Intermetallics 93 (2018) 209–216

Contents lists available at ScienceDirect

Intermetallics

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

First principles study of the structural phase stability and magnetic order in various structural phases of Mn_2FeGa

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ARTICLE INFO

Keywords:
Magnetism
Transition metal alloys and compounds
Phase stability
Electronic band structure

ABSTRACT

We investigate the structural and magnetic properties of Mn_2FeGa for different phases (cubic, hexagonal and tetragonal) reported experimentally using density functional theory. The relative structural stabilities, and the possible phase transformation mechanisms are discussed using results for total energy, electronic structure and elastic constants. We find that the phase transformation form hexagonal to ground state tetragonal structure would take place through a Heusler-like phase which has a pronounced electronic instability. The electronic structures, the elastic constants and the supplementary phonon dispersions indicate that the transition from the Heusler-like to the tetragonal phase is of pure Jahn-Teller origin. We also describe the ground state magnetic structures in each phase by computations of the exchange interactions. For Heusler-like and tetragonal phases, the ferromagnetic exchange interactions associated with the Fe atoms balance the dominating antiferromagnetic interactions between the Mn atoms leading to collinear magnetic structures. In the hexagonal phase, the directions of atomic moments are completely in the planes with a collinear like structure, in stark contrast to the well known non-collinear magnetic structure in the hexagonal phase of Mn_3Ga, another material with similar structural properties. The overwhelmingly large exchange interactions of Fe with other magnetic atoms destroy the possibility of magnetic frustration in the hexagonal phase of Mn_2FeGa. This comprehensive study provides significant insights into the microscopic physics associated with the structural and magnetic orders in this compound.

1. Introduction

Mn_2YZ compounds in Heusler and Heusler-like structures have been in the attention of spintronics community due to their multiple possible applications in spin-transfer torque random access memory (STT-MRAM) [1], spin valves [2], magnetic tunnel junction [3], spin gapless semiconductor [4] and magnetic shape memory effect [5]. Such traits of Mn_2YZ compounds are artefacts of various possible structures in which the systems can crystallise as well as of different orientations of the Mn spins giving rise to interesting magnetic configurations [5–14]. Among the compounds in this family, Mn_3Ga [15–19] and Mn_2NiGa [5,14] have been studied extensively. Mn_2NiGa is a recently discovered ferrimagnetic shape memory system which martensitically transforms to a low temperature tetragonal structure through a series of complex modulated phases of orthorhombic and monoclinic symmetries [14]; the martensitic transformation being driven by phonon softening and Fermi surface nesting [20]. Mn_3Ga, on the other hand, is found to crystallise in a cubic Cu_3Au-like [17], a hexagonal DO_{19} [21] and a tetragonal DO_{22} phase [16,22], resulting in a high perpendicular magneto-crystalline anisotropy in the DO_{22} phase and a large Exchange Bias in the DO_{19} phase, which are useful for STT-MRAM [16] and magnetic tunnel junction [21] applications, respectively. First-principles Density Functional Theory (DFT) calculations predicted a Heusler-like metastable structure in Mn_3Ga with a half-metallic gap, which phase transforms to the DO_{22} structure [11,12]. This phase, however, has not yet been synthesised experimentally. Comprehensive DFT calculations inferred that the phase transition from DO_{19} to DO_{22}, as observed in the experiments [17], happens via the Heusler-like phase [18]. First-principles computations of the magnetic exchange interactions [19] and the magnetic anisotropy [16] concluded that the novel magnetic properties of Mn_3Ga in DO_{19} and DO_{22} structures are due to non-collinear magnetic structures arising out of frustrations due to geometry as well as competing exchange interactions between in-plane and out-of-plane Mn atoms.

Inspite of enough promises towards a variety of magnetism related applications, both Mn_3Ga and Mn_2NiGa have low saturation magnetisations originating from the predominantly antiferromagnetic interactions between the Mn atoms. This hinders the exploitations of their

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https://doi.org/10.1016/j.intermet.2017.12.010
Received 10 July 2017; Received in revised form 20 September 2017; Accepted 6 December 2017

complete potentials in the respective applications. The low saturation magnetisation in Mn_3Ga limits it's applicability in potential permanent magnet applications, inspite of having strong uniaxial magnetic anisotropy and large Curie temperature. For Mn_2NiGa, much lower saturation magnetisation [5,7], in comparison to Ni_2MnGa, the prototype magnetic shape memory system in the Heusler family, is an obstacle to obtain significant magnetic field induced strain required for actuator applications. Attempts have, therefore, been made to combat the dominant antiferromagnetic interactions in these systems by replacing one of the Mn with ferromagnetic elements like Co and Fe. Complete replacement of one Mn atom by Fe, resulting in the compound Mn_2FeGa, was expected to circumvent the problems. Synthesis of Mn_2FeGa, however, exhibited several important aspects of structure-property relationship. Various crystallographic phases with possible magnetic structures were observed and predicted experimentally. Gasi et al. [10] reported an inverse tetragonal Heusler structure with a low saturation magnetic moment and a high Curie temperature for samples annealed at 400 °C. The system behaved like an exchange spring which was attributed to the distribution of Fe atoms among the Mn sites resulting in two different magnetic states of Fe. A Cu_3Au-like structure was observed when the system was annealed at 800 °C. A giant tuneable Exchange Bias was later obtained in the inverse tetragonal structure with a saturation magnetisation as low as 0.09 μ_B/f.u. [23] suggesting a near compensation of moments from Mn and Fe atoms. DFT calculations, like Mn_3Ga, predicted a meta-stable inverse Heusler phase for Mn_2FeGa, which transforms to the inverse tetragonal structure observed in the experiments [11,12]. The electronic structure of inverse Heusler Mn_2FeGa revealed a pronounced instability associated with the minority spin band [12]. However, unlike Mn_2NiGa, the transformation from inverse Heusler to inverse tetragonal phase didn't turn out to be volume conserving, implying the possibility of absence of shape memory effect in this system. Investigations into sputter deposited thin films of Mn_2FeGa [24] find that the system crystallises either in inverse tetragonal or in the Cu_3Au-like cubic phase. Mossbauer spectroscopy on epitaxial thin films suggested that Fe might be statistically distributed among the two Mn sites leading to a low spin moment in the inverse tetragonal phase [25]. Heteroepitaxially grown thin films of Mn-Fe-Ga with composition near that of Mn_2FeGa also exhibited strong perpendicular anisotropy and moderate coercivity suggesting that this system can be used in mid-range permanent magnet applications [26]. Like Mn_3Ga, this system could also be synthesised in DO_{19}-type hexagonal structure which yielded a giant Exchange Bias field upto 1.32 kOe [27]. The large Exchange Bias was attributed to the presence of substantial ferromagnetic matrix due to Fe-Mn pairs in an antiferromagnetic host.

The experimental observations clearly indicate that investigations into the phase stability, sub-lattice occupancy and magnetic properties of Mn_2FeGa would be insightful. The following issues, in particular, are worth looking into, in order to understand the physics associated with Fe substitution in either Mn_3Ga or in Mn_2NiGa, the two compounds having very different functional aspects: (i) the energetics of various phases observed experimentally or are predicted theoretically but not observed experimentally, (ii) the magnetic interactions among three different magnetic atoms and their dependencies on the sub-lattice occupancies of the atoms in different structural phases. This can be particularly relevant in the hexagonal phase where the Fe atom has more than one choice of the crystallographic site it can occupy, and (iii) the effect of anti-site disorder on the magnetic properties. In this paper, we have undertaken a DFT based comprehensive investigation into the structural and magnetic properties of the four crystallographic phases of Mn_2FeGa, the Cu_3Au-like, the hexagonal DO_{19}-like, the inverse Heusler and the inverse tetragonal. Emphasis has been given on identifying the magnetic structure in the hexagonal phase as it is supposed to be most complex in this phase as was observed in Mn_3Ga. We have computed the magnetic exchange interactions in each structural phase in order to understand the magnetic structures. The electronic structures of the structural phases are computed and analysed in order to provide a possible picture of the phase transformations. The elastic constants and the phonon dispersion relations for select phases are computed to supplement the analysis from the energetics and the electronic structures. In this work, we have not incorporated anti-site disorder in order to avoid dealing with prohibitively large number of possible configurations, in particular for the hexagonal structure. In absence of concrete quantitative estimate of the anti-site disorder from the experiments, this is justified. The paper is organised as follows: in the section 2, computational details are given. The results and discussion are presented in section 3 followed by conclusions.

2. Calculational details

All calculations were performed with spin-polarised density functional theory (DFT) based projector augmented wave (PAW) method [28] as implemented in Vienna Ab-initio Simulation Package (VASP) [29,30]. Perdew-Burke-Ernzerhof (PBE96) implementation of Generalised Gradient Approximation (GGA) for exchange and correlation [31] part in the Hamiltonian was used throughout. An energy cut-off of 500 eV and a Monkhorst-Pack [32] 25 × 25 × 25 k-mesh for Cu_3Au-like and inverse Heusler structures, a 15 × 15 × 13 k-mesh for the tetragonal structure and a 13 × 13 × 11 k-mesh for the hexagonal structure were used for self consistent calculations. Larger k-meshes were used for the densities of states calculations of all the structures. The k-meshes used were 29 × 29 × 29 for Cu_3Au-like and inverse Heusler, 19 × 19 × 17 for tetragonal and 15 × 15 × 13 for hexagonal structures. For all calculations, the total energy convergence criteria and the force convergence criteria were set to 10^{-6} eV and to 10^{-2} eV/Å respectively. The elastic constants were calculated from the second derivatives of the total energies with respect to the strain tensors [33].

The magnetic pair exchange parameters were calculated with multiple scattering Green function formalism as implemented in SPRKKR code [34]. In here, the spin part of the Hamiltonian is mapped to a Heisenberg model

$$H = -\sum_{\mu,\nu}\sum_{i,j} J_{ij}^{\mu\nu}\,\mathbf{e}_i^{\mu}\cdot\mathbf{e}_j^{\nu} \tag{1}$$

μ, ν represent different sub-lattices, i, j represent atomic positions and $\mathbf{e}_i^{\mu}$ denotes the unit vector along the direction of magnetic moments at site i belonging to sub-lattice μ. The $J_{ij}^{\mu\nu}$s are calculated from the energy differences due to infinitesimally small orientations of a pair of spins within the formulation of Liechtenstein et al. [35]. In order to calculate the energy differences, full potential spin polarised scaler relativistic Hamiltonian with angular momentum cut-off $l_{max} = 3$ is used along with a converged k-mesh for Brillouin zone integrations. The Green's functions are calculated for 32 complex energy points distributed on a semi-circular contour. The energy convergence criterion is set to 10^{-5} eV for the self-consistency. The equilibrium lattice parameters and optimised atomic positions as obtained from the PAW calculations are used to obtain the self-consistent potentials in the multiple scattering Green's function method.

3. Results and discussions

3.1. Structural parameters and magnetic structures in various crystallographic phases

Experimentally, Mn_2FeGa has been observed to crystallise in three different phases, the Cu_3Au-like, the tetragonal DO_{22} like and the hexagonal DO_{19} [10,27], depending on the annealing temperature. DFT calculations predicted a inverse Heusler phase [11,12,36], yet undetected in experiments. In these investigations, the possible site-specific magnetic structures associated with different structural phases have been indicated through indirect evidences. In this sub-section, we present results on the structural properties and possible ground state magnetic structures, along with atomic moments for all four structural