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<https://aip.scitation.org/doi/10.1063/1.4905173>

DOI: 10.1063/1.4905173

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Effects of Ga substitution on the structural and magnetic properties of half metallic Fe₂MnSi Heusler compound

S. S. Pedro,^{1,a)} R. J. Caraballo Vivas,¹ V. M. Andrade,¹ C. Cruz,¹ L. S. Paixão,¹ C. Contreras,¹ T. Costa-Soares,^{1,b)} L. Caldeira,² A. A. Coelho,³ A. Magnus G. Carvalho,⁴ D. L. Rocco,¹ and M. S. Reis¹

¹Instituto de Física, Universidade Federal Fluminense, Niterói-RJ, Brazil

²IF Sudeste MG, Campus Juiz de Fora - Núcleo de Física, Juiz de Fora-MG, Brazil

³Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas - Unicamp, Campinas-SP, Brazil

⁴Laboratório Nacional de Luz Síncrotron, CNPEM, Campinas-SP, Brazil

(Received 29 September 2014; accepted 16 December 2014; published online 5 January 2015)

The so-called half-metallic magnets have been proposed as good candidates for spintronic applications due to the feature of exhibiting a hundred percent spin polarization at the Fermi level. Such materials follow the Slater-Pauling rule, which relates the magnetic moment with the valence electrons in the system. In this paper, we study the bulk polycrystalline half-metallic Fe₂MnSi Heusler compound replacing Si by Ga to determine how the Ga addition changes the magnetic, the structural, and the half-metal properties of this compound. The material does not follow the Slater-Pauling rule, probably due to a minor structural disorder degree in the system, but a linear dependence on the magnetic transition temperature with the valence electron number points to the half-metallic behavior of this compound. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4905173>]

I. INTRODUCTION

Heusler alloys have been attracting considerable attention nowadays, specially due to their remarkable properties, with applications in magneto-optical, magnetocaloric, and magnetoelectric systems, as well in solar cells, thermoelectrical, and spintronic devices, just to name a few examples.¹ These systems are well known also for exhibiting a very curious shape memory behavior, defined as the ability of the material to come back to its original state or form after deformation by a change in its temperature and magnetic field.¹

A very interesting particular class of Heusler compounds is known as half-metals: compounds with conduction electrons that are 100% spin polarized. They have a gap in one spin band at the Fermi level, whereas the other spin band has a strongly metallic behaviour, which results in a complete spin polarization of the conduction electrons. Therefore, these materials are considered hybrids between metals and semiconductors. This feature of half-metals is well explored for spintronic-based devices.²⁻⁴

However, for functional applications, not only a high spin polarization but also a T_C near room temperature and stability of the $L2_1$ structural phase (to minimize atomic disorder effects) is highly desired. In general, half-metals obey the Slater-Pauling rule,⁵ which relates the magnetic moment with the number of valence electrons in the compound.

Many materials with Heusler structure present half-metal features, and Fe₂MnR (R = Si and Ga) compounds are reported to present such properties.^{2,6-8} In these compounds, the magnetic properties are mainly dominated by Mn and Fe

atoms, where its d subshells are incomplete. The magnetic, structural, and electronic properties of the Fe₂MnSi and Fe₂MnGa Heusler alloys have been investigated.^{2,6-8} The Fe₂MnSi Heusler compound is a half-metallic ferromagnet ordered in the full Heusler $L2_1$ structure, with T_C around 220 K,^{2,6,7} while Fe₂MnGa can be found in two distinct structures: fcc -type and the $L2_1$ phase, presenting half-metallic features only in the $L2_1$ phase. The magnetic transition temperature T_C for the latter is far above room temperature, around 800 K as previously reported.⁸ As far as we know, there is no report in the literature of the properties related to the substitution of Si by Ga in the Fe₂MnSi compound and how this substitution can change the properties of the parent phases.

In the present study, the crystal structure and magnetic properties were investigated in the Fe₂MnSi Heusler compounds, in order to quantify the physical effects of Ga substitution. In this way, X-ray diffraction and EDS were used to characterize the crystal structure and the sample composition. Since the Curie temperature for the Fe₂MnSi and Fe₂MnGa is known and reported in the literature, we intend to obtain T_C near room temperature by tuning the Ga content in the compound. In addition, we intend from structural and magnetic studies to estimate how the density of states at Fermi level supposedly changes with this substitution, verifying if the half-metallic character of the undoped Fe₂MnSi compound remains with Ga substitution.

II. EXPERIMENTAL DETAILS

Bulk polycrystalline ingots of the compound Fe₂MnSi_{1-x}Ga_x ($x = 0, 0.02, 0.04, 0.09, 0.12, 0.20, 0.30, \text{ and } 0.50$) were synthesized at UFF by melting pure Fe, Mn, Si, and Ga pieces in arc furnace with water-cooled refrigeration under Ar atmosphere. The purity of the raw materials was

^{a)}Also at Instituto de Física, Universidade do Estado do Rio de Janeiro, Rio de Janeiro-RJ, Brazil. Electronic mail: sandrapedro@uerj.br.

^{b)}Also at IF Sudeste MG, Campus Juiz de Fora - Núcleo de Física, Juiz de Fora-MG, Brazil.

99.99 wt. % or higher. The mass of the reactants was calculated in stoichiometric quantities for 2 g of sample, with exception of Mn, which was added in 3% excess of the stoichiometry to compensate loss during melting process. To promote volume homogeneity, the ingots were remelted at least two times, then wrapped in tantalum foils and sealed in a quartz tube under Ar atmosphere for annealing at 1323 K during three days, and then were quenched in cold water. The weight loss after melting and annealing was below 1%.

One small piece of each annealed ingot was separated for powder X-ray diffraction experiments, to verify the crystal structure, and energy dispersive spectroscopy (EDS), to define the elemental composition of the prepared samples. X-ray powder diffraction data were obtained at room temperature using a Bruker AXS D8 advance diffractometer with Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$), 40 kV and 40 mA at UFF. Data were collected in the $20^\circ < 2\theta < 85^\circ$ range in Bragg-Brentano geometry, with a step size of 0.02° . EDS experiments were performed on a Bruker microanalysis system mounted on a SEM microscope TESCAN Vega SBU at Laboratório de Caracterização de Materiais at IF - Sudeste MG. Magnetization data were acquired as a function of temperature and magnetic field using a commercial Superconducting Quantum Interference Device (SQUID, from Quantum Design[®]) at UNICAMP.

III. RESULTS

A. Characterization and crystal structure

Heusler alloys are ternary X_2YZ compounds, where X and Y are usually transition metals and Z is a main group element (containing elements that belong to the *s* and *p* blocks). These compounds crystallize in the cubic space group $Fm\bar{3}m$ (space group 225) with Cu_2MnAl structure¹ (also known as $L2_1$ type). This structure consists of four interpenetrating *fcc* sublattices with four atoms as basis, two of which are equally occupied by the X element. In $Fe_2MnSi_{1-x}Ga_x$, the Fe atoms occupy the 8c Wyckoff position at (0.25, 0.25, 0.25); Mn atoms are located in the 4a site (0, 0, 0), and the Ga and Si atoms are assumed to randomly occupy the 4b site (0.5, 0.5, 0.5).

The energy dispersive X-ray spectroscopy (EDS) was used to determine the sample compositions. We performed the measurement at several points on the polished surface of each sample. The average values are in very good agreement with the nominal compositions.

Figure 1 exhibits the X-ray diffractograms of $Fe_2MnSi_{1-x}Ga_x$ measured at room temperature. The characteristic reflections show that the obtained samples are in accordance to what was described above. Evidences of secondary phases were not detected.

The powder X-ray diffraction data were refined by Rietveld method with the PowderCell software, using the Fe_2MnSi structural data (ICSD Code No. 186 061) as basis, and it was obtained that the cell parameter *a* tends to increase with the substitution of Si by Ga, from $a = 5.6627 \text{ \AA}$ ($x = 0$) to 5.7359 \AA ($x = 0.5$). The reason for the increasing of the cubic cell parameter is directly related with the atomic radii of Ga and Si, since the atomic radius of Ga is larger than Si.

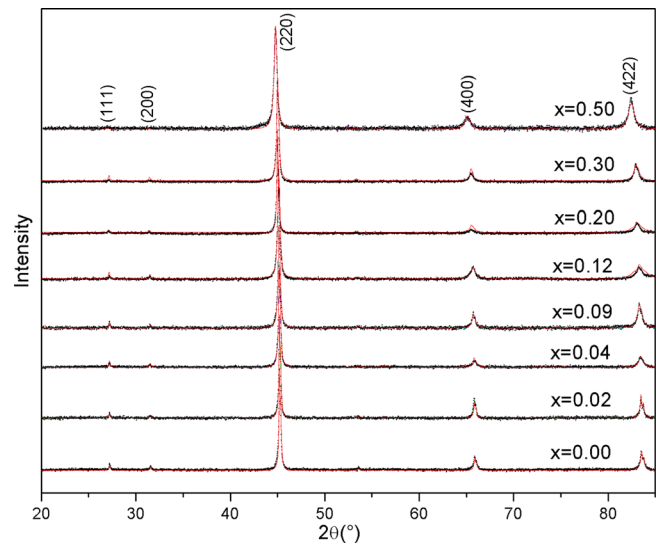


FIG. 1. Powder X-ray diffraction patterns of the $Fe_2MnSi_{1-x}Ga_x$ and the respective refinements. The black lines are the observed patterns and the red lines are the calculated ones by Rietveld refinement.

This tendency can be seen in Figure 2, where the lattice parameter *a* obtained from Rietveld refinement is shown as a function of Ga content. By increasing Ga content, we observed that the reflections are shifted for lower angles; the same behavior was reported in Fe_2MnSi where Si was replaced by Ge.⁹ From the figure, we can see that the cell parameter *a* increases linearly with the Ga content within the concentration studied range, in agreement with the Vegard's law.¹⁰ However, there is no evidence of changes in the crystal structure for Si substitution up to $x = 0.50$. The cell parameter *a* value for $x = 1.0$ (Fe_2MnGa) estimated by linear extrapolation using the concentration dependence is about 5.8053 \AA . This result is very close to the value of 5.808 \AA reported by Kudryavtsev and co-workers.⁸

The degree of atomic ordering can be roughly estimated from the occurrence of the (111) and (200) reflections and their relation with the (220) reflection: as more intense these reflections are, more ordered is the structure, which features a superlattice.¹ The (111) and (200) reflections are observed

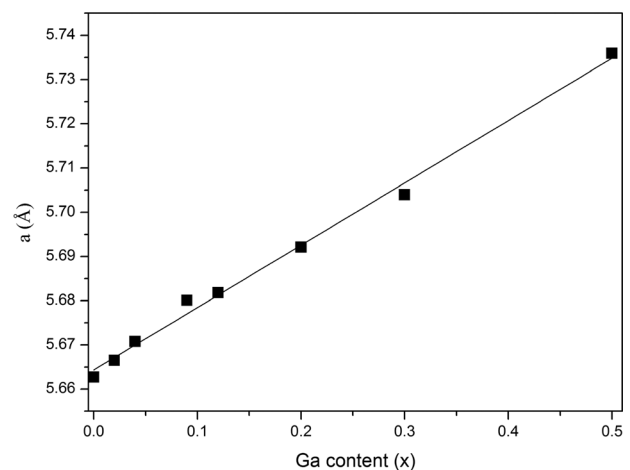


FIG. 2. Lattice parameter *a* variation vs. Ga content. The straight line is the linear fit of the data.

for the samples with $x \leq 0.3$, but the intensities are relatively low when compared with the (220) reflection, which indicates the existence of a certain degree of disorder between the Fe and Si/Ga in the structure.^{4,11,12} These reflections are absent for the sample with a high Ga content ($x=0.5$). Due to the weak superlattice reflections, it is a difficult task to estimate the degree of order from the observed intensities from x-ray diffraction,¹³ but other sophisticated techniques using synchrotron radiation, for example, can bring a better understanding of the order-disorder degree in the structure. Due to the changes in the lattice parameter with the Ga content, with a increasing around 1% with increasing x , it is expected substantial changes in the density of states (DOS) at Fermi level.

B. Magnetic properties

Figure 3 shows the temperature dependence of the magnetic susceptibility ($\chi = M/H$) for the $\text{Fe}_2\text{MnSi}_{1-x}\text{Ga}_x$ compounds for an applied magnetic field of 200 Oe. These compounds exhibit a magnetic behavior involving a transition from a paramagnetic state at high temperature to a ferromagnetic ordered state, with the transition temperature dependent on the Ga content. The transition does not present detectable thermal hysteresis and has a second order character, in spite to be sharp for low magnetic field.

Based on obtained data from the magnetic measurements, the concentration dependence of T_C for the $\text{Fe}_2\text{MnSi}_{1-x}\text{Ga}_x$ compound is shown in Figure 4. The Curie temperatures were obtained from the first derivative of the magnetization at 200 Oe. At $x=0$, T_C is 224 K. It is clear from Figures 3 and 4 that the ferro-paramagnetic transition temperature is (almost) linearly decreasing by increasing Ga content, down to a minimum of 112 K for $x=0.50$. In spite to what would be expected, within the studied x range (from $x=0-0.50$), the value of T_C becomes lower than the value of the parent compound and the Ga doping interval chosen was not enough to bring T_C to room temperature, as can be seen in Figure 4.

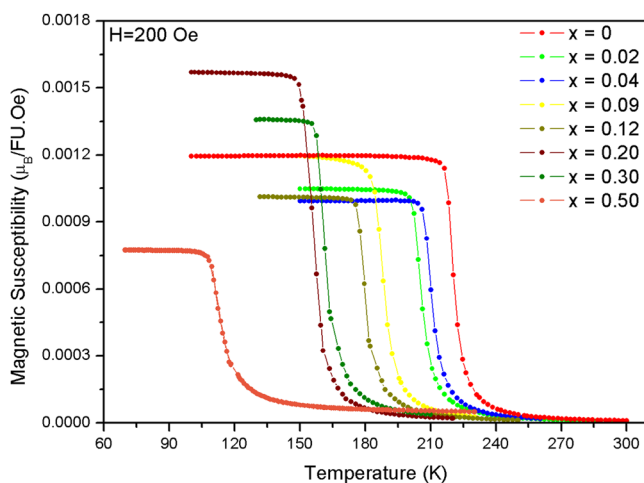


FIG. 3. Magnetic susceptibility curves for the $\text{Fe}_2\text{MnSi}_{1-x}\text{Ga}_x$ ($x=0, 0.02, 0.04, 0.09, 0.12, 0.20, 0.30$, and 0.50) Heusler compounds measured at 200 Oe.

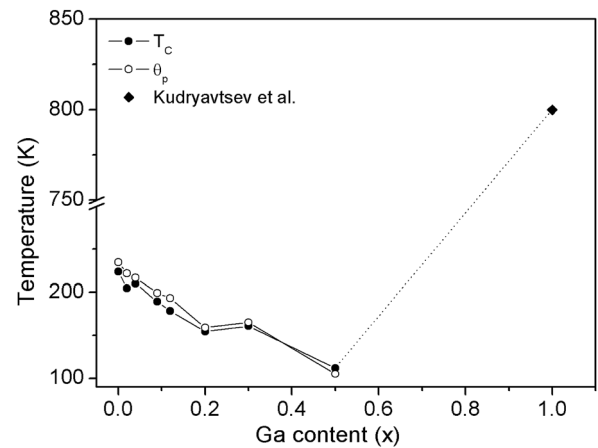


FIG. 4. The Curie temperature (T_C) and paramagnetic Curie temperature (θ_p) of the $\text{Fe}_2\text{MnSi}_{1-x}\text{Ga}_x$ Heusler compounds.

The paramagnetic Curie temperatures were calculated for all samples from the fitting of the linear segment of the inverse susceptibility $1/\chi$ data as a function of temperature. The obtained values are shown in Figure 4.

Figure 5 shows the magnetic field dependence of the magnetization up to 50 kOe for $x=0.02, 0.12$, and 0.50 samples at 4 K. There is a clear tendency of magnetization reduction by increasing Ga content, but the saturation is not reached up to 50 kOe. However, the magnetic saturation can be estimated from M vs. $1/H$ curves (not shown) and is $2.11, 1.98$, and $1.45 \mu_B/\text{FU}$ for $x=0.02, 0.12$, and 0.50 samples, respectively (see inset of Figure 5).

IV. DISCUSSION

The generalized Slater-Pauling rule is a known rule to determine if a system has a half-metal character based only in electrons counting. In this rule, the total magnetic moment M_t for a X_2YZ compound can be expressed as $M_t = Z_t - 24$, where Z_t is the number of valence electrons in the system.⁵

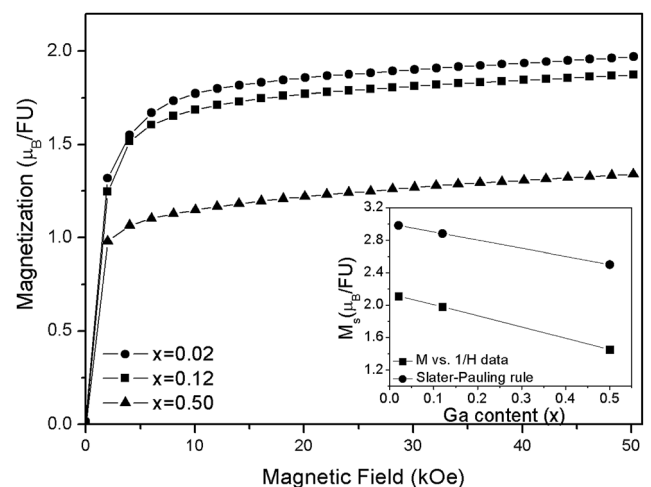


FIG. 5. Magnetic field dependence on the magnetization of $\text{Fe}_2\text{MnSi}_{1-x}\text{Ga}_x$ for $x=0.02, 0.12$, and 0.50 samples at $T=4$ K. Inset: the magnetization saturation M_s as a function of the Ga content. The squares are the values estimated from M vs. $1/H$ experimental data; the circles are the values estimated from the Slater-Pauling rule.

To follow this rule, according to Galanakis and Dederichs,⁵ it is assumed that there are 12 occupied spin down states for unit cell and the total magnetic moment M_t (related to the number of uncompensated spins) is given by:

$$M_t = Z_t - 2n_{\downarrow}, \quad (1)$$

where n_{\downarrow} is the number of electrons in the spin down state (2 times 12, equals to 24).

In this way, it is a convention to suppose that the extra electrons (uncompensated spins) occupy the spin up states only. In X_2YZ compounds, the spin magnetic moment per unit cell becomes strictly integer for half-metallic ferromagnets. However, this situation changes for compounds with non-integer site occupancies, like quaternary compounds stabilized in the $L2_1$ phase.^{14–16} In such cases, the magnetic moment may become non-integer depending on the composition, even for half-metallic state. If the total magnetic moment obtained from the Slater-Pauling rule is close to the obtained from M vs. H measurements, this is an indication of the half-metallic character of the compound.

Fe_2MnSi has a total of $(2 \times 8) + 7 + 4 = 27$ valence electrons in the unit cell and, accordingly, Fe_2MnGa has 26 (Ga contributes with 3 valence electrons); for this reason, the magnetic moment is expected to vary linearly from $3 \mu_B$ to $2 \mu_B$ by increasing Ga content in the $\text{Fe}_2\text{MnSi}_{1-x}\text{Ga}_x$. As early mentioned, the magnetic moments estimated from M vs. $1/H$ curves at 4 K and 50 kOe for $x = 0.02, 0.12,$ and 0.50 samples are $2.11, 1.98,$ and $1.45 \mu_B$ per unit formula, respectively. These values are far from the expected ones according to the Slater Pauling rule of $2.98, 2.88,$ and $2.50 \mu_B/FU$, respectively, but the decrease of the magnetic moment with the Ga concentration is clearly visible, as can be seen in the inset of Figure 5. The difference between the estimated values and the experimental ones is quite large. Such discrepancies may be attributed to a partial atomic disorder in the structure, since the formed structures do not constitute a superlattice, as confirmed by the low intensity of the (111) and (200) diffraction peaks. The same behaviour was observed for Nakatani and co-authors,¹⁸ who studied the magnetic and structural properties of the $\text{Co}_2\text{FeAl}_x\text{Si}_{1-x}$ Heusler alloy. In that work, the authors report spin polarization and saturation magnetization dependences on the Si by Al substitution, but the half-metallicity of the compound is preserved even for a partially disordered state, besides the saturation magnetization values do not follow the Slater-Pauling rule. In this way, atomic disorder effects may explain why the Slater-Pauling rule is not followed by our samples, but our system still remains half-metallic, since both parent compounds Fe_2MnSi and Fe_2MnGa exhibit half-metal behavior.

According to a work conducted by Graf and co-authors,¹⁷ there is a linear dependence on the Curie temperature T_C with the magnetic moment on half metallic Heusler alloys. In the same work, the authors also showed that T_C increases for half-metallic compounds with the valence electron number. The decreasing of T_C with decreasing x is supposedly related to a decreasing in the magnetic moment caused by changes in the number of valence electrons in the system.¹³ This tendency was observed in our $\text{Fe}_2\text{MnSi}_{1-x}\text{Ga}_x$ series, as can be seen

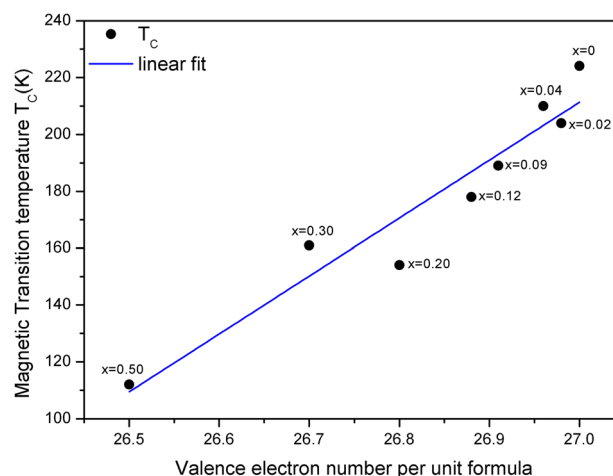


FIG. 6. The magnetic transition temperature (T_C) shows an increasing on the valence electron count with an approximately linear dependence. The line is the linear fit of the data points.

in Figure 6, where the magnetic transition temperature T_C presents an almost linear dependence as a function of the number of valence electrons count. Such behaviour reinforces the hypothesis of the half-metallic behaviour of the $\text{Fe}_2\text{MnSi}_{1-x}\text{Ga}_x$ series, despite the Slater-Pauling rule is not followed by this series due to a minor structural disorder in the system.

V. CONCLUSIONS

The substitutional series of the Heusler compound $\text{Fe}_2\text{MnSi}_{1-x}\text{Ga}_x$ was synthesized and investigated experimentally. The obtained phase crystallizes in the cubic $L2_1$ structure and the lattice parameter a increases linearly with increasing of Ga content. The Curie temperature changes significantly with Ga content in the $0 \leq x \leq 0.5$ range, but the Ga doping interval chosen was not enough to bring T_C to room temperature. The compounds do not follow the Slater-Pauling rule, probably due to a minor disorder degree in the system, but the almost linear dependence on the magnetic transition temperature with the valence electron number reinforces the half-metallic behaviour of the compound, such as the parent phases Fe_2MnSi and Fe_2MnGa . Samples with $x > 0.5$ were prepared, but x-ray diffraction analysis revealed the appearing of additional peaks, indicating the existence of secondary phases or structural changes in these samples. Other studies will be performed concerning electronic structure investigation of these samples and with samples containing higher Ga doping ($x > 0.5$) with the aim of solving the structure and tuning T_C near room temperature.

ACKNOWLEDGMENTS

Access to Laboratório de Caracterização de Materiais at IF-Sudeste MG (Juiz de Fora, Brazil), Laboratório de Difração de Raios-X at IF - UFF (Niterói, Brazil), and Laboratório de Baixas Temperaturas at UNICAMP (Campinas, Brazil) is gratefully acknowledged by all authors. The authors also acknowledge FAPERJ, FAPESP, CAPES, CNPq, and PROPPI-UFF for financial support.

- ¹T. Graf, C. Felser, and S. S. P. Parkin, *Prog. Solid State Chem.* **39**, 1 (2011).
- ²M. Hiroi, I. Yano, K. Sezaki, I. Shigeta, M. Ito, H. Manaka, and N. Terada, *J. Phys.: Conf. Ser.* **400**, 032021 (2012).
- ³B. Hamad and Q.-M. Hu, *Phys. Status Solidi B* **248**, 2893 (2011).
- ⁴S. Wurmehl, G. H. Fecher, H. C. Kandpal, V. Ksenofontov, C. Felser, H.-J. Lin, and J. Morais, *Phys. Rev. B* **72**, 184434 (2005).
- ⁵I. Galanakis and P. H. Dederichs, *Phys. Rev. B* **66**, 174429 (2002).
- ⁶M. Kawakami, *Physica B* **186–188**, 1037 (1993).
- ⁷T. Ersez, G. T. Etheridge, and T. J. Hicks, *J. Magn. Magn. Mater.* **177–181**, 1351 (1998).
- ⁸Y. V. Kudryavtsev, N. V. Uvarov, V. N. Iermolenko, I. N. Glavatsky, and J. Dubowik, *Acta Mater.* **60**, 4780 (2012).
- ⁹L. Zhang, E. Brück, O. Tegus, K. H. J. Buschow, and F. R. de Boer, *Physica B* **328**, 295 (2003).
- ¹⁰L. Vegard, *Z. Phys.* **5**, 17 (1921).
- ¹¹Y. Du, G. Z. Xu, X. M. Zhang, Z. Y. Liu, S. Y. Yu, E. K. Liu, W. H. Wang, and G. H. Wu, *Europhys. Lett.* **103**, 37011 (2013).
- ¹²L. Hongzhi, Z. Zhiyong, M. Li, X. Shifeng, L. Heyan, Q. Jingping, L. Yangxian, and W. Guangheng, *J. Phys. D: Appl. Phys.* **40**, 7121 (2007).
- ¹³R. Y. Umetsu, A. Okubo, X. Xu, and R. Kainuma, *J. Alloys Compd.* **588**, 153 (2014).
- ¹⁴G. H. Fecher, H. C. Kandpal, S. Wurmehl, C. Felser, and G. Schönhense, *J. Appl. Phys.* **99**, 08J106 (2006).
- ¹⁵Y. Du, G. Z. Xu, E. K. Liu, G. J. Li, H. G. Zhang, S. Y. Yu, W. H. Wang, and G. H. Wu, *J. Magn. Magn. Mater.* **335**, 101 (2013).
- ¹⁶B. Hamad, Z. Charifi, H. Baaziz, and F. Soybalp, *J. Magn. Magn. Mater.* **324**, 3345 (2012).
- ¹⁷T. S. Graf, S. S. P. Parkin, and C. Felser, *IEEE Trans. Magn.* **47**, 367 (2011).
- ¹⁸T. M. Nakatani, A. Rajanikanth, Z. Gercsi, Y. K. Takahashi, K. Inomata, and K. Hono, *J. Appl. Phys.* **102**, 033916 (2007).