Intermetallics 80 (2017) 10–15

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Competition of XA and $L2_1B$ ordering in Heusler alloys Mn_2CoZ (Z = Al, Ga, Si, Ge and Sb) and its influence on electronic structure

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ARTICLE INFO

Article history:
Received 22 June 2016
Received in revised form
13 August 2016
Accepted 6 October 2016

Keywords:
Magnetic alloys
Electronic structure
Phase stability
Ab-initio calculations

ABSTRACT

Competition between the highly-ordered XA structure and disordered $L2_1B$ structure in Heusler alloys Mn_2CoZ (Z = Al, Ga, Si, Ge, Sb) has been investigated. The relative stability of the two structures strongly depends on the main group element Z. When Z belongs to Al or Ga, the XA structure is stabler, but when Z belongs to Si, Ge or Sb, the $L2_1B$ structure gains stability and is lower in energy. This is related to the different number of valence electrons in main group element Z, which influences the DOS structure near the Fermi level and changes $N(E_F)$. The energy difference ΔE between the XA and $L2_1B$ structures may be used to estimate the tendency to form $L2_1B$ structure in different Heusler alloys qualitatively. A large negative ΔE is preferable to retard the A-C site disorder and retain the highly-ordered XA structure. That is just the case in Mn_2CoAl. A robust half-metallicity is observed in Mn_2CoSi, Mn_2CoGe and Mn_2CoSb, they are always half-metallic under either XA or $L2_1B$ structure. But in Mn_2CoAl and Mn_2CoGa, their spin gapless semiconducting character will be destroyed and replaced by a half-metallic state if $L2_1B$ disorder occurs. Finally, these results suggest that the $L2_1B$ structure should be considered together with XA structure when discussing the electronic structure of "inverse" Heusler alloys.

1. Introduction

In recent years, the Mn_2-based Heusler alloys have attracted much attention for their interesting properties and possible applications in many technical fields. One important application of Mn_2-based Heusler alloys is spintronic materials, till now quite a few Mn_2-based Heusler alloys have been reported to be half-metals or spin gapless semiconductors (SGSs). Some typical examples are Mn_2VAl, Mn_2VSi, Mn_2FeZ (Z = Al, Sb), Mn_2CoZ (Z = Al, Ga, Si, Sb), Mn_2CuSb, Mn_2ZrSi, etc. [1–12]. The half-metallic materials have a 100% spin polarization of the conduction electrons at the Fermi level E_F and are of great importance in spintronics. SGS is an intermediate state between the well known half-metallic ferromagnets and gapless semiconductors. In case of SGS, one spin channel has an open band gap at E_F like a half-metal but the other spin channel has a zero-width gap like a gapless semiconductor [5,13], thus the conducting electrons or holes are not only 100% spin polarized but also easily excited. Among these Mn_2-based Heusler alloys, Mn_2CoZ (Z = Al, Ga, In, Si, Ge, Sn, Sb) are particularly interesting, for they are not only predicted to be half-metals/SGSs theoretically, but also can be realized experimentally [4,5,14]. It has been found that the unique properties of Mn_2CoZ alloys are strongly related to the preferred occupation of Mn and Co atoms in the cubic lattice of Heusler alloys [15].

Heusler alloys crystallize in a highly-ordered cubic structure and have a stoichiometric composition of X_2YZ, where X and Y are transition metal elements, and Z is a main group element. In Heusler alloys there are four 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. The transition metal elements X, Y enter A, B, C sites and main group element Z always enters D sites in the cubic lattice. The site preference of transition metal elements is usually determined by the number of their valence electrons: atoms with more electrons tend to occupy the A and C positions while the atoms with fewer electrons prefer the B position [16]. So in Mn_2CoZ the most possible structure is that one Mn and one Co occupy (A, C) sites and the other Mn enters the B site. In previous literature, people usually assume that Mn and Co occupy the A and C sites respectively [4,17],

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http://dx.doi.org/10.1016/j.intermet.2016.10.001
0966-9795/

which results in a highly-ordered XA structure (Hg_2CuTi-type, space group No.216), as shown in Fig. 1.

However, a new possible structure named $L2_1B$ may also be considered when discussing the electronic structure and magnetic properties of Heusler alloys Mn_2CoZ. The $L2_1B$ structure evolves from the ordered XA structure [18,19]. In $L2_1B$ type Mn_2CoZ, one Mn and one Co occupy the A and C sites randomly rather than respectively, which results in space group Fm-3m, the same to the $L2_1$ structure. In Fig. 1, we compared the crystal structures of $L2_1B$ and XA type Mn_2CoAl as an example. In some Fe-based Heusler alloys, the $L2_1B$ structure is found to has a lower total energy compared with XA structure and is stabler [20]. In some Mn_2-based Heusler alloys, the $L2_1B$ structure may increase the total energy slightly, but due to the effect of enthalpy of mixing, it can still be observed in actual samples at room temperature [19]. It has also been found that the $L2_1B$ structure can affect the electronic and magnetic properties of Heusler alloys obviously [21]. Thus it is quite meaningful to investigate the electronic structure and stability of half-metallicity in Heusler alloys under possible $L2_1B$ structure.

In this paper, we investigated the competition between $L2_1B$ and XA ordering in Heusler alloys Mn_2CoZ (Z = Al, Ga, Si, Ge, Sb). A close relation between the phase stability of $L2_1B$ structure and main group element Z has been observed. $L2_1B$ structure is more preferable in several Mn_2CoZ alloys. But the half-metallicity in them is robust under either XA or $L2_1B$ structure.

2. Calculation methods

The electronic structures of Mn_2CoZ (Z = Al, Ga, Si, Ge, Sb) were calculated by using CASTEP code based on pseudopotential method with a plane-wave basis set [22,23]. The interactions between the atomic core and the valence electrons were described by the ultrasoft pseudopotential [24]. The electronic exchange–correlation energy was treated under the generalized-gradient-approximation (GGA) [25]. Supercell approach is used for the calculations of $L2_1B$ structure. The random occupation of Mn and Co at (A, C) sites is treated in a 16-atom supercell, which resulting in a chemical formula of $Mn_8Co_4Z_4$. The detail can be found in Fig. 1. For all cases, a plane-wave basis set cut-off of 500 eV was used. A mesh of $20 \times 20 \times 20$ or $16 \times 16 \times 16$ *k*-points was employed for Brillouin zone integrations in the XA and $L2_1B$ structures, 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.

3. Results and discussions

3.1. Competition between $L2_1B$ and XA ordering in Mn_2CoZ

First, We investigated the site preference of Mn and Co in Mn_2CoZ (Z = Al, Ga, Si, Ge, Sb) and compared the phase stability of XA and $L2_1B$ structures. During structural optimization, we

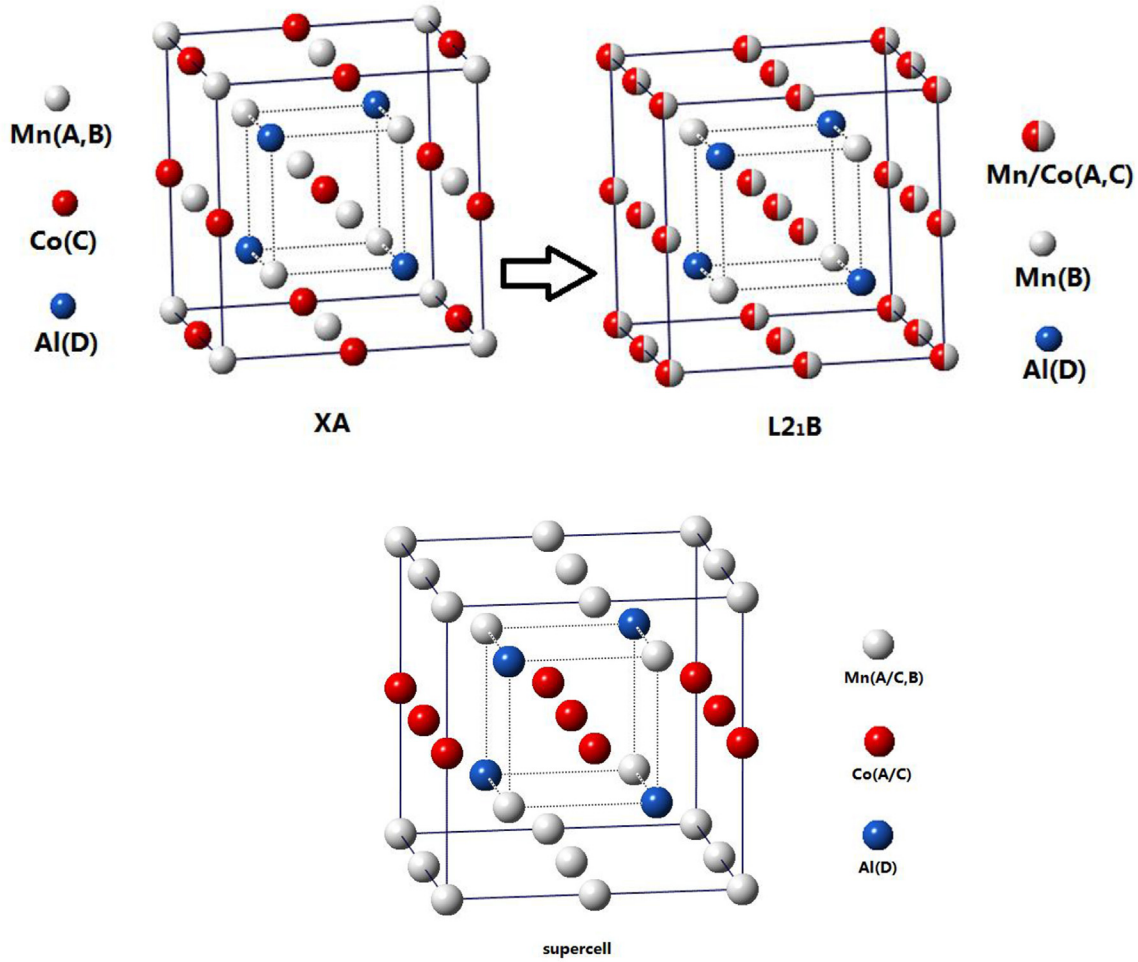

Fig. 1. Crystal structures of XA and $L2_1B$ type Mn_2CoAl, in the $L2_1B$ structure, Mn and Co occupy A, C sites randomly, the $L2_1B$ supercell indicates the exact structure used for calculation, in which Mn and Co atoms occupy four A and four C sites alternately.