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Electronic structure, magnetic properties and martensitic transformation in all-d-metal Heusler alloys Zn_2YMn (Y = Fe, Co, Ni, Cu)

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ABSTRACT

The site preference, electronic structure, magnetic properties and martensitic transformation of all-d-metal Heusler alloys Zn_2YMn (Y = Fe, Co, Ni, Cu) have been investigated by first-principles calculations. In these alloys $L2_1$ structure is found to be more stable compared with XA, in which two Zn atoms prefer occupying the equilibrium A, C sites in the lattice. The total spin moments of Zn_2YMn are all larger than $3\mu_B$ and mainly come from the contribution of Mn. The contributions from Zn atoms are small for its low-lying d states, which do not hybridize with the d states of other atoms directly. Further calculation reveals that the tetragonal martensitic type Zn_2YMn (Y = Fe, Co, Ni) can relax the total energy and are more stable than the cubic phase. The energy difference ΔE_M between the cubic austenite and tetragonal martensite is as high as 0.31 eV in Zn_2FeMn and decreases as Y atom varies from Fe to Ni. In martensitic type Zn_2FeMn and Zn_2CoMn, a quite large c/a ratio is observed, which is preferable for transformation strain effect.

1. Introduction

All-d-metal Heusler alloys are a series of newly reported materials composed completely of transition metal elements [1]. As we know, classic Heusler alloys have an stoichiometric composition of X_2YZ, where X and Y are transition-metal elements, and Z is a main-group element. The transition metal X, Y and main group element Z occupy Wyckoff positions namely A (0, 0, 0), B (0.25, 0.25, 0.25), C (0.5, 0.5, 0.5) and D (0.75, 0.75, 0.75), respectively, and form highly ordered structure. But in full-d Heusler alloys, the Z atom is also a transition metal element. In 2015, Liu et al. synthesized all-d-metal Heusler alloy Ni_2MnTi and realized martensitic transformation in Co-doped Ni-Mn-Ti alloys [1]. These results can greatly enlarge the family of Heusler alloys. In classic Heusler alloys, hybridization between the d electrons from transition metal and p electrons from main-group element is important for the physical properties of Heusler alloys [2–5]. But in all-d-metal Heusler alloys, the situation can be quite different. Then it is quite interesting to investigate the electronic structure of all-d-metal Heusler alloys, which can help to understand the properties of these alloys deeply.

In fact, all-d-metal Heusler alloys have already been observed in Zn_2-based alloys. For example, Zn_2AuAg and Zn_2CuAu were found to crystallize in ordered $L2_1$ or disordered B2 structure depending on the processing methods [6,7]. These results suggest that all-d-metal Heusler materials can be formed in different alloy systems beyond Ni-Mn based and may be a new branch of Heusler alloys.

However, till now there are few reports on the properties of Zn_2YZ Heusler alloys. The main obstacle is the zinc loss to vaporization during alloying, which is a well known problem in metallurgy [8]. Then it is difficult to prepare Zn-based Heusler alloys using normal arc-melting method. Also, Zn_2CuAu and Zn_2AgAu are nonmagnetic, which restricts their applications as magnetic materials like ferromagnetic shape memory alloys (FSMAs).

Then it can be quite meaningful to design a series of ferromagnetic Zn_2YZ all-d-metal Heusler alloys and investigate their electronic, magnetic properties and also martensitic transformation theoretically. In this paper, we selected Zn_2YMn (Y = Fe, Co, Ni, Cu) for investigation, in which Fe, Co, Ni and Mn can contribute spin moments and help to realize ferromagnetism in these alloys.

2. Computational methods

The electronic properties of Zn_2YMn (Y = Fe, Co, Ni, Cu) were calculated using CASTEP code based on pseudopotential method with a plane-wave basis set [9,10]. The interactions between the atomic core and the valence electrons were described by the ultra-soft pseudopotential [11]. The electronic exchange–correlation

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energy was treated under the generalized-gradient-approximation (GGA) [12]. In the calculations, a plane-wave basis set cut-off of 500 eV was used. For Brillouin zone integrations, k-meshes of 20 × 20 × 20 and 18 × 18 × 20 *k*-points were employed for the cubic austenitic and tetragonal martensitic phases, respectively. These parameters ensured good convergences for total energy. The convergence tolerance for the calculations was selected as a difference on total energy within 1×10^{-6} eV/atom.

In the calculations, to reach the stable ground state, we have considered ferromagnetic (FM), paramagnetic (PM) and antiferromagnetic (AFM) coupling between the partial spin moments of magnetic atoms like Mn and Co or Mn and Fe.

3. Results and discussions

3.1. Atomic ordering in cubic Zn_2YMn

As we know, in classic Heusler alloys X_2YZ, the atomic ordering of transition metal atoms X and Y can be determined by the number of their valence electrons further: atoms with more electrons tend to occupy the equilibrium A and C positions while the atoms with fewer electrons prefer the B position, the main group element Z always occupies the D position [13]. This results in two kinds of highly-ordered structures in Heusler alloys: One is $L2_1$ (Cu_2MnAl-type), in which two X atoms occupy A and C positions and Y, Z atoms enter B and D positions, respectively. The other is XA (Hg_2CuTi-type), in which the two X atoms occupy A and B positions and Y, Z atoms locate at C and D positions, respectively [14]. In all-d-metal Heusler alloys, there is no main group element, then it is interesting to investigate the site preference in them. In Fig. 1, we presented the crystal structure of XA and $L2_1$ type Zn_2FeMn as examples.

In Fig. 2 we presented the calculated total energies (E) of $L2_1$ and XA type Zn_2YMn (Y = Fe, Co, Ni, Cu) as functions of the lattice constant a. For each structure, the FM, AFM and PM curves were all presented for comparison. It is clear that in Zn_2YMn alloys studied, the $L2_1$ structure is lower in energy compared with XA and is more stable, in which two Zn atoms occupy the A, C sites. This agrees well with the observation in Zn_2AuAg and Zn_2CuAu [6,7]. This conclusion can be helpful in the design of new all-d-metal Heusler alloys. The energy difference ΔE between XA and $L2_1$ structures has been listed in Table. 1, which is as high as 0.24 eV in Zn_2FeMn, then decreases in the sequence of Fe, Co, Ni and Cu. In Zn_2CuMn, the ΔE is only 0.04 eV, this is a small value and may be related to the similar number of valence electrons and electronic structure between Cu and Zn. The derived equilibrium lattice constants for $L2_1$ and XA type Zn_2YMn have been listed in Table. 1, a increasing tendency of the lattice is observed as Y atom varies from Fe to Cu.

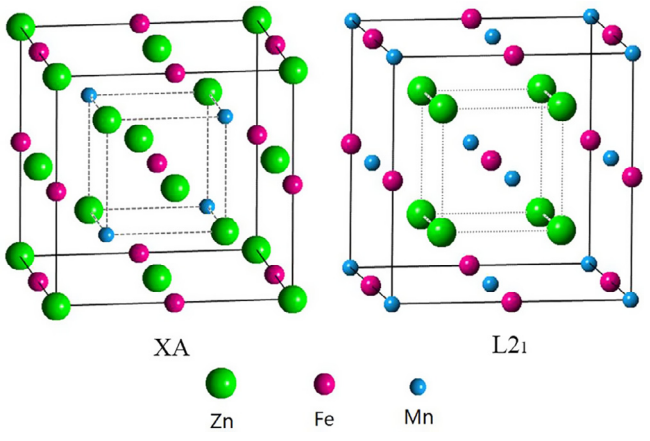

Fig. 1. Crystal structures of XA and $L2_1$ type Zn_2FeMn.

3.2. Electronic and magnetic properties

In $L2_1$ type Zn_2YMn, the magnetic structure is different and depends on composition. In Zn_2FeMn, the FM $L2_1$ curve has the lowest total energy, the energy difference between FM and AFM states is 0.25 eV. But in the other three alloys, the FM and AFM calculations finally converged to the same ground state, despite the starting spin moment configuration of the magnetic atoms. The calculated total and partial spin moments for $L2_1$ type Zn_2YMn are listed in Table. 1, the results for the XA type alloys are also presented for comparison. It may be noticed that the general properties of them are similar.

The total moments of Zn_2YMn are all larger than $3\mu_B$ and comparable to some typical Heusler alloys like Ni_2MnGa [15]. The large total moment mainly comes from the Mn partial moment. In Table 1, it can be found that the spin moment of Mn increases with increasing atomic number of Y atom and contributes most to the total moment. While the partial moment of Y atoms decreases from $2.30\mu_B$ in Zn_2FeMn to $0.03\mu_B$ in Zn_2NiMn, and in Zn_2CuMn, a small negative moment of $-0.17\mu_B$ at Cu site is observed. The partial moment of Zn is insensitive to composition, it remains about $-0.20\mu_B$ in $L2_1$ type Zn_2YMn. All this makes Zn_2FeMn having the largest total moment in these alloys.

Magnetic properties of Zn_2YMn can be explained further based on their electronic structure. In Fig. 3, we presented the total and partial density of states (DOS) for $L2_1$ type Zn_2YMn. In the total DOS, it can be found that these DOS structures share similar characters. In the energy region below −6 eV, a isolated DOS peak is observed in both spin-up and -down directions, which is quite pronounced and less populated. This peak mainly comes from the contributions of Zn 3d states and is separated from the d states of other atoms by a low DOS region as wide as 3 eV. Then the direct hybridization between the d states of Zn and Mn, Y atoms can be weak. This is different from classic Heusler alloys, in which the hybridization between the d states of transition metal atoms may be strong [16].

The d states from Mn and Y atoms spread in the region from −4 to +3 eV, the Mn d states show obvious exchange splitting in the BCC crystal field. In majority spin channel, the DOS peaks are basically below the Fermi level and occupied, but in the minority spin, the antibonding peak locates high above the Fermi level, which introduce large partial spin moment on Mn site in these alloys. The PDOS of Y atom is different in Zn_2YMn and changes with the composition. For the d states of Fe, the minority DOS is high above E_F and a DOS peak locates just at the Fermi level position. But for Co, Ni and Cu, the minority states moves to low energy gradually with increasing number of valence electrons and a flat low DOS region is observed around the Fermi level. That is why only Fe has a large partial moment in these alloys, as can be seen in Table. 1.

Finally, the s and p states of Zn have also been presented to show more detail on the hybridization in Zn_2YMn. It is clear that the s states of Zn locate mainly below -5eV while the p states locate in the energy region from −4 to +1 eV. Then a hybridization between the p states of Zn and d states of other transition metal atoms can be expected. This is similar to the p-d hybridization in classic Heusler alloys between main group element and transition metal [2,3] and also means that Zn may be used to substitute for main group elements in Heusler alloys, if we can inhibit its volatilization.