OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 8, No. 9-10, September – October 2014, p. 916 - 920

First-principles calculations on structural and electronic properties of $Al_{18}Mg_3M_2$ phases (M = Sc, Ti, Cr, Mn and Zr)

XIAO-MING DU[a,*], ZHEN BIAO DONG[a], PING MA[b], ER-DONG WU[b]
[a]*School of Materials Science and Engineering, Shenyang Ligong University, Shenyang 110159, China*
[b]*Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016 , China*

The plane-wave ultrasoft pseudopotential method based on the density-functional theory has been used to calculate the crystal, electronic structures and the stability of $Al_{18}Mg_3M_2$ (M = Sc, Ti, Cr, Mn and Zr) compounds with cubic structure. The calculated results show that stability of $Al_{18}Mg_3M_2$ componds decreases in the order $Al_{18}Mg_3Mn_2 < Al_{18}Mg_3Cr_2 < Al_{18}Mg_3Ti_2 < Al_{18}Mg_3Sc_2 < Al_{18}Mg_3Zr_2$. The density of states and charge density analyses show that the bondings of $Al_{18}Mg_3M_2$ compounds have both covalent and ionic properties and the all crystals exhibit a metallic feature. The bonding nature of $Al_{18}Mg_3M_2$ compounds is investigated, showing stronger covalent bonding between transition metal atoms and Al than between Al and Al, between Mg and Al.

(Received February 26, 2014; accepted September 11, 2014)

Keywords: $Al_{18}Mg_3M_2$ compounds, First-principle calculation, Stability, Electronic structure

1. Introduction

The development of the industry of alloys of non-ferrous metals is due to the demand for such materials in many domains of technology. The characteristic properties of alumnium alloys such as high specific strength, good formability, good corrosion resistance and potential recycling make them to be applied in many facilities of the shipbuilding industry, in the construction of moderately loaded elements of aeroplanes and vehicles, as well as in the chemical and food industry, and also in building engineering [1-3]. Al-Mg alloys usually contain additives of transition metals, such as Mn, Cr, Sc, Ti and Zr and other metals. Small concentrations of transition metals increase the tensile strength [4,5], corrosion resistance [6] of these alloys. For the purpose of obtaining aluminum P/M materials strengthened by solid solution of Mg and dispersion of transition metal compounds, Fujii, et. al. [8] worked on rapidly solidified Al-Transition metals with addition of Mg Rapid solidification.

Alought many researches have been done on improvement of mechanical propersites for Al-Mg alloys by adding transition metals, the investigation of the microstructures of Al-Mg-Transition metal alloys and interactions between Al and transition metal atoms was scarce to our knowledge. Kerimov et al. [9,10] established for the first time the crystal structures of the ternary intermetallic Al-Mg-Transition metal (Ti, V, Cr, Mo, W, Ta) compounds using X-ray powder analysis, which have been found to crystallize in cubic symmetry. Zhang et al. [11] reported that the elastic and electronic properties of cubic $Al_{18}Ti_2Mg_3$ phase from the first principle calculation. Howerev, the results mentioned above have not given the systemical explaintions of the structural stability and bonding nature in Al-Mg-Transition metal compounds so far. In this paper, we attempt to calculate the structural and electronic properties of $Al_{18}Mg_3M_2$ (M = Sc, Ti, Cr, Mn and Zr) compounds based on an ab initio method in order to revealing natural properties of the compounds from atomic or electronic scale.

2. Computational methods

The calculations were performed using Quantum-ESPRESSO plane-wave code based on density functional theory [12]. The exchange – correlation potential was evaluated by the generalized gradient approximation (GGA) of PW91 adopted for all elements in our models by adopting the Perdew–Burke–Ernzerhof parameters [13,14]. Ultrasoft psudopotentials [15] represented in reciprocal space are used. The kinetic energy cut-off value for plane-wave expansions was set as 500eV for all the calculations. For all structures the lattice parameters, the volume and the atom positions were allowed to relax simultaneously. The sampling integration over the first Brillion zone was conducted by using the Monkhorst–Pack method [16] with 6×6×6 special *k*-point mesh for cubic $Al_{18}Mg_3M_2$ Phases (M = Sc, Ti, Cr, Mn and Zr). Convergence with respect to the *k*-point sampling for the Brillouin zone (BZ) integration was tested independently on the five phases using regular meshes of increasing density. Tests indicated that the total energy converges to 2 meV/atom. Pulay density mixing scheme was applied for the electron energy minimization process. The valence electronic configurations were Al ($3s^23p^1$), Mg ($2p^63s^2$), Ti ($3s^23p^63d^24s^2$), Cr ($3s^23p^63d^54s^1$), Mn ($3s^23p^63d^54s^2$), Sc ($3s^23p^63d^14s^2$), Zr ($4s^24p^64d^25s^2$) in the calculations. The convergence criteria for geometry optimization were as follows: electronic self-consistent field (SCF) tolerance less than 5.0×10^{-5} eV/atom, Hellmann–Feynman force below 0.01eV/⊕, maximum stress less than 0.05GPa and displacement within 2.0×10^{-4}⊕. After the structures are optimized, the total energies are recalculated self-consistently with the tetrahedron method [17]. The latter technique is also used to calculate the electronic density of states (DOS).

3. Results and discussions

3.1 Crystal structures

The $Al_{18}Mg_3M_2$ (M = Sc, Ti, Cr, Mn and Zr) compound crystallizes in the cubic structure with the space group Fd-3m (No.227). The unit cell has 184 atoms in which the Al atoms occupy the 48f (0.4843,0.125,0.125) and 96g (0.0584,0.0584,0.3252) Wyckoff sites, the transition metal atoms occupy 16d (0.5,0.5,0.5) sites and the Mg atoms occupy the 8a (0.125,0.125,0.125)sites and 16c (0,0, 0) sites, as shown in Fig. 1. The original crystal configurations in present work are chosen from the X-ray diffraction results given in Ref. [9]. Starting from the above crystal structure, the structural optimization was first performed by full relaxation of cell shape and atomic positions. The obtained equilibrium lattice constants were listed in Table 1, where the available experimental results were also presented. It can be seen that the structural parameters of $Al_{18}Mg_3M_2$ (M = Ti, Cr, Mn) phases were in accordance with the experimental data [9,10]. Also, Zhang et al. [11] reported that the lattice constant of $Al_{18}Mg_3Ti_2$ with the same structure as this study was 14.7967 ⊕ obtained from the first principle calculation, which is in good agreement with our calculated results.

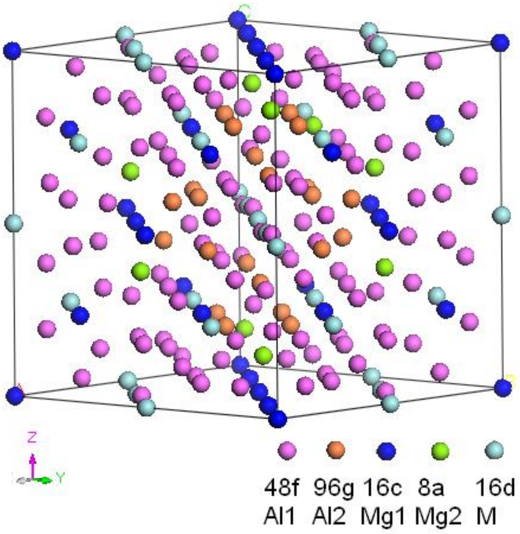


Fig. 1. Crystal structure of $Al_{18}Mg_3M_2$ (M = Sc, Ti, Cr, Mn and Zr).

Table 1. Optimized results for $Al_{18}Mg_3M_2$ (M = Sc, Ti, Cr, Mn and Zr) including equilibrium lattice constants, total energy E_{tot}, formation enthalpy ΔH.

Compounds	Lattice constants (⊕)		E_{tot} (eV)	ΔH (kJ/mol)
	Cal.	Exp.[9]		
$Al_{18}Mg_3Sc_2$	15.0636	-	-12891.7763	-18.50
$Al_{18}Mg_3Ti_2$	14.8095	14.77	-14204.9378	-17.95
$Al_{18}Mg_3Cr_2$	14.5280	14.53	-17652.0648	-15.82
$Al_{18}Mg_3Mn_2$	14.6424	14.53	-10395.4889	-13.07
$Al_{18}Mg_3Zr_2$	15.1129	-	-12903.9264	-21.84

3.2 Formation enthalpies

In order to understand the formation stability of the ternary intermetallic compound, the formation enthalpies of $Al_{18}Mg_3M_2$ (M = Sc, Ti, Cr, Mn and Zr) compounds were calculated according to the following expressions [18]:

$$\Delta H=(E_{\mathrm{tot}}-N_{\mathrm{Al}}E_{\mathrm{tot}}(\mathrm{Al})_{\mathrm{solid}}-N_{M}E_{\mathrm{tot}}(\mathrm{M})_{\mathrm{solid}}-N_{\mathrm{Mg}}E_{\mathrm{tot}}(\mathrm{Mg})_{\mathrm{solid}})/(N_{Al}+N_{\mathrm{M}}+N_{\mathrm{Mg}}) \tag{1}$$

where E_{tot} is the total energy of $Al_{18}Mg_3M_2$ in equilibrium lattice per unit ; $E_{tot}(Al)_{solid}$, $E_{tot}(M)_{solid}$ and $E_{tot}(Mg)_{solid}$ are the total energy of fcc Al, transition metals and hcp Mg in their stable state per unit cell, respectively; N_{Al} , N_M and N_{Mg} refer to the numbers of Al, transition metals and Mg atoms in unit cell of $Al_{18}Mg_3M_2$, repectively. In the present work, we calculate the single atomic energy by the following method: at first, the energy of a pure metal crystal in the solid state was calculated, then the energy was divided by the number of atoms involved in the crystal, and this result is the energy of a single atom in the pure metal. The calculated energies of Al, Mg, Ti, Cr, Mn, Sc and Zr pure metals for our considered systems were -52.7863 eV, -978.5108 eV, -1606.2525 eV, -2468.2879 eV, -654.4715 eV, -1277.8963 eV and –1280.5356 eV, respectively. The calculated formation enthalpies of $Al_{18}Mg_3M_2$ phases are listed in Table 1. Generally, the lower the formation enthalpy is, the more stable the crystal structure is. The $Al_{18}Mg_3Zr_2$ compound has the highest stability. For 3d transition metals, it was found that the formation enthalpies of $Al_{18}Mg_3M_2$ (M = Sc, Ti, Cr, Mn) compounds increased with the increase of the atomic number of transition metals in compounds, indicating that the stability of the compounds decreases correspondingly. The formation enthalpy of $Al_{18}Mg_3Ti_2$ from Zhang et al. [11] was -17.26 kJ/mol obtained by GGA method, which is in good agreement with the presently calculated values (Table 1).

3.3 Electronic structure

In order to investigate intrinsic mechanism for structural stability and electronic bonding nature, the density of states (DOS) and the charge density distribution for The $Al_{18}Mg_3M_2$ (M = Sc, Ti, Cr, Mn and Zr) compounds were calculated. Fig. 2 shows the total densities of states (TDOS) and partial densities of states (PDOS) for $Al_{18}Mg_3M_2$ compounds with the energy from -12 eV to 4 eV, in which Fermi level was set to zero. The most remarkable feature of the total densities of states for these compounds is that all the compounds exhibit metallic characteristics. The values of the total DOS at the Fermi level ($N(E_F)$) were 16.42, 16.91, 19.12, 21.06, 15.90 electron states /eV for $Al_{18}Mg_3Sc_2$, $Al_{18}Mg_3Ti_2$, $Al_{18}Mg_3Cr_2$, $Al_{18}Mg_3Mn_2$ and $Al_{18}Mg_3Zr_2$, respectively, which are mainly contributed by electrons from transition metal atoms (3d) or (4d), Al1 (3p), Al2 (3p), Mg1 (2p) and Mg2 (3s) orbits. In general, $N(E_F)$ on DOS plot can be used to characterize the activity of valance electrons of the atoms in crystal. Namely, the smaller $N(E_F)$, the less is change probability of the electronic structures of the crystal when external conditions change, thus the crystal has the higher stability [19]. It is shown that the stability of $Al_{18}Mg_3M_2$ componds decreases in the order $Al_{18}Mg_3Mn_2 < Al_{18}Mg_3Cr_2 < Al_{18}Mg_3Ti_2 < Al_{18}Mg_3Sc_2 < Al_{18}Mg_3Zr_2$. The conclusion consists with the forementioned result from energetic analysis.

The overall shapes of the total DOSs for $Al_{18}Mg_3M_2$ (M = Sc, Ti, Cr, Mn and Zr) compounds are similar to each other, except that the location and number of sharp peaks below Fermi level are different. These differences may result from the bonding interactions between different neighbor atoms. We can see that Al and Mg atoms at different crystal sites exhibit different density of states. Especially, at the energy near the Fermi level, more electrons of Mg1 atoms occupy p orbit while more electrons of Mg2 atoms occupy s orbit, and less electrons of Al1 and Al2 atoms occupy s orbit. In the region of −5 eV to Fermi level, strong hybridizations between Al(3p) orbit and transitoion metal (3d or 4d) orbit appear for $Al_{18}Mg_3M_2$ compounds, indicating that there exist strong bonding interactions between Al atoms and transitoion metal atoms. The first bonding peak on total DOS located at −1.27 eV, -1.27 eV, -1.94 eV, -1.90 eV and -1.38 eV, respectively, is due to the strong interaction of transition metal (3d or 4d), Al (3p) and Mg (2p). The slight interaction between Mg (s) and Al (p) also occurs. In the lower energy range from −10 eV to −5 eV, the total DOS is dominantly contributed by 3p, 3s states of Al atoms and 2p, 3s states of Mg atoms, which indicates s-p hybridization of Al-Al, Al-Mg and Mg-Mg bonds. Obviously, the lower density states of Mg imply that Al-Al interaction is stronger than that of Al-Mg and Mg-Mg.

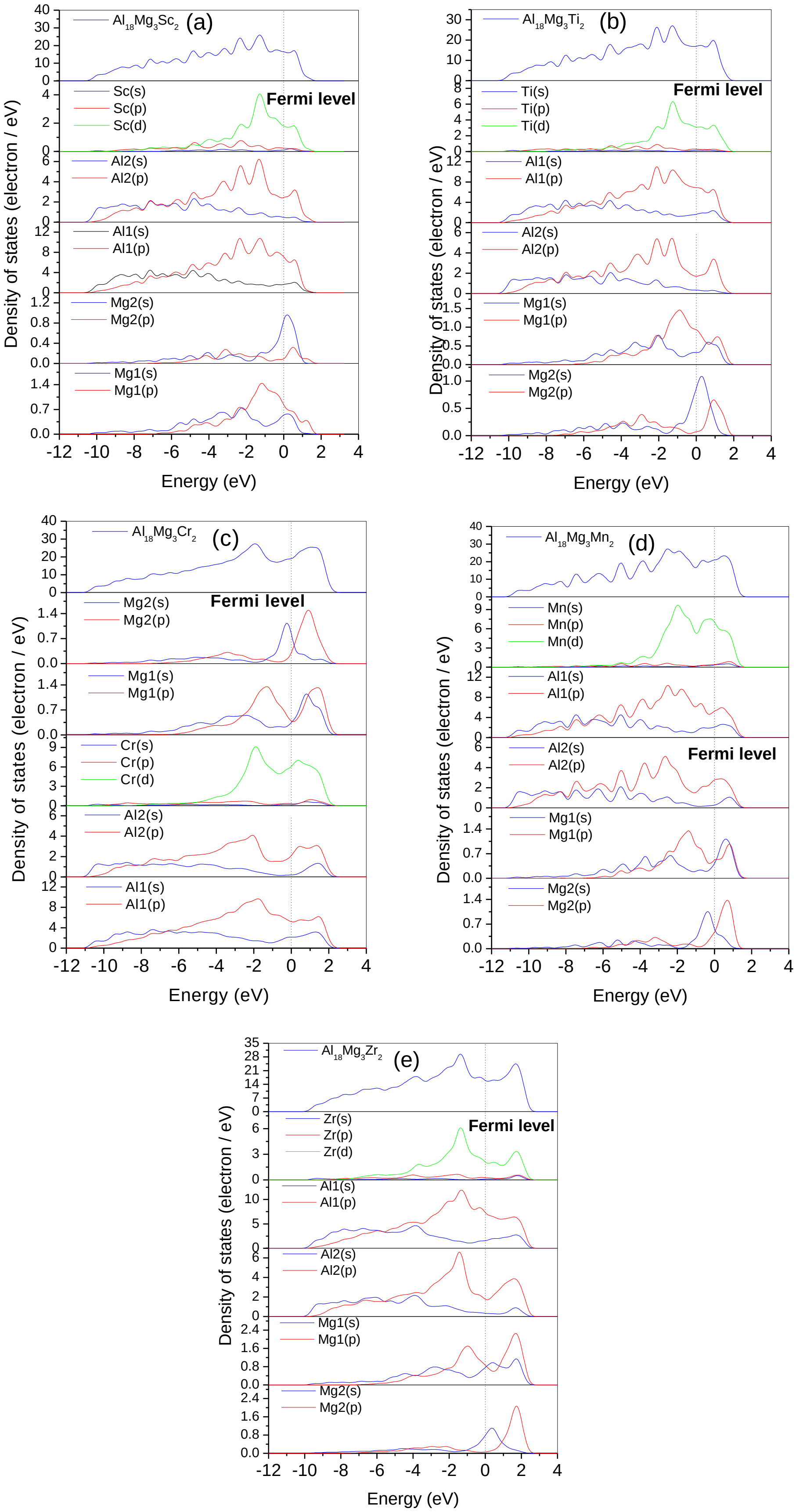
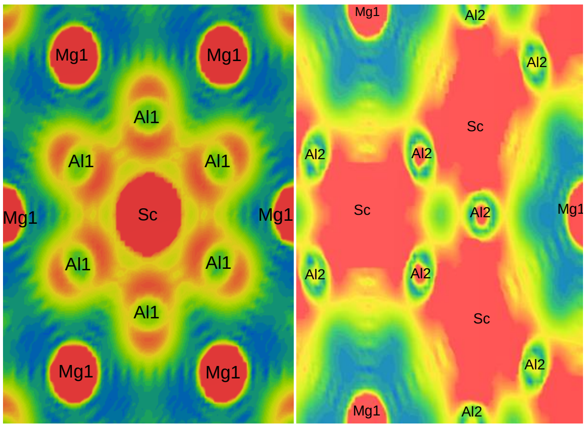


Fig. 2. The total and partial density states of $Al_{18}Mg_3M_2$ (M = Sc, Ti, Cr, Mn, and Zr), (a) $Al_{18}Mg_3Sc_2$, (b) $Al_{18}Mg_3Ti_2$, (c) $Al_{18}Mg_3Cr_2$, (d) $Al_{18}Mg_3Mn_2$, (e) $Al_{18}Mg_3Zr_2$.

To visualize the nature of the bond character and to explain the charge transfer and the bonding properties of the $Al_{18}Mg_3M_2$ compounds, we have investigated change of the charge density distribution. Considering the $Al_{18}Mg_3M_2$ series studied here exhibit similar features, accordingly we have only documented such plots for $Al_{18}Mg_3Sc_2$ compound. Fig. 3 shows the charge-density contour on the (111) plane with different position for $Al_{18}Mg_3Sc_2$ compound. From Fig. 3, it is clear that Sc atoms are surrounded by Al1 atoms with spherical regions (Fig. 3 (a)), implying that valence electron charge from Sc atoms is almost fully transferred to Al1 atoms, and the Sc-Al1 interaction is apparently ionic. However, there exists the overlap for the charge density between Sc and Al2 (Fig. 3 (b)), between Al and Al atoms and between Al and Mg atoms, shown as in Fig. 3. This indicates a covalent bonding between Sc and Al2, between Al and Al atoms and between Al and Mg atoms. And Sc-Al2 interactions are relatively stronger than that of Al-Al and Al-Mg. Clearly the stronger covalent interactions between transition metal atoms and Al atom have weakened the interactions between Al atom and Al atom and between Al atom and Mg atom. Therefore, a small quantity of transition metal atoms in $Al_{18}Mg_3M_2$ compounds may improve significantly their mechanical properites. According to those analyses, $Al_{18}Mg_3M_2$ (M = Sc, Ti, Cr, Mn, and Zr) compouds exhibit a mixture characteristic of ionic and covalent bonding.



(a) Sc-Al1 interactions (b) Sc-Al2 interactions

Fig. 3. Contour map of the electron density on the (111) plane with different position for $Al_{18}Mg_3Sc_2$.

4. Conclusions

In conclusion, the investigation on the structural, electronic properties and stability of $Al_{18}Mg_3M_2$ (M = Sc, Ti, Cr, Mn, and Zr) compouds has been performed by using the first-principles total-energy calculations based on DFT. The calculated lattice parameters have a great agreement with experimental results. The calculated enthalpies of formation reveal that the stability of $Al_{18}Mg_3M_2$ componds decreases in the order $Al_{18}Mg_3Mn_2 < Al_{18}Mg_3Cr_2 < Al_{18}Mg_3Ti_2 < Al_{18}Mg_3Sc_2 < Al_{18}Mg_3Zr_2$. Electronic densities of states have shown that $Al_{18}Mg_3M_2$ componds exhibit metallic characteristics and a mixture characteristic of ionic and covalent bonding. And the stronger covalent interactions between transition metal atoms and Al atom have weakened the interactions between Al atom and Al atom and between Al atom and Mg atom.

Acknowledgement

The authors gratefully acknowledge the financial support from the program for Shenyang Ligong University Key Course Opening Fund in Materials Processing Engineering, China and the program for Liaoning Excellent Talents in University (LNET), China (LJQ2012016).

References

[1] M. Tokarski, Ślask, Katowice, 1986.
[2] L. A. Dobrzański, WNT, Warsaw, 2004.
[3] L. A. Dobrzanski, K. Kasprzak, J. Sokolowski, Proceedings of the 13th International Scientific Conference “Achievements in Mechanical and Materials Engineering” AMME’2005, Gliwice-Wisła, 2005, 143-146.
[4] V. I. Elagin, V. V. Zakharov, T. D. Rostova, Met. Sci. Heat Treat. **34**, 37 (1992) .
[5] S. Lathabai, P. G. Lloyd, Acta Mater. **50**, 4275 (2002).
[6] M. N. Ishaq, S. T. A. Shah, S. Ali, Coden: Jnsmac **46**, 39 (2006).
[7] H. Fujii, M. Sugamata, J. Kaneko, M. Kubota, Keikinzoku **50**, 330 (2000).
[8] K. M. Kerimov, S. F. Dunaev, E. M. Sljusarenko, J. Less-Common Met. **133**, 297 (1987).
[9] K. M. Kerimov, S. F. Dunaev, J. Less-Common Met. **153**, 267 (1989).
[10] F. Y. Zhang, M. F. Yan, Y. You, C. S. Zhang, H. T. Chen, Physica B **408**, 68 (2013).
[11] http://www.pwscf.org.
[12] B. Hammer, L. B. Hansen, J. K. Norkov, Phys. Rev. B **59**, 7413 (1999).
[13] J. A. White, D. M. Bird, Phys. Rev. B **50**, 4954 (1994).
[14] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[15] H. J. Monksorst, J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[16] P. E. Blochl, O. Jepsen, O. K. Andersen, Phys. Rev. B **49**, 16223 (1994).
[17] N. I. Medvedeva, Y. N. Gornostyrev, D. L. Novikov, O. N. Mryasov, A. J. Freeman, Acta Mater. **46**, 3433 (1998).
[18] Y. Imai, M. Mukaida, T. Tsunoda, Intermetallics **8**, 381 (2000).

---

[*] Corresponding author: du511@163.com