic exist between Mg–Cu and Cu–Cu atoms in MgCu_2 .

Charge density distribution maps on the (1 1 0) plane for MgCu_2 are shown in Fig. 4. The (1 1 0) plane intersects the

Cu tetrahedral, containing the [1 1 1] close-packing direction and unit layers of Laves phase mentioned before. The contour lines are plotted from 0 to $0.6 \text{ e}/\text{\AA}^3$ with $0.03 \text{ e}/\text{\AA}^3$ intervals. Higher density region corresponds to the core electron distribution of Mg and Cu atoms that contributes relatively little to the bonding and is omitted in the charge density distribution map. Mg atoms are almost spherical, but Cu atoms are a little deformed as shown in Fig. 4. The obvious overlap of electron densities between Cu–Cu indicates a covalent bonding between them. In contrast to the Cu–Cu bonding, there is no overlap of electron densities around Mg atoms. The almost uniform electron distribution around Mg atoms is like a metallic bonding and can be well described by the nearly free electron model. These results are consistent with those from the DOS analysis explicated above. The height of charge density at the bond midpoint between Cu–Cu was found to be $0.33 \text{ e}/\text{\AA}^3$, whereas the height of charge density at the bond midpoint between Mg–Cu is only $0.13 \text{ e}/\text{\AA}^3$. It could be

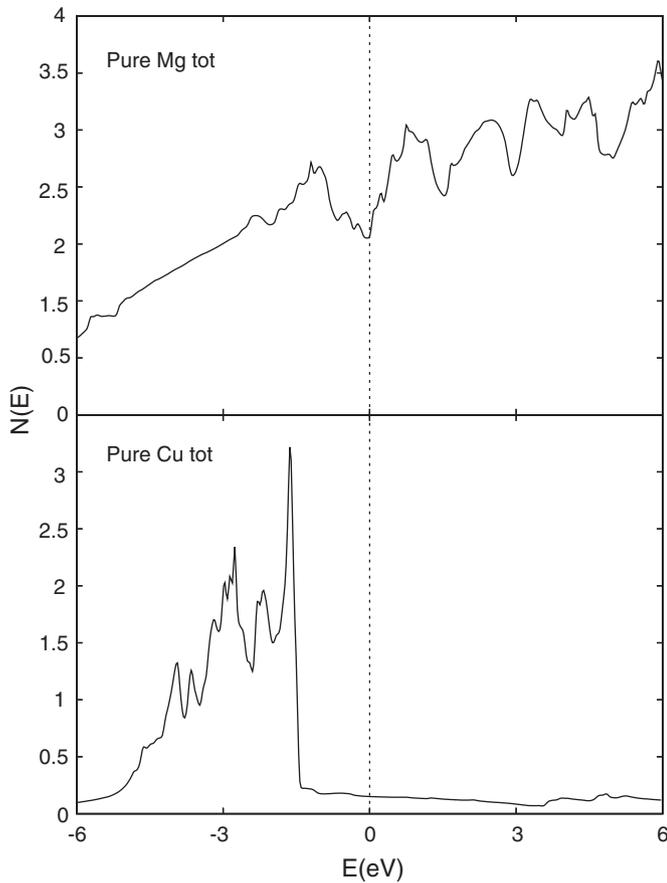


Fig. 3. The total density of states for pure Mg and Cu.

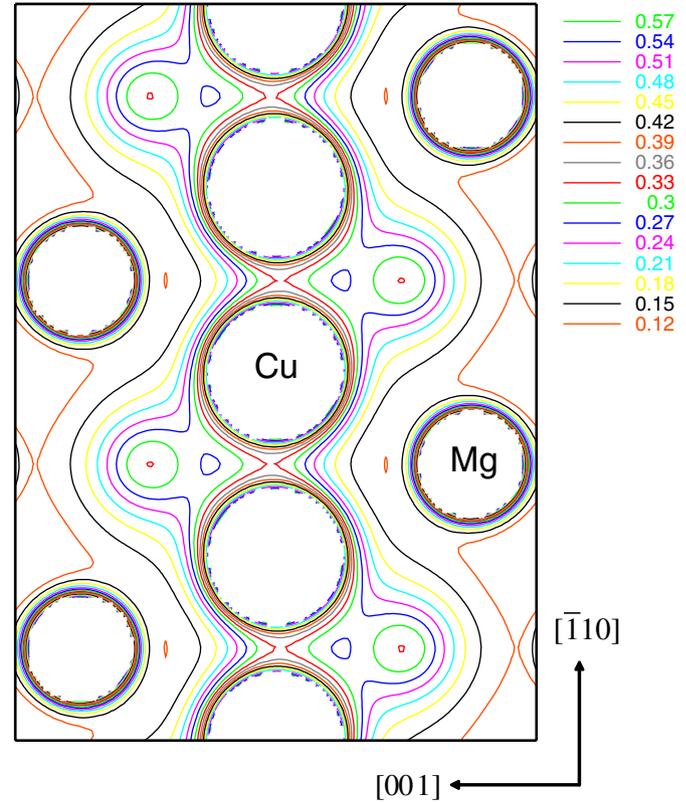


Fig. 4. The charge density distribution map on the (110) plane of MgCu_2 compound. The contour lines are plotted from 0 to $0.6 \text{ e}/\text{\AA}^3$ intervals. Lines near atoms correspond to higher charge density.

assumed that the bonding between Mg–Cu is much weaker than that between Cu–Cu in the MgCu_2 compounds. This could be explained from the point of view of the C15 Laves phase structure. The nearest neighboring sites of Cu are occupied by 6 Cu atoms in the C15 Laves compounds MgCu_2 . The atomic distance between the nearest Cu–Cu atoms is 4.670 a.u., which is 3.3% shorter than that in pure Cu (4.831 a.u.) with an h.c.p. structure. Compared with the atomic distance between the next nearest Mg–Cu atoms (5.576 a.u.), the Cu–Cu covalent bonding is thus stronger than that between the Mg–Cu atoms which is a mainly metallic bonding in MgCu_2 .

A similar phenomenon was observed from charge density distribution maps for TiCo_2 and TiCr_2 . There is also an overlap of electron densities between the smaller atoms (Cu, Cr and Co) and a relatively even electron distribution among the larger atoms (Mg and Ti) for all the three Laves compounds. Table 1 lists the height of charge density at the bond midpoint and atomic distances of the nearest and next-nearest neighboring atoms of the three compounds. It is shown numerically that the covalent bonding between two smaller atoms is stronger than the bonding between a larger atom and a smaller one. Evaluating the heights of charge density at the bond midpoint and atomic distances values listed in Table 1, it could be said that the covalent bonding in TiCo_2 is the

strongest, while that in MgCu_2 is the weakest among the three Laves compounds. It is also worth noting that the hybridization between the smaller atoms is stronger in these Laves compounds than that in their corresponding pure metals, due to the reduction of atomic distances in these compounds.

Bonding type and bonding strength change upon the formation of compounds. Laves phases can be therefore understood from their thermodynamic properties. Enthalpies of formation of these Laves phases were deduced from ab initio calculation of total energy. Table 2 lists the calculated and experimental enthalpies of formation of these compounds. The enthalpy of formation is the difference between the total energy of the compound and the sum of the total energies of the constituents in proportion to the composition. For a Laves phase AB_2 , the energy per atom is given by $\Delta H = (E_{\text{AB}_2} - E_{\text{A}} - 2E_{\text{B}})/3$. These calculated values are found to be in good agreement with the experimental data. The enthalpy of formation is closely related to the bond energies of the compound and reflects the change of bonding energy on the formation of compounds. It is shown that the enthalpy of formation of TiCo_2 is the largest, while those of MgCu_2 and TiCr_2 are comparatively much smaller. There seems to be no direct relationship between the enthalpy of formation and bonding strength of Laves compounds. Melting points

Table 1

The heights of charge density at the bond midpoint and atomic distances of nearest and next-nearest neighboring atoms of three Laves compound and its corresponding pure metals

MgCu ₂	Cu–Cu: 0.33 e/Å ³	Cu–Cu: 4.670 a.u.	Mg–Cu: 0.13 e/Å ³	Mg–Cu: 5.576 a.u.
Pure Cu	Cu–Cu: 0.26 e/Å ³	Cu–Cu: 4.831 a.u.		
TiCr ₂	Cr–Cr: 0.39 e/Å ³	Cr–Cr: 4.632 a.u.	Ti–Cr: 0.23 e/Å ³	Ti–Cr: 5.431 a.u.
Pure Cr	Cr–Cr: 0.35 e/Å ³	Cr–Cr: 4.762 a.u.		
TiCo ₂	Co–Co: 0.42 e/Å ³	Co–Co: 4.471 a.u.	Ti–Co: 0.23 e/Å ³	Ti–Co: 5.243 a.u.
Pure Co	Co–Co: 0.34 e/Å ³	Co–Co: 4.718 a.u.		

Table 2

The calculated and experimental enthalpies of formation of MgCu₂, TiCr₂ and TiCo₂

Compounds	Calculated enthalpies of formation (kJ/mol)	Experimental enthalpies of formation (kJ/mol) [11]
MgCu ₂	−43.3	−35.1
TiCr ₂	−37.6	−27.9
TiCo ₂	−89.6	−102

Table 3

Related Properties of MgCu₂, TiCr₂ and TiCo₂

Compounds	Melting point (°C)	Lattice constant (Å)	Atom radius ratio r_A/r_B	Percentage deviating from theory values of r_A/r_B
MgCu ₂	520	7.034	1.254	2%
TiCr ₂	1400	6.943	1.14	−7%
TiCo ₂	1250	6.701	1.168	−5%

of the three compounds are listed in Table 3. As melting point can be a measure of bonding energy, the higher melting point corresponds well to stronger hybridization or bonding in these Laves compounds.

Although the bonding nature in Laves phases is previously considered to be metallic, the bonding nature is rather complicated as per the results of our research. Other results of Laves phases also show this complexity. Ormeci et al. [6] calculated the charge densities in C15 HfV₂ and NbCr₂ based on a full potential muffin-tin orbital method, but showed the bonding is only weakly directional for these compounds. Hafner [7] theoretically studied the valence density map of CaAl₂ that has a C15 structure by pseudopotential method and also found a covalent bonding between the smaller Al atoms. Kubota et al. [8] performed a charge density study of MgCu₂ by the maximum entropy method and demonstrated a similar result that strong covalent bonding exists between Cu–Cu atoms while electrons are distributed similarly to metallic bonding between Mg and Cu atoms.

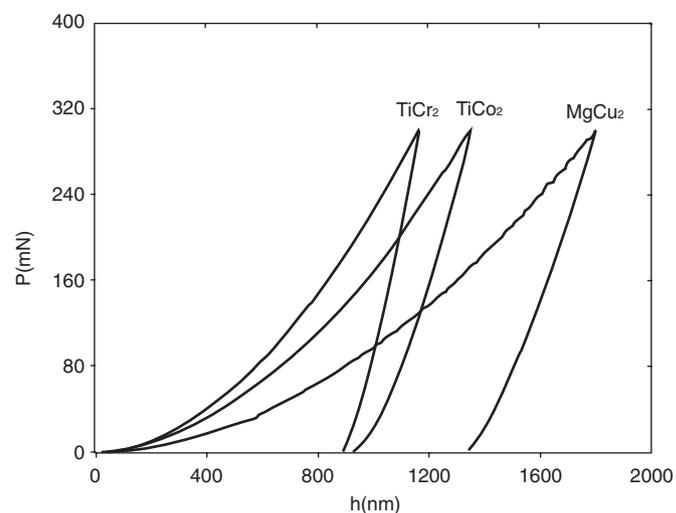


Fig. 5. Load vs. displacement curve of (a) MgCu₂, (b) TiCr₂ and (c) TiCo₂.

3.2. Mechanical properties test

Load versus indenter displacement curves of MgCu₂, TiCr₂ and TiCo₂ obtained by nano-indenter are plotted in Fig. 5. With a maximum load of 300 mN, the curves of those materials exhibit similar shapes. However, the maximum penetration depth of the Berkovich indenter is much larger for MgCu₂ than those of TiCr₂ and TiCo₂ and the unloading curve of MgCu₂ is not as steep as those of TiCr₂ and TiCo₂. In addition, the residue indenter displacement of MgCu₂ is the largest of the three materials. Table 4 lists the hardness and reduced the Young's module results of TiCr₂, TiCo₂ and MgCu₂ calculated from the nano-indenter tests. Numerically, the hardness of MgCu₂ is only half of that of TiCr₂ and TiCo₂ and the values of TiCr₂ and TiCo₂ are approaching to each other. The results of reduced Young's moduli also show a similar trend.

The process of indentation contact is usually explained by a plastic-elastic model [9] that accounts for the stretch, distortion and breaking of atomic bonding. Of the three Laves phase compounds, MgCu₂, which has the least height of charge density at the bond midpoint between the nearest atoms Cu–Cu (weakest covalent bonding of the three compounds) and the lowest melting point of the three compounds, has the least value of hardness and reduced Young's modulus among them. While the height of charge

Table 4
Mechanical properties of MgCu₂, TiCr₂ and TiCo₂

Compounds	TiCr ₂	TiCo ₂	MgCu ₂
Hardness <i>H</i>	1199.28	1020.01	519.30
Reduced Young's modulus <i>E</i> (GPa)	231.56	230.436	95.862

density at the bond midpoint between the nearest atoms Cr–Cr (Co–Co) and the melting point of TiCo₂ and TiCr₂ approach each other, hardness and reduced Young's module of TiCo₂ are also close to those of TiCr₂. Earlier discussion of electronic structure shows that a strong covalent bonding exists between the nearest atoms of the three C15 Laves phase compounds and this covalent bonding is dominant compared with metallic bonding between different kinds of atoms. Therefore, differences in mechanical properties can be explained by the differences in bonding characteristics. As larger hardness and reduced Young's module values generally concur with stronger bonding strength, these mechanical results testify theoretical calculation findings.

The relationship between electronic structure and mechanical properties in the three C15 Laves phase compounds is consistent with our former research on ZrCr₂ [10], which showed that C15 is a ground-state phase, whereas C36 is an intermediate phase and C14 the high-temperature phase. It is evident that the covalent bonding in these Laves phase compounds plays an important role in determining their mechanical properties.

4. Conclusion

The Bonding Character and mechanical behavior of C15 Laves phase compounds MgCu₂ were investigated in the paper and were compared with those of TiCo₂ and TiCr₂. Ab initio calculations have been performed to calculate the density of states (DOS) and charge density distribution of MgCu₂ based on the method of augmented plane waves plus local orbitals (APW + lo). The results reveal a covalent bonding between Cu–Cu and a metallic bonding between Mg–Cu in MgCu₂ which is a compound of main group element Mg and transition metal element Cu. In TiCr₂ and

TiCo₂, which are compounds of two transition metal elements, there exist covalent bonding between Cr–Cr (Co–Co) and hybridization of atomic orbitals between Ti–Cr (Ti–Co), which is indication of covalent component. Theoretical calculation of the enthalpy of formation of the three compounds is deduced by the difference between total energy of compounds and pure metals. It is shown that enthalpy of formation is related to the bonding strength difference in the formation of Laves phase.

Hardness and reduced Young's moduli of the three compounds are measured by nano-indenter. It is shown that the hardness of TiCr₂ is slightly larger than that of TiCo₂ and is much larger than that of MgCu₂, which can be interpreted as the difference in cohesive energy in these compounds that can be related to melting point. The elastic moduli of TiCr₂ and TiCo₂ are close to each other and are much larger than that of MgCu₂ in that the covalent bonding strength of MgCu₂ is the least among the three.

Acknowledgment

This research was sponsored by the National Nature Science Foundation of China (Project number 50271040).

References

- [1] K. Schwarz, P. Blaha, G.K.H. Madsen, *Comput. Phys. Commun.* 147 (2002) 71.
- [2] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.
- [3] P.E. Blochl, O. Jepsen, O.K. Andersen, *Phys. Rev. B* 49 (1994) 16223.
- [4] W.C. Oliver, G.M. Pharr, *J. Mater. Res.* 7 (1992) 1564.
- [5] J. Sun, B. Jiang, D.J. Smith, *Phys. Rev. B* 69 (2004) 214107.
- [6] A. Ormeci, F. Chu, J.M. Wills, T.E. Mitchell, R.C. Albers, D.J. Thoma, S.P. Chen, *Phys. Rev. B* 54 (1996) 12753.
- [7] J. Hafner, *J. Phys. F: Metal Phys.* 15 (1985) 1879.
- [8] Y. Kubota, M. Takata, M. Sakata, T. Ohba, K. Kifune, T. Tadaki, *Jpn. J. Appl. Phys. 1-Regular Papers Short Notes Rev. Papers* 38 (1999) 456.
- [9] K.L. Johnson, *Contact Mechanics*, Cambridge University Press, Cambridge [Cambridgeshire], New York, 1985.
- [10] J. Sun, B. Jiang, *Philosophical Magazine* 84 (2004) 3133.
- [11] J.H. Zhu, C.T. Liu, L.M. Pike, P.K. Liaw, *Intermetallics* 10 (2002) 579.