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Theoretical study of the electronic and magnetic properties of $Co_2Cr_{1-x}V_xAl$

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ABSTRACT

We have investigated the electronic and magnetic properties of the doped Heusler alloys $Co_2Cr_{1-x}V_xAl$(x=0, 0.25, 0.5, 0.75, 1) using first-principles density functional theory within the generalized gradient approximation (GGA) scheme. The calculated results reveal that with increasing V content the lattice parameter slightly increases; both cohesive energy and bulk modulus increase with increasing x. The magnetic moment of the Co(Cr) sites increases with V doping; the total spin moment of these compounds linearly decreases. We also have performed the electronic structure calculations for $Co_2Cr_{1-x}V_xAl$ with positional disorder of Co–Y(Cr,V)-type and Al–Y(Cr,V)-type. It is found that formation of Al–Y-type disorder in $Co_2Cr_{1-x}V_xAl$ alloys is more favorable than that of Co–Y-type disorder. Furthermore, we found that $Co_2Cr_{1-x}V_xAl$ of the $L2_1$-type structure have a half-metallic character. And the stability of $L2_1$ structure will enhance, however, the Curie temperature decreases as the V concentration increases. The disorder between Cr(V) and Al does not significantly reduce the spin polarization of the alloys $Co_2Cr_{1-x}V_xAl$.

1. Introduction

Since 1903, when Heusler [1] first reported on ferromagnetic properties of the Cu_2MnAl compound, the Heusler alloys are permanently attractive for many investigators due to their potential for applications in magnetic field sensors and spintronics devices [2] as well as the diverse magnetic phenomena [3,4]. And the electronic and magnetic properties of the Heusler compounds are still an important subject because these ferromagnetic materials are predicted to be half metallic ferromagnets and consequently can be used in tunnel magnetoresistance (TMR) device [5] or current-perpendicular-to-plane giant magnetoresistance (CPP-GMR) devices [6].

The full-Heusler alloys [7] have the type X_2YZ, where X and Y represent transition elements, and Z represents a sp element. Their crystal structure is $L2_1$, which consists of four fcc sublattices. However, these alloys transform into the B2 (disorder between Y and Z atoms) or A2 (disorder between X, Y and Z atoms) structure or a combination of the above structures, depending on their thermodynamic equilibrium. Amongst the broad class of the Heusler alloys, the Co-based Heusler alloys Co_2YZ are especially attractive for their predicted high spin polarization and high Curie temperature [8] as well as varying magnetic moments at Co site depending on the constituents Y and Z [9–11], making them attractive for various industrial applications.

Currently, the most promising half-metallic ferromagnetic materials with high Curie temperature are believed to be $L2_1$-type full-Heusler alloys [1]. X-ray diffraction [12] shows that the ordered $L2_1$ structure becomes more stable with increasing vanadium concentration in $Co_2Cr_{1-x}V_xAl$. The experimental results [12] indicate that the concentration dependence of $Co_2Cr_{1-x}V_xAl$ alloys reveals that the spin polarization P decreases from 0.62 to 0.5 with increasing vanadium concentration from x = 0.0 to x =0.5 and then to 0.48 at x = 1.0, whereas the saturation magnetization measured at 5 K for $Co_2Cr_{1-x}V_xAl$ alloy changes from 1.4 to 2.0 μ_B when x increases from 0.0 to 0.5 and then becomes 1.4 μ_B for x = 1.0. Obviously, the total magnetic moments do not obey the Slater–Pauling behavior. For Co_2CrAl alloys, several possible reasons for the reduction in the spin polarization of these alloys have been proposed [13,14]. However, the band structure was reported only for Co_2CrAl and Co_2VAl compounds with the ordered $L2_1$ structure. And it is found that these compounds are half metallic and follow a Slater–Pauling behavior [15] where the total spin magnetic moment per unit cell in $\mu_B(M_t)$ scales with the total number of valence electrons (Z_t) following the rule: $M_t=Z_t-24$. In spite of the theoretical predictions, it is difficult to demonstrate their half metallicity in experiments due to the sensitivity of spin polarization to structural disorder, surface/interface stoichiometry, etc. [12,16,17]. To understand the relevant microscopic mechanisms and find new quaternary Heusler alloy systems which form a stable ordered $L2_1$ structure

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with high spin polarization and high Curie temperature for spintronic applications, it is indispensable to investigate and discuss the electronic and magnetic properties of $Co_2Cr_{1-x}V_xAl$ with ordered and disordered structures.

In this work we report systematic investigations of the effects of V-doping on the electronic structure and magnetic properties of Co_2CrAl as well as the effects of disordered (antisite) defects of Co–Y(Cr, V)-type and Y(Cr, V)–Al-type. In the following section, we summarize the computational details. The calculated geometrical structures, magnetic moments and electronic structures are analyzed in Section 3. The conclusions are given in Section 4.

2. Computational details

Self-consistent band structure calculations were carried out using the scalar-relativistic full potential linearized augmented plane wave method (FLAPW) provided by Blaha et al. [18,19] (Wien2k). The exchange-correlation functional was taken within the generalized gradient approximation (GGA) in the parametrization of Perdew et al. [20]. The energy threshold between the core and valence states was set to -7.0 Ry. Here 2.3 a.u. were considered for the muffin-tin radii (RMT) of all the atoms, and this resulted in nearly touching spheres. The number of plane waves was restricted to $R_{MT} \times k_{\max} = 7$. And 455 irreducible k points for Brillouin zone integration are used which gives convergence of 0.01 mRy/f.u.

The ordered, mixed compounds may have the general formula sum $Co_8(Y_{(1-x)}Y'_x)_4Al_4$ with Y = Cr and Y′ = V. These structures have integer occupation of Y with x=0.0, 0.25, 0.5, 0.75 , 1.0. The theoretical lattice constants were obtained using the projector-augmented wave (PAW) method [21] in the generalized gradient approximation (GGA) as it is implemented in Vienna ab initio Simulation Package (VASP) [22,23]. The atomic geometries are fully optimized by performing minimizations of the Hellmann–Feynman forces on atoms and stressed on the supercell. The relaxations of lattices are stopped until the forces on each ion are converged to less than 0.01 eV/Å. All the geometry relaxations were performed with an cut-off 350 eV to ensure proper convergence of the stress tensor.

3. Results and discussions

3.1. Crystal structures and magnetic properties of ordered $Co_2Cr_{1-x}V_xAl$

First, we calculated the structural and magnetic properties of $Co_2Cr_{1-x}V_xAl$(x=0, 0.25, 0.5, 0.75, 1) with ordered $L2_1$ structure (see Fig. 1). We carried out a structural optimization by relaxing the internal coordinates and cell parameters. In Table 1, we show the calculated structural parameters and magnetic moments for different compositions by using GGA method. It can be seen that the lattice parameter increases with increasing V content in agreement with experiments [24], while the calculated lattice parameters are less than 0.5% smaller compared to the experimental values [25–27]. The present results in Co_2CrAl are in good agreement with the lately reported [28]. The calculated results obtained for different V contents in the doped compounds shows that the local magnetic moments are determined by the actual value of x. The spin magnetic moment of Co(Cr) atoms varies in different doped compounds from $0.77\,\mu_B(1.56\,\mu_B)$ to $0.89\,\mu_B(2.19\,\mu_B)$, and the spin magnetic moment of V atoms slightly increases from -0.18 to $0.20\,\mu_B$. The increase of the local magnetic moment is explained as being a result of a enhanced exchange splitting Co(Cr) due to hybridization. And the total spin moment of these compounds in the ferromagnetic ground states linearly decreases. It is found the Curie temperature (T_C) of the Heusler compounds decreases linearly as the total spin moment decreases [29]. Thus, the Curie temperature decreases as the V concentration increases.

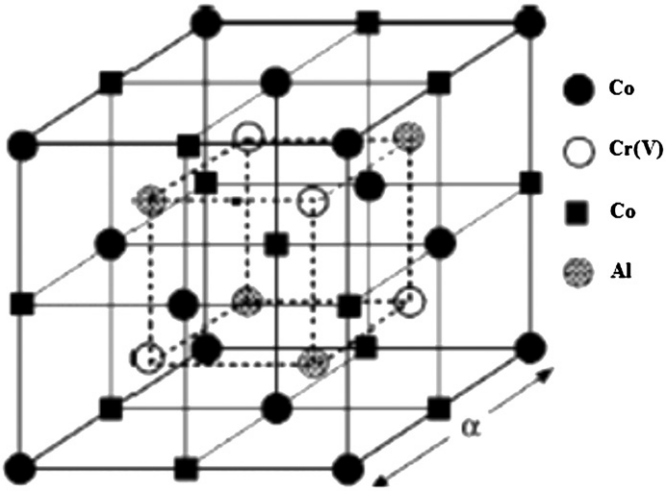

Fig. 1. Crystal structure of the ordered $Co_2Cr_{1-x}V_xAl$. The lattice consists of four fcc sublattices. The unit cell is that of a fcc lattice with four atoms as basis: X at (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, Y at $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$, and Z at $(\frac{3}{4}\frac{3}{4}\frac{3}{4})$ in Wyckoff coordinates.

To investigate the stability of ordered $Co_2Cr_{1-x}V_xAl$, we study the bulk modulus and cohesive energy. The lattice constants and bulk modulus are calculated by fitting energy volume data to Murnaghan equation of state [30]. The results are summarized in Fig. 2. Obviously, both cohesive energy and bulk modulus increase with the concentration of V, thus, with the increase of x, the stability of $L2_1$ structure will enhance. The results are compatible with the following band calculation.

3.2. Atomic disorder effects

Next, we discuss the effects of disordered (antisite) defects of Co–Y(Cr, V)-type and Y(Cr, V)–Al-type in $Co_2Cr_{1-x}V_xAl$. The atomic disorders are implemented by exchanging a position of Y atom with Co atom (Co–Y type disorder) and Al atom (Y–Al type disorder), so as to generate different chemical environments surrounding each inequivalent Y and Co(Al) site while keeping the concentration of Y/Co(Al) sites fixed. The antisite (AS) concentration is defined as the ratio of the concentration of Co(Al) in Cr/V positions divided by the total concentration of Co(Al). We have performed the calculation for two concentrations corresponding to 12.5% of the disorder between Co and Y atom and 25% of the disorder between Y and Al atom. Such calculations can provide useful information about the electronic and magnetic properties. In Fig. 3, we show the total energy difference between the Co–Y-type (Y–Al-type) disordered and ordered $L2_1$-type $Co_2Cr_{1-x}V_xAl$ which corresponds to a change in energy due to the Co–Y-type (Y–Al-type) disorder from ordered $L2_1$ structure. The calculated results reveal that with increasing V content the dE is substantially enhanced for both Co–Y(Cr, V)-type and Y(Cr, V)-Al-type disorders. A larger dE indicates a lower possibility of the Co–Y-type (Y–Al-type) disorder. Thus, with increasing V content the stability of $L2_1$ structure will enhance. The results are compatible with experiments [12]. The enhancement of stability can be mainly attributed to the less valence electron in V than that in Cr. Because dE increases as the valence electron charges around Y atom decrease [31]. The valence electron charges (4.74 in Co_2VAl vs. 5.46 in Co_2CrAl) around V(Cr) are evaluated by