First-Principles Study on the Electronic Structure and Elastic Properties of YCu, DyCu and YAg

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The electronic structure and elastic properties of YCu, YAg, and DyCu were studied by full-potential linearized augmented plane wave method (FP-LAPW) on the basis of the density functional theory (DFT). The generalized gradient approximation (GGA) is applied for YCu, YAg, and the LDA+U is applied for DyCu. The density of states at the Fermi energy, $N(E_F)$, are 1.08, 1.09, and 1.04 states/(eV unit cell) for YCu, YAg and DyCu, respectively. The elastic constants were calculated. The values for Pugh's criterion are 2.30, 2.05 and 3.00 for YCu, DyCu and YAg, respectively. All of them are larger than 1.75, indicating the ductile manner of these materials. The calculated value of the anisotropy is close to 1, indicating highly isotropic behavior. [doi:10.2320/matertrans.MB200816]

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1. Introduction

The B2 (CsCl-type structure) intermetallic compounds have been extensively studied for several decades due to their high oxidation resistance, high stiffness and high strength for elevated temperature engineering applications.¹⁻³⁾ Most of the B2 polycrystalline intermetallic compounds usually possess little or no tensile ductility at room temperature if they are fully ordered and exactly stoichiometric.¹⁻³⁾ However, a new family of fully ordered, stoichiometric binary rare-earth intermetallic compounds denoted as *RM* (where *R* is a rare-earth element, and *M* is a main group or transition metal element) has recently been found to be ductile at room temperature.⁴⁾ For example, the tensile testing of polycrystalline YCu specimens produces elongations as high as 11% before failure; DyCu has an intermediate ductility, 16% elongation before failure; while YAg is the most ductile, producing 20% elongations before failure.⁵⁾ Besides YCu, DyCu and YAg, nine other *RM* intermetallics are also ductile.⁴⁾ These *RM* intermetallics with high ductility are promising high-temperature structural materials due to their high-temperature strength and corrosion resistance. Furthermore, the studies on the mechanism of the high ductility in *RM* intermetallics may offer insights into alloy modifications that could improve the ductility of other intermetallic compounds.⁵⁻⁷⁾

So far, many experimental works have been done to reveal the origin of the high ductility in *RM* intermetallics. However, the mechanism has not been well understood. In addition to the experimental work, first-principles calculations based on density functional theory (DFT) have been used to reveal the electronic structure, structural and physical properties of *RM*. For example, the bulk and defect properties of YAg and YCu have been calculated to explain the ductility.⁸⁾ And the phase stability and pressure-induced phase transition in YCu were also studied.⁹⁾ As is known, YCu, DyCu and YAg have the same crystal structure, but

they show different room-temperature ductility. The comparative analysis of electronic structure may be beneficial to understand the different ductility in *RM* intermetallics. However, as a typical member of ductile *RM*, the electronic structure of DyCu has not been studied due to the partially filled 4*f* level in Dy atom, which usually results in absurd calculation results. Fortunately, the recently developed LDA+U method takes into account orbital dependence of the Coulomb and exchange interactions which is absent in the LDA or GGA, and is known to give a correct description of the systems where *f*-electrons are well localized.^{10,11)} In this paper, we present first-principles calculations of YCu, DyCu and YAg. The comparative analysis of their electronic structures and elastic properties were performed. The ductile behavior of these intermetallics is predicted on the basis of the calculated results. The aim of our work is to extend the understanding of the anomalous ductility in *RM* intermetallics.

2. Computational Method

The presented calculations were performed by using the full-potential linearized augmented plane wave method (FP-LAPW) as implemented in the latest WIEN2k code.¹²⁾ The structures of YCu, DyCu and YAg are all primitive cubic crystal lattice, with B2 (CsCl-type) structure, belonging to the space group $Pm\bar{3}m$.^{4,13)} Figure 1 illustrates the crystal structure of *RM*. It is clear that the *M* atoms are positioned at the center of the cubic cell (0.5, 0.5, 0.5) and *R* atoms occupy (0, 0, 0) positions at the eight corners of the cubic cell. In our calculations, the exchange and correlation effects are treated using the generalized gradient approximation (GGA) for YCu and YAg, while the LDA+U method is used for DyCu. It is known that Dy atom with localized 4*f* electrons is belong to strongly correlated systems. The generalized gradient approximation (GGA) can not be applied for strongly correlated systems, however, the recently developed LDA+U method takes into account orbital dependence of the Coulomb and exchange interactions which is absent in

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Fig. 1 Crystal structure of *RM* intermetallics.

the GGA and is known to give a correct description of the strongly correlated systems.¹⁰⁾ The radii of spheres for Y, Dy, Cu and Ag have been chosen as 2.5, 2.7, 2.2 and 2.5 atomic units, respectively. The energy that separates the valence states from the core states were all chosen to be -6.0 Ryd (-81.6 eV). 1000 k -points are used in the whole Brillouin zone. During the self-consistency cycle, the total energy is converged to within $10 \mu\text{Ry/f.u.}$ In the LDA+U method, U is set as 0.52 Ry for DyCu. There are three independent elastic constants for cubic crystal, C_{11} , C_{12} and C_{44} . In the present work, the elastic constants were calculated by the strain-energy method. An appropriate set of strains was applied to the undeformed unit cell lattice with the relaxed structure. Then, the elastic constants were determined from the resulting change in total energy on the deformation.^{14,15)}

3. Results and Discussion

As a first step, the total energies of YCu, DyCu and YAg with different volumes are calculated respectively in order to determine the equilibrium structural parameters. This is performed by applying hydrostatic pressure by varying volume with the constant ratio of $a : b : c = 1 : 1 : 1$. The point of crystal energy minimum is corresponding to the equilibrium. The volume variations applied were -10 , -5 , 0 , $+5$ and $+10\%$ of the experimental volume. The energy vs. volume curves of YCu, DyCu and YAg are shown in Fig. 2. The equilibrium lattice constant can be obtained by fitting the total energy vs. volume data to Murnaghan equation.¹⁶⁾ The results are listed in Table 1. For comparison, the corresponding experimental values are also presented. The calculated equilibrium lattice constant of YCu, DyCu and YAg are 3.473 , 3.459 and 3.632 Å, respectively. For calculated equilibrium volumes, the values are 41.882 , 41.403 and 47.920 Å³ for YCu, DyCu and YAg respectively. As shown in the table, the calculated lattice constants and equilibrium volumes are in good agreement with those experimental values. Thus, we can conclude that the computation parameter and conditions selected in this calculated work should be suitable.

The total and partial densities of states (DOS) of YCu, YAg and DyCu are plotted in Figs. 3(a), (b) and (c), respectively. It can be seen that the DOSs at the Fermi level are all higher than zero, 1.08 states/(eV unit cell) for YCu, 1.09 states/(eV unit cell) for YAg, and 1.04 states/(eV unit cell) for DyCu, respectively. Hence, they have obvious metallic character.¹⁷⁾ As shown in the figure, for YCu and DyCu, the large occupied peak is located at about -3.0 eV

Fig. 2 Calculated total energy vs. relative volume/f.u. of (a) YCu, (b) DyCu and (c) YAg. V_0 is the corresponding experimental volume.

Table 1 The experimental and calculated structural parameters for YCu, DyCu and YAg, respectively.

	<i>RM</i>	<i>a</i> (Å)	Volume (Å ³)
YCu	Experimental ¹³⁾	3.476	41.999
	Present calculation	3.473	41.882
DyCu	Experimental ⁴⁾	3.460	41.422
	Present calculation	3.459	41.403
YAg	Experimental ¹³⁾	3.619	47.399
	Present calculation	3.632	47.920

below the Fermi level, which is dominated by the Cu d -state according to the results of partial DOSs. But for YAg, the large occupied peak is to shift to the energy -5.0 eV, which is dominated by the Ag d -state. The states above the Fermi level are mainly due to Y d -state in YCu and YAg, and Dy d -state in DyCu, respectively. In binary alloys, it is important to analyze the bonding character near the Fermi level. As shown in Fig. 3, the Fermi energy of YCu, DyCu and YAg lies near a local minimum, which means that the bonding is relatively insensitive to local distortions.¹⁸⁾ In contrast, the Fermi energy of NiAl, a typical intermetallic with brittle behavior, is located at the peak in the DOS. Thus, the difference in ductility between RM ductile intermetallics and the other brittle intermetallics may be partially explained by their difference in Fermi level.

Knowledge of the elastic properties of materials promotes the understanding of the fundamental aspects of mechanical deformation and structural properties of crystals. Above all, we can predict the mechanical properties by the elastic constants, particularly, the ductility/brittleness of the materials. The calculated elastic constants of YCu, DyCu and YAg have been listed in Table 2. For a comparison, the corresponding experimental values are also presented. From Table 2, it is analyzed that the calculated elastic constants of YCu and YAg are very close to the experimental value. On the basis of the fact, though it is lack of reports for DyCu, we should think that the calculated values of elastic constants for DyCu are credible.

Table 2 The calculated and experimental elastic constants, bulk modulus K , anisotropy, and Poisson's ratio for YCu, YAg and DyCu.

	YCu		YAg		DyCu
	Calculated	Experimental ⁸⁾	Calculated	Experimental ⁸⁾	Calculated
C_{11} (GPa)	110.7	113.4	107.3	102.4	106.1
C_{44} (GPa)	35.3	32.3	37.9	37.2	46.3
C_{12} (GPa)	50.7	48.4	58.4	54.0	42.3
K (GPa)	70.7	70.1	74.7	70.5	63.6
Anisotropy	1.18	0.99	1.55	1.54	1.45
ν	0.31	0.30	0.35	0.35	0.29

Fig. 3 The total and partial density of states of *RM* intermetallics: (a) YCu, (b) YAg and (c) DyCu.

The polycrystalline shear modulus is associated with the resistance to plastic deformation while the bulk modulus represents the opposition to bond rupture, so the ratio K/G (bulk modulus K divided by the shear modulus G) may be considered as a criterion of the ductility/brittleness performance of materials.¹⁹⁾ This criterion is named as Pugh's criterion. For materials with melting temperature above

900°C, its ductility (ability to plastic deformation without fracture) can be characterized by high K/G ratio (> 1.75), while low K/G is representative of brittleness.^{8,20)} The melting temperatures of YCu, YAg and DyCu are 935, 1160 and 955°C, respectively. They are all greater than 900°C. Using the relation between the bulk modulus and shear modulus and the relation between Poisson's ratio ν , and the elastic constants, the K/G ratio can be calculated as follows:

$$\frac{K}{G} = \frac{2}{3} \left(\frac{1 + \nu}{1 - 2\nu} \right) \quad (1)$$

$$\nu = \frac{C_{12}}{C_{11} + C_{12}} \quad (2)$$

The calculated values are 2.30 for YCu, 3.00 for YAg and 2.05 for DyCu, respectively. According to the Pugh's criterion, they should be ductility at room temperature, which is consistent with the experimental work.⁴⁻⁷⁾ The elastic anisotropy is also calculated in this work. The expression for the anisotropy is:

$$A = 2 \frac{C_{44}}{C_{11} - C_{12}} \quad (3)$$

The value of the anisotropy is also listed in Table 2. Unlike other B2 intermetallics, the elastic anisotropy of *RM* intermetallics is close to 1, and lies between the brittle B2 intermetallics ($A > 2$) and B2 ionic compounds ($A < 0.7$), indicating a more isotropic behavior.⁸⁾ The values of the anisotropy and Poisson's ratio of the ductile *RM* intermetallics are very close to the BCC metals (W, $A = 1.00$, $\nu = 0.28$; Mo, $A = 0.90$, $\nu = 0.29$).^{4,21)} The more isotropic nature of the *RM* compounds may account for the absence of the brittleness as compared with the strong anisotropy ($A > 2$ or $A < 0.7$), and provides additional support to that *RM* intermetallics are a new class of materials, which are different from the other B2 structural intermetallics.

4. Summary

In conclusion, the electronic structure and elastic properties of YCu, DyCu and YAg were studied by the first-principles calculations. Based on the results of density of states and elastic properties, their ductility is predicted. These ductile *RM* intermetallics are different from the other ordinary brittle B2 intermetallics. They exhibit more isotropic behavior, very close to the BCC elemental metals.

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REFERENCES

- 1) C. T. Liu, E. P. George, P. J. Maziasz and J. H. Schneibel: *Mater. Sci. Eng. A* **258** (1998) 84–98.
- 2) N. S. Stoloff, C. T. Liu and S. C. Devis: *Intermetallics* **8** (2000) 1313–1320.
- 3) D. B. Miracle: *Acta Metall. Mater.* **41** (1993) 649–684.
- 4) K. Gschneidner, A. Russell, A. Pecharsky, J. Morris, Z. Zhang, T. Lograsso, D. Hsu, C. H. Chester, Y. Y. Ye, A. Slager and D. Kesse: *Nature Mater.* **2** (2003) 587–590.
- 5) Z. Zhang, A. M. Russell, S. B. Biner, K. Gschneidner and C. C. H. Lo: *Intermetallics* **13** (2005) 559–564.
- 6) A. M. Russell, Z. Zhang, T. A. Lograsso, C. C. H. Lo, A. O. Pecharsky, J. R. Morris, Y. Ye, K. A. Gschneidner and A. J. Slager: *Acta Mater.* **52** (2004) 4033–4040.
- 7) A. M. Russell, Z. Zhang, K. A. Gschneidner, T. A. Lograsso, A. O. Pecharsky, A. J. Slager and D. C. Kesse: *Intermetallics* **13** (2005) 565–571.
- 8) J. R. Morris, Y. Y. Ye, Y. B. Lee, B. N. Harmon, K. A. Gschneidner and A. M. Russell: *Acta Mater.* **52** (2004) 4849–4857.
- 9) Y. J. Shi, Y. L. Du, G. Chen and G. L. Chen: *Phys. Lett. A* **368** (2007) 495–498.
- 10) V. I. Anisimov, F. Aryasetiawan and A. I. Lichtenstein: *J. Phys.: Condens. Matter.* **9** (1997) 767–808.
- 11) H. Harima: *J. Magn. Magn. Mater.* **226–230** (2001) 83–84.
- 12) P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka and J. Luitz: *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties*, Karlheinz Schwarz, Techn. (Universität Wien, Austria, ISBN 3-9501031-1-2, 2001).
- 13) M. Diviš and J. Kuriplach: *Physica B* **205** (1995) 353–364.
- 14) K. B. Panda and K. S. Ravi Chandran: *Acta Mater.* **54** (2006) 1641–1657.
- 15) B. B. Karki, L. Stixrude, S. J. Clark, M. C. Warren, G. J. Ackland and J. Crain: *Am. Mineralogist* **82** (1997) 51–60.
- 16) F. D. Murnaghan: *Proc. Natl. Acad. Sci. USA* **30** (1944) 244–247.
- 17) J. Y. Wang and Y. C. Zhou: *Phys. Rev. B* **69** (2004) 144108–144102.
- 18) Y. Wu and W. Hu: *Eur. Phys. J. B* **60** (2007) 75–81.
- 19) S. F. Pugh: *Philos. Mag.* **45** (1954) 823–844.
- 20) L. Vitos, P. A. Korzhavyi and B. Johansson: *Phys. Rev. Lett.* **88** (2002) 155501–155504.
- 21) Y. G. Zhang, Y. F. Han, G. L. Chen, J. T. Guo, X. J. Wang and D. Feng: *Structural materials of intermetallic compounds*. Beijing, China, ISBN 7-118-02321-3, 2001.