Electronic and Magnetic Effects on Cu Doping Ti_2NiAl Heusler Alloy: A First-Principles Study

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(Received November 5, 2013; in final form June 18, 2014)

We investigate the effect of the electronic and magnetic properties on nonmagnetic Cu-3d atoms doping the Heusler alloy $Ti_2Ni_{1-x}Cu_xAl$ ($0 \leq x \leq 1$) using first-principles calculations. The optimized lattice constants are consistent with the Vegard law, and energies of doped systems become more lower as the increase of x concentration. A critical transition diagram from half-metallic to metallic characters is discussed. In addition, the magnetic interactions between p and d states are illustrated. Finally, magnetic moments are given as a function of x value, which implies that the Slater–Pauling rule is obeyed at low Cu content ($x \leq 0.2$).

DOI: 10.12693/APhysPolA.126.795

PACS: 71.20.Gj; 61.72.S–; 81.30.–t; 75.50.Cc

1. Introduction

Full-Heusler compounds appear with the chemical formula X_2YZ, where X and Y are transition metal and Z is a *sp* element. When the valence of the X is larger than Y, the structure is the well known $L2_1$ one and its prototype is Cu_2MnAl [1]. When the valence of the Y elements is the largest, the compounds crystallize in the so-called XA structure, where the prototype is Hg_2TiCu [1], which is also known as inverse Heusler compounds. Recently, several inverse Heusler alloys have confirmed to be half-metallicity by using first-principles electronic structure calculations [2–8]. Among them, the magnetization is usually confined to the transition metal atom, and the total magnetic moment is integer values that accords with the Slater–Pauling rule [9, 10]. Additionally, the large exchange interaction between transition metal atoms leads to the formation of band gap and the integer moment. Therefore, the magnetic properties of these systems strongly depend on the transition metal 3d atoms, including nonmagnetic and magnetic 3d atom, and *sp* atoms. Early measurements [11] on several quaternary Heusler alloys as well as recent studies on $AuMnSn_{1-x}Sb_x$ [12] have demonstrated the importance of *sp* electrons in establishing the magnetic properties. On the other hand, the importance of the nonmagnetic 3d atoms for the magnetism was revealed recently by the experimental studies [13, 14]. Particularly, Galanakis et al. [15] confirmed that a phase transition occur from a ferromagnetic to an antiferromagnetic state close to the stoichiometric ($x \approx 1$) when the nonmagnetic 3d-Cu atoms are doped to $Co_{1-x}Cu_xMnSb$ and $Ni_{1-x}Cu_xMnSb$ alloys. At present, the authors show the influence of electronic and magnetic properties for nonmagnetic Cu-doped to $Ti_2Ni_{1-x}Cu_xAl$. We have to note here that Ti_2NiAl is a half-metallicity with ferromagnetic states and has been extensively studied theoretically [16, 17].

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The purpose of the given work is to investigate the influence of the nonmagnetic 3d atoms on the electronic and magnetic properties of the half-metallic Heusler alloy Ti_2NiAl. Simultaneously, we explore the transition between half-metallic and metallic at zero temperature, and discuss the physical mechanisms behind the transition.

2. Computational method

The electronic structure calculations are performed using the full-potential nonorthogonal local-orbital minimum-basis band-structure scheme (FPLO) [18, 19] and employing the virtual crystal approximation (VCA) to simulate the disorder. All calculations were done within the scalar relativistic approximation. The general gradient approximation of exchange-correlation functional was chosen to be that parameterized by Perdew–Burke–Ernzerhof [20]. The number of k-points in the whole Brillouin zone was set to $25 \times 25 \times 25$ in order to ensure the convergency of the results. For a self-consistent field iteration, the convergence criterion was set to both the density (10^{-6} code specific units) and the total energy (10^{-8} He). In addition, more detailed calculations in FPLO-VCA method can be seen from Ref. [21].

3. Results and discussion

3.1. Lattice constants and stability

We have used the optimized lattice constants for $Ti_2Ni_{1-x}Cu_xAl$ system. The lattice constants are displayed as a function of x concentration in Fig. 1, meanwhile, we also give lattice constants which follow the Vegard law. The contrary of both curves shows they are consistent with each other, the tiny discrepancy ascribes to interatomic complex interactions. In addition, we have given the change of energy as a function of Cu dopant in Fig. 2, the results indicate the energies become more lower as increasing x content. Meanwhile, we can see also a transition occurrence between half-metallic and metallic characters as Cu concentration up to ≈ 0.2.

The electronic and magnetic properties of parent Heusler alloy Ti_2NiAl have been extensively studied earlier. Here we focus on the effect of the Cu doping on the electronic and magnetic characteristics of Ti_2NiAl, and

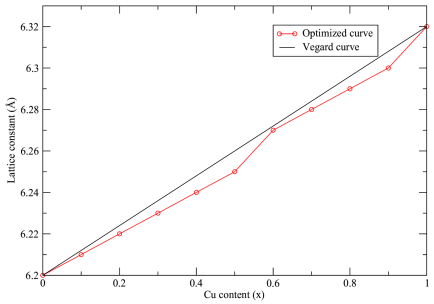

Fig. 1. The changes of lattice constants as functions of Cu concentration in $Ti_2Ni_{1-x}Cu_xAl$. Let us note that the Vegard curve is given to compare with the optimized lattice constants.

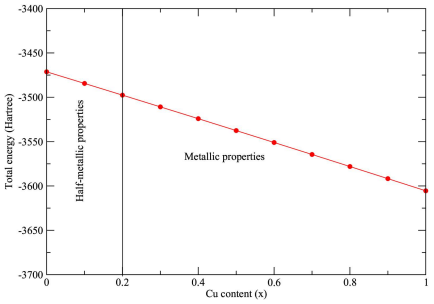

Fig. 2. The total energy changes of $Ti_2Ni_{1-x}Cu_xAl$ with increased Cu content. The transition points between the half-metallic and metallic characters also are offered.

we discuss the origin of the observed transition from half--metallic to metallic. The discussion is divided into two parts. Firstly, we study the influence of the Cu doping on electronic properties. Secondly, we focus on changes of the magnetic moment including also a discussion on the role played by the Cu atoms.

3.2. Effect of Cu doping on electronic properties of Ti_2NiAl

In Fig. 3, we present the total density of states (DOS) in $Ti_2Ni_{1-x}Cu_xAl$ as a function of the Cu content. It can be seen that the band gap in minority-spin states is retained around $x \leq 0.2$, and the total DOS shifts slowly to occupied states, which is consistent well with obtained results in Fig. 2, namely, the energy of $Ti_2Ni_{1-x}Cu_xAl$ is much lower as Cu content increases. The reason for this phenomenon is that more electrons filled the occupied states. In order to further explore the cause of trend, we give the total and atom-resolved DOS to analysis in Fig. 4. It is clear that the Ti-3d states offer a main contribution to the total DOS around the Fermi level, while for virtual atom the contribution of 3d states gradually decrease with increase of Cu content, but they play a main contribution to total DOS from -2 to -4 eV below the Fermi level. In unoccupied states, the Ti-3d states offer a main contribution to total DOS. Surprisedly, the contribution of virtual atom 3d states gradually decreases with Cu concentration, owing to the cause that d^{10} orbital is filled fully by electrons. Only Al-3p states have little contribution to total ones.

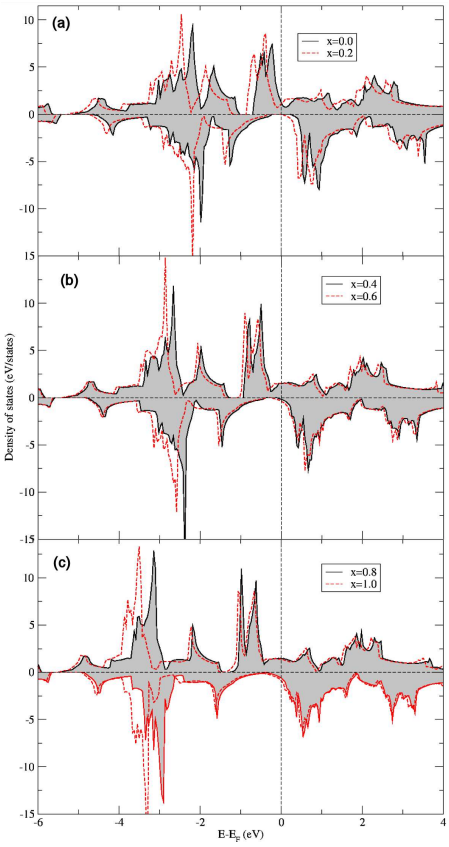

Fig. 3. The changes of total density of states with increased Cu dopant.

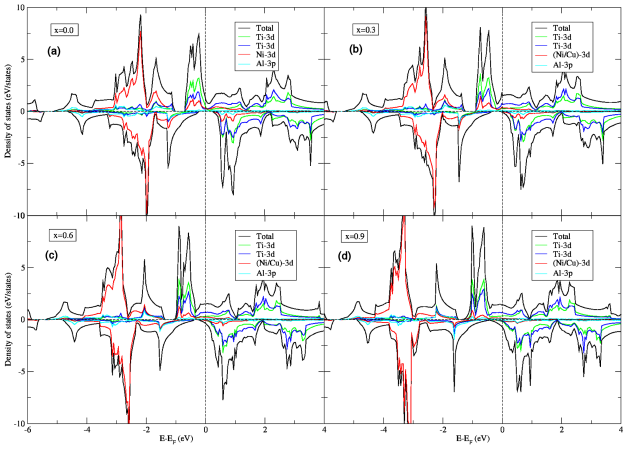

Fig. 4. Total and partial density of states, and the contribution of partial density of states to total ones with increased Cu contents are offered.

3.3. Magnetic properties

In the following, we will discuss the magnetic moments as a function of Cu content. In Fig. 5, we present the total and atom-resolved magnetic moments in $Ti_2Ni_{1-x}Cu_xAl$ as a function of x value. As seen from Fig. 5a, for $x = 0$ the corresponding parent compound is half-metallic with total integer magnetic moment of 3 μ_B for Ti_2NiAl. As the Cu concentration increases, the total spin magnetic moment follows the Slater–Pauling rule around $x \leq 0.2$ and then deviates from the Slater–Pauling curve. Thus

the half-metallicity is retained up to the particular value of the Cu concentration and is dominated by the ferromagnetic Ruderman–Kittel–Kasuya–Yosida (RKKY)--type exchange mechanism [15]. This can also be seen from the total DOS shown in Fig. 3, where the Fermi level crosses the minority-spin states for the corresponding value of x. Furthermore, the variation of the total magnetic moment is around 0.6 μ_B, which mainly comes from the Ti atoms located in 4b sites, whereas this is rather small in other atoms. The induced moment for other atoms only weakly depends on the x concentration. This is due to the fact that the Ti atoms at 4a sites have the same octahedral symmetry with the virtual atom, they are nearest-neighbour atoms and d-orbital hybridizes firstly with each other. However, with the increase of the Cu content, more electrons occupy the majority-spin states for Ti at 4b sites so that the spin magnetic moments improve gradually. For the virtual atom, the magnetic interactions become weaker and weaker, resulting in the exchange splitting disappearance. Finally, there is leading to the transition with half-metallic and metallic characters. It should be noted that as seen from Fig. 5b, the Ti moment located in 4a sites is insensitive to the moment of virtual revealing of the small interaction with virtual atom. In a word, the magnetic interactions of systems strongly depend on the Cu content. In fact, the nature that Cu dopant affects the half-metallicity ascribes to the competition between RKKY-type coupling and superexchange coupling.

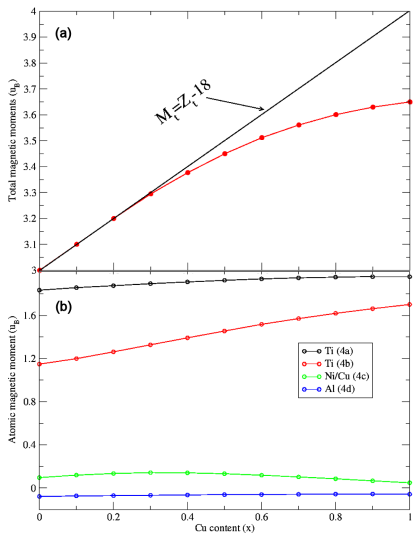

Fig. 5. Total and atomic magnetic moments as fuction of Cu content are displayed. Let us note that the Slater–Pauling rule is indicated to compare with the calculated magnetic moments.

4. Conclusion

In conclusion, we have studied the effect of electronic and magnetic properties for nonmagnetic Cu atom doping Ti_2NiAl within density functional theory. Results indicate that $Ti_2Ni_{1-x}Cu_xAl$ energy lowers as the x content increases. In addition, the magnetic interactions of studied system strongly depend on the Cu content, the half-metallic character is preserved under the $0 \leq x \leq 0.2$ interval, and corresponding spin magnetic moments obey the Slater–Pauling rule, while the nature that Cu dopant affects the half-metallicity ascribes to the competition between RKKY-type coupling and superexchange coupling. Thus, these findings can be used as a practical tool to design materials with given physical properties.

Acknowledgments

This work is financially supported by the National Natural Science Foundation of China (No. 11161027 and No. 11164013). This work was also supported by International Science and Technology Cooperation Program of Gansu province in China (No. 1104WCGA195).

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