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First-principles investigations of electronic, magnetic and thermodynamic properties of Heusler alloy $Co_2Mn_{1-x}Ti_xSn$

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ABSTRACT

Using first-principles density functional theory based method we have investigated the electronic, magnetic and thermodynamic properties of Heusler alloy $Co_2Mn_{1-x}Ti_xSn$. From analysis of elastic constants, we find that the cubic $L2_1$ phase is stable and all the alloys prone to ductility for $Co_2Mn_{1-x}Ti_xSn$ alloy. The total magnetic moment decreases with increasing x, in agreement with the generalized Slater-Pauling rule. Band structure calculations show that the minority DOS exhibits a gap around Fermi level confirming the half-metallic character of the material for all the concentrations studied and the Fermi level can be shifted within the minority spin gap by changing the Ti concentration. The Curie temperature T_C estimated from the effective exchange constant J_0 decreases with x, and qualitatively accords with the experimental values. Finally, by using a quasi-harmonic Debye model, the temperature dependent bulk modulus, heat capacity and coefficient of thermal expansion have been obtained in the present work.

1. Introduction

Co-based Heusler alloys have attracted considerable attention for their potential use as applicable materials in the field of spin-electronics and magnetoresistive devices. They are particularly of interest because of their predicted full spin polarization at the Fermi edge, making them so-called half-metallic ferromagnets (HMFs) [1]. Several kinds of Co-based Heusler alloys have been investigated and reported to HMFs based on theoretical calculations [2–6]. A great advantage of those compounds is the possibility to specifically tune the position of the Fermi level and thus their electronic and magnetic properties by partial substitution of elements in the parent phase [7–9]. Co-based Heusler compounds have the formula Co_2 YZ, where Y may be Ti, V, Cr, Mn or Fe and Z may be Al, Ga, Si, Sn or another main group metal. Co-based Heusler alloys that are predicted to be half-metallic ferromagnets show a Slater-Pauling behavior of the magnetization which means that the saturation magnetization scales linearly with the number of valence electrons [2]. Furthermore, Co-based Heusler alloys exhibit high Curie temperatures (T_C) and easy grow on substrates which are very important requirement for the application of the material in electromagnetic devices.

Co_2 MnSn and Co_2 TiSn are excellent examples of a Heusler-type alloy, in which the local environment profoundly influences the electronic and magnetic properties. The phase separation appearing in the quaternary Heusler series Co_2 Mn_{1-x} Ti_xSn is reported [10]. The quaternary compounds have a dendritic microstructure which was formed during the solidification process as a result of a phase separation into a Co_2MnSn-enriched and a Co_2TiSn-enriched Heusler phases. Pronounced changes in the magnetic and electronic properties take place with varying composition. The stability, electronic and thermodynamic properties of Co_2Mn_{1-x} Ti_xSn are very important and essential for material design and development. However, there is a lack of thorough research focused on the stability and thermodynamic properties of $Co_2Mn_{1-x}Ti_xSn$. So, the first principles calculations and quasi-hormonic approximation are desirable to study the $Co_2Mn_{1-x}Ti_xSn$ Heusler alloy and some significant relations between the macroscopic thermodynamics and the microscopic electronic properties for the alloys are also desirable to be found.

2. Computational details

First-principles calculations of $Co_2Mn_{1-x}Ti_xSn$ are performed in

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a plane-wave basis set using the projector augmented wave (PAW) [11,12] method in the generalized gradient approximation (GGA) as it is implemented in the Vienna *ab initio* simulation program (VASP) [13,14] program. The 16 atoms in the $L2_1$ unit cell composed of eight Co, four Mn/Ti, and four Sn atoms were taken for the self-consistency calculations. The Ti addition was carried out by a gradual replacement of those four Mn atoms by Ti atoms. In such a way, one of the four Mn atoms is replaced by an Ti atom results in $x = 0.25$, etc. in the Co_2 $Mn_{1-x}Ti_xSn$ formula. A plane-wave basis and projector augmented-wave pseudopotentials are used, with Cod^8s^1, Mnd^6s^1, Ti d^3s^1 and Sn s^2p^2 electrons treated self-consistently. The Brillouin zone integration is performed using Monkhorst-Pack grids of $12 \times 12 \times 12$ to obtain higher quality state densities. In our calculations the spin-orbit interaction and noncollinear spin configuration are neglected.

The exchange interactions are investigated here by the spin polarized relativistic Korringa-Kohn-Rostoker package Munich SPRKKR [15] which allows to calculate the exchange coupling parameters by mapping the system onto a Heisenberg Hamiltonian. From the Heisenberg pair exchange coupling parameters J_{ij}, we then estimate the Curie temperatures within the mean field approximation (MFA). Additionally, it provides the coherent potential approximation (CPA) to be used for disordered systems. This method was used to estimate the influence of disorder on the magnetic structure. To investigate the thermodynamic properties of the $Co_2Mn_{1-x}Ti_xSn$, we apply here the quasi-harmonic Debye model by the GIBBS program [16]. Given the energy of a solid (E) as a function of the molecular volume (V), the gibbs program uses a quasi-harmonic Debye model to generate the Debye temperature $\Theta(V)$, obtains the non-equilibrium Gibbs function $G^*(V;P.T)$, and minimizes G^* to derive the thermal equation of state (EOS) $V(p,T)$ and the chemical potential $G(p,T)$ of the corresponding phase. Other macroscopic properties are also derived as a function of p and T from standard thermodynamic relations.

3. Results and discussion

Generally, the Heusler structure can be looked on as four interpenetrating facecentered cubic (fcc) lattices, A(0, 0, 0), B(1/4, 1/4, 1/4), C(1/2, 1/2, 1/2) and D(3/4, 3/4,3/4) sites in Wyckoff coordinates; the $L2_1$ phase of Co_2 YSn in which Co occupy the A and C sites and Y and Sn occupy B and D sites, respectively. By fitting the optimized total energies vs volume values to the Murnaghans EOS, we obtain the equilibrium lattice constants a, bulk modulus B_0, and pressure derivative of bulk modulus B_0 for $Co_2Mn_{1-x}Ti_xSn$. We summarized our results and the experimental values in Table 1. It can be clearly seen that our calculated lattice constants are all in a close agreement with the experimental values. We thus confirm that the present first principles calculations are accurate and believable. The calculated total energies vs volume curve is accurate enough to be input into the expression of the Gibbs energy. With increasing Ti concentration, the lattice constant increases slightly due to larger atomic radius of Ti as compared to Mn.

Table 1
The calculated lattice constant (a) in Å, bulk modulus (B_0) in GPa and its derivative (B') in comparison with other experimental data for $Co_2Mn_{1-x}Ti_xSn$.

Alloys	a	B_0	B'
$x = 0$	5.987 6.010[a] 5.984[b] 5.999[d]	163.75	5.81
$x = 0.25$	6.016	161.74	4.88
$x = 0.75$	6.061	168.06	6.18
$x = 1$	6.080 6.060[a] 6.073[c] 6.051[d]	163.86	4.55

[a] Reference [10].
[b] Reference [17].
[c] Reference [18].
[d] Reference [19].

The elastic constants of solids provide a link between the mechanical and the dynamic properties and give important information about the nature of the force action in a solid. In particular, they provide information about the stability and stiffness of materials. For a cubic crystal, there are only three independent elastic constants, namely C_{11}, C_{12} and C_{44}, and the cubic material will not be mechanically stable unless $C_{11}+2C_{12}>0$, $C_{11}-C_{12}>0$, $C_{44}>0$. The Voigt modulus and Reuss modulus is the upper limit and the lower limit of the actual effective moduli respectively, and the Voigt-Reuss-Hill modulus is an arithmetic average of Voigt modulus and Reuss modulus [20]. For a cubic phase, the Voigt shear modulus G_V, Reuss shear modulus G_R, Voigt-Reuss-Hill shear modulus G, bulk modulus B, Youngs modulus E, Zener's anisotropy parameter A and Possions ratio σ are given by

$$G_V = (C_{11} - C_{12} + 3C_{44})/5,$$

$$G_R = 5(C_{11} - C_{12})C_{44}/[4C_{44} + 3(C_{11} - C_{12})],$$

$$G = (G_V + G_R)/2,$$

$$B = (C_{11} + 2C_{12})/3,$$

$$E = 9BG/(3B + G),$$

$$A = 2C_{44}/(C_{11} - C_{12})$$

$$\sigma = (3B - 2G)/2(3B + G).$$

The three elastic constants C_{11}, C_{12} and C_{44} can be obtained directly by first principles calculations, and all the remaining quantities G_V, G_R, G, B, E, A and σ can be calculated by the above equations. All the above mentioned quantities by the first principles calculations are given in Table 2. From analysis of C_{11}, C_{12} and C_{44}, we find that the alloys all fulfill the Born criteria, indicating that the cubic $L2_1$ phase is stable for them. The bulk modulus calculated from the theoretical values of the elastic constants $B = (C_{11}+2C_{12})/3$ is also listed in Table 2, and it has nearly the same value as the one obtained from energy minimization. The ratio between the bulk and the shear modulus (B/G), has been proposed to predict brittle or ductile behavior of materials. A high B/G value indicates a tendency for ductility and if $B/G>1.75$, the ductile behavior is predicted. The ratio for Co_2 Mn_{1-x} Ti_xSn is all larger than 1.75, which indicated that all the alloys are prone to ductility. It is known that the deviation of Zeners anisotropy parameter (A) from unit 1 indicates the degree of elastic anisotropy. Co_2 MnSn has the highest degree of elastic anisotropy among the alloys with the largest Zeners anisotropy parameter $A = 2.08$.

The band structures of Co_2 Mn_{1-x} Ti_xSn are illustrated in Fig. 1 and the left- and right-hand panels exhibit the majority and the minority spin states, respectively. The dispersed bands from −2 eV to 2 eV are due to the strong hybridization of Co d and Mn(Ti) d electrons, including a contribution from Sn p states in the occupied valence states. At Γ there is a series of twofold degenerate states derived from Co and Mn(Ti) d states and threefold degenerate states derived from the hybridization of Co and Mn(Ti) d states with the Sn p states. The majority spin band structure is strongly metallic for all the concentrations studied. For $x = 0$ and 0.25, the minority "valence band maximum" (VBM) is slightly above the Fermi level, leading to a nearly half-metallic behavior. For $x = 0.75$ and 1, the minority spin band structure shows a semiconducting gap around the Fermi level, leading to a half-metallic