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Microscopic origin of ferro-antiferromagnetic transition upon non-magnetic substitution in $Ru_2(Mn_{1-x}V_x)Ge$ full Heusler alloys

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ABSTRACT

On the basis of first-principle simulations of interatomic magnetic exchange interactions, we show that the transition from antiferromagnetic order in Ru_2MnGe to ferromagnetic order in vanadium substituted $Ru_2Mn_{1-x}V_xGe$ is due to a progressive increase of the first-nearest neighbor (NN) ferromagnetic coupling between Mn atoms. The revealed mechanism is quite unusual since commonly one would expect, and indeed it has been proposed earlier, that the transition scenario is due to the suppression of some relevant interactions by the non-magnetic substitution or chemical disorder effects. Here, using our ab-initio calculated exchange parameters and performing finite temperature Monte Carlo statistical simulations on a disordered lattice, we describe the experimental magnetic phase diagram for the full range of vanadium concentrations, including the variation of the ordering temperature and the onset of finite magnetization in the ground state. Since the observed changes in the Mn–Mn magnetic interactions are continuous with increasing V content, we argue that there is a threshold concentration of V substitutions where the critical fluctuations associated with frustration effects on the fcc lattice could be studied experimentally.

1. Introduction

The transition between ferromagnetic (FM) and antiferromagnetic (AFM) ordering upon the change of some external parameter (pressure, applied field, temperature) attracts considerable interest in the field of magnetism due to the possibility of the fine tuning of the material properties, the investigation of magnetic frustration effects, quantum criticality and a variety of other properties related to the magnetic instabilities. One of the prominent examples is the FM-AFM transition in FeRh alloys, which leads to a huge magneto-caloric effect resulting in intensive experimental and theoretical studies during the recent decade [1–4]. The occurrence of the FM-AFM transition in this material is highly sensitive to the stoichiometry and alloy disorder [5]. It seems that the ferromagnetic state in this material becomes stabilized due to the high magnetic polarization of itinerant Rh, which does not possess an intrinsic magnetic moment, whereas the exchange interactions between the localized magnetic moments of Fe tend to stabilize the AFM state [1,4]. Metallic alloys close to FM-AFM transitions attract nowadays also a considerable practical interest due to their potential applications in electronics as materials for fast magnetic recording.

The mechanisms driving an AFM or FM compound to AFM-FM transition may be rather different. Usually it is achieved by substituting a magnetic element with another one, which introduces a strong exchange coupling of opposite sign as compared to the magnetic matrix. A well known example is the spin-spiral antiferromagnet $MnAu_2$ [6], which became of interest recently [7,8], since the substitution of a small amount of Fe for Mn may drive system to a ferromagnetic ground state [9]. On the basis of ab-initio calculations it has been confirmed that Fe has a very strong FM interaction with their neighboring Mn moments changing the energy balance towards the FM state [10]. The other examples and first-principles studies of the AFM-FM transition caused by substitutions, specifically in some half-Heusler alloys, can be found in Refs. [11,12]. It more or less obvious that if an FM (AFM) intermetallic compound, say X_nY_m … (where X is a magnetic element) is soluble with another magnetic element X' such that X'_nY_m … is AFM (FM), one can expect to find a critical region of the concentration of X', where the alloy $(X,X')_nY_m$ goes through an FM-AFM

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(AFM-FM) transition.

Another more complex source for the AFM-FM instability may be magnetic disorder. Beside the well-known case of FeRh, an interesting example is the full Heusler alloy Ni_2MnAl, which is ferromagnetic in the fully ordered state, but gradually turns into the antiferromagnetic state upon increasing the chemical disorder between the Mn and Al sites [13]. First-principles analyses revealed that the mechanism of this transition is a competition of the FM coupling between the Mn moments on proper sites and the AFM coupling between proper Mn sites and Mn anti-sites on the Al sublattice [14,15].

The AFM-FM transition might occur also due to more subtle effects related to a reconstruction of the electronic structure caused by applied pressure or by substituting a non-magnetic element into the system. In this case it is often not easy to guess the relevant mechanism without ab-initio based studies. Moreover, systems in the vicinity of AFM-FM instability might develop critical fluctuations associated with a quantum phase transition.

In this work we present a study of the microscopic mechanism of the recently discovered AFM-FM transition [16] in the full Heusler alloy $Ru_2(Mn_{1-x}V_x)Ge$, where the transition occurs upon doping with non-magnetic vanadium atoms into the originally antiferromagnetically ordered alloy Ru_2MnGe with a Néel temperature of 316 K [15] just above room temperature. This finding was not obvious since vanadium is soluble in the Heusler structure $Ru_2(Mn_{1-x}V_x)Ge$ over the full composition range from $x = 0.0$ to $x = 1.0$ and for $x = 1.0$ the compound Ru_2VGe has an ordinary paramagnetic ground state [16]. Below the critical V concentration, $x = 0.3–0.4$, the Néel temperature decreases with V doping, above this concentration in the ferromagnetic state one observes an increase of the Curie temperature up to $x = 0.5$, followed by a gradual decrease until the disappearance of the magnetic order around $x = 0.8$ [16]. The original interpretation of this non-monotonous behavior has been based on the assumption that vanadium atoms concentrate in certain [111] planes and strongly decrease the second nearest neighbor antiferromagnetic coupling between the Mn moments, which stabilizes the 2nd kind antiferromagnetic ground state on the Mn fcc sublattice. Later the problem of the evolution of magnetism in $Ru_2(Mn_{1-x}V_x)Ge$ alloys has been studied using synchrotron-based Compton scattering experiments [17]. It was found that the vanadium substitution induces changes in the electronic structure and the topology of the Fermi surface, which presumably decreases indirect AFM and enhances direct FM d-d exchange [17]. Recently, we studied [18] the exchange interactions between localized Mn moments in the high temperature paramagnetic state for the whole series of Ru_2MnX with X = Si, Ge, Sb, and Sn and found the importance of the long-range interactions (beyond first- and second NN shells) for a proper explanation of the experimental Néel temperature in this series and for that of effects of magnetic frustration. However, the question of how the non-magnetic vanadium influences the Mn–Mn exchange interactions remained open.

Magnetic Heusler alloys in general are subject of intensive studies during the past few decades due to both their importance for modern technology and for a fundamental understanding of magnetism [19–21]. In particular, the inter-atomic exchange interactions and a variety of underlying microscopic mechanisms responsible for them have intensively been investigated for Heusler alloys with local atomic moments (e.g. see Ref. [22]). The experimentally established pronounced phenomena like AFM-FM transition or non-monotonous variation of the Curie temperature of $Ru_2(Mn_{1-x}V_x)Ge$ [16,17] provides an excellent opportunity to test the state-of-the-art ab-initio methodologies and our general understanding to describe magnetism in metallic alloys at finite temperatures.

We calculate the distant inter-atomic exchange interactions between localized Mn moments in the high temperature paramagnetic state of $Ru_2(Mn_{1-x}V_x)Ge$ using ab-initio methods (see Methodology section) based on the Green Function formalism and Local Spin Density Approximation (LSDA) [21] taking into account the effects of chemical disorder on the Mn–V sublattice in the whole concentration range $x = 0.0–1.0$. Then we perform Monte-Carlo simulations on a disordered lattice with a Heisenberg Hamiltonian to construct the magnetic phase diagram of $Ru_2(Mn_{1-x}V_x)Ge$. We find that approach predicts a stabilization of the ferromagnetic ground state as well as the increase of the Curie temperature in the interval $x = 0.4–0.5$ followed by a vanishing total magnetization. The mechanism of the stabilization of the FM state and other experimentally observed properties are revealed and discussed in detail in section “Results and Discussion”.

2. Methodology

Our first principles investigation is based on the Local Spin-Density Approximation and the Korringa-Kohn-Rostoker (KKR) method in Atomic Sphere Approximation (ASA) [23,24]. The experimental lattice constants of the $L2_1$ full Heusler structure of $Ru_2(Mn_{1-x}V_x)Ge$ as provided in Ref. [16] has been used during the calculations. The electronic structure calculations were converged with 2109 nonequivalent *k*-points in the irreducible wedge of Brillouin zone (IBZ) and around 10^4 *k*-points in IBZ were used to derive magnetic exchange interactions. The partial waves in the KKR-ASA calculations have been expanded up to $l_{max}=3$ *(spdf – basis)* inside the atomic spheres, with an equal radius of the ASA spheres for all non-equivalent atomic sites.

Atomic disorder within the Mn–V sub-lattice has been treated in the framework of the single-site coherent potential approximation (CPA) [24]. The CPA has been also used to model the high-temperature paramagnetic state above the magnetic ordering temperature in the framework of the Disordered Local Moment (DLM) scheme [25].

The magnetic exchange interaction constants, J_{ij}, of the classical Heisenberg Hamiltonian:

$$H = -\sum_{i,j\in\{Mn\}} J_{ij}\vec{e}_i\vec{e}_j \tag{1}$$

where $\vec{e}_i$ is the unit directional vector of magnetic moment at the *i*-th site of the Mn sublattice, calculated using the magnetic force theorem [26] implemented in the bulk Korringa-Kohn-Rostokker band structure method as described in Ref. [27]. The exchange constants were derived from the Disordered Local Moment (DLM) reference state [25].

Subsequently, we performed Monte Carlo simulations with the Hamiltonian (1) on a cluster of 4096 Mn atoms (14 × 14 × 14 primitive cells of the underlying magnetic fcc lattice) employing periodic boundary conditions and using a conventional Metropolis algorithm. For the simulation of finite temperature magnetic properties of the chemically disordered $Ru_2(Mn_{1-x}V_x)Ge$ alloys the Mn–V fcc sublattice was randomly filled with magnetic atoms according their partial occupation numbers. This computational scheme has previously been used successfully by the authors to predict and explore the finite temperature magnetic properties in a number of Mn-based metallic alloys and intermetallics with localized Mn spin moments [28–30] including full Heusler alloys [14,18] with chemical disorder.

3. Results and discussion

The parent Ru_2MnGe compound is an antiferromagnet with

Néel temperature of 316 K and a high degree of the chemical order [31]. The Mn atoms have fairly localized moments of about 3 μ_B/Mn and occupy one of the four interpenetrating fcc sub-lattices of the $L2_1$ full Heusler structure. The antiferromagnetic interactions on the fcc lattice are frustrated and the so-called 2nd kind AFM structure of Ru_2MnGe found in experiment becomes stabilized due to the competition of the 1st, 2nd and 3rd nearest neighbor (NN) exchange interactions [32] in accordance with the well known Moran-Lopez et al. [33] phase diagram of the classical Heisenberg model. In Ref. [18], however, it was shown that also longer distance exchange interactions (beyond the 3rd NN shell, in particular, strong 4th NN ones) provide an essential contribution to the Néel temperature. The speciality of the second kind of AFM ordering on an fcc lattice is that the actual values of the interatomic interactions do not fix the mutual orientation of the spins in the four simple cubic antiferromagnetic sublattices, leaving the system essentially frustrated. It has been shown that one of the mechanisms which removes frustration might be a higher order biquadratic exchange interaction, which has been estimated to have a positive value in Ru_2MnGe.

In Fig. 1 we show the calculated exchange interactions in $Ru_2(Mn_{1-x}V_x)Ge$ alloys up to the 4th NN shell. The vanadium atoms do not possess intrinsic magnetic moments and thus the Mn–Mn interactions are sufficient to describe the magnetic properties of the system. From the values given for $x = 0$, one can see that the dominating interaction in the parent Ru_2MnGe alloy is the antiferromagnetic second nearest-neighbor one, which is more than two times larger in magnitude than the ferromagnetic 1st NN interaction, being the reason for the stability of 2nd kind AFM structure.

When vanadium is alloyed in the Mn sublattice the magnetic moment of Mn gradually increases with increasing V concentration, see Fig. 2 showing the calculated local Mn moment in paramagnetic DLM state. In the dilute limit, close to the stoichiometric Ru_2VGe composition, the local Mn moment increases by almost 20% compared to the parent Ru_2MnGe (from 3.05 μ_B to almost 3.6 μ_B) implying a tendency of increasing localization of the *d*-electrons. From Fig. 1 one can see that the 2nd, 3rd, and 4th NN interactions remain almost unchanged in the concentration range from $x = 0.0$ to $x = 0.3–0.4$. Dramatic changes occur, however, to the 1st NN ferromagnetic exchange interactions. It shows a gradual increase with *x* and becomes of similar size as the 2nd NN AFM interaction in the critical region where experiment finds the stabilization of the FM ground state. Thus the AFM-FM transition upon alloying with V occurs due to a promotion of the direct 1st NN ferromagnetic exchange, rather than due to the suppression of the AFM coupling as was originally proposed in Ref. [16]. The mechanism for the AFM-FM transition proposed here (promoting of the direct FM exchange coupling) is in-line with the discussion given earlier on the basis of the Compton scattering experiments [17].

The 2nd NN AFM coupling might be understood as the indirect exchange between the Mn moments mediated by the *p*-states of Ge, although the complete analogy with the Anderson-Kanamori type super-exchange models must be taken with a great care in the case of the metallic Heusler alloys, see the discussion in Refs. [18,34]. The 1st NN coupling is in turn due to the direct hybridization between the Mn *d*-states. Our direct calculations of the exchange interactions thus suggest that the stabilization of the FM state in $Ru_2(Mn_{1-x}V_x)Ge$ is due to a promotion of the direct *d*-*d*-interaction in terms of the terminology given in Ref. [16]. The only difference in the two kinds of explanations is that we find that the indirect "*sp*-*d*" AFM interactions are not suppressed until $x = 0.4$. However, the suppression of the AFM interaction, which starts in the region $x > 0.4$, plays a considerable role in the experimentally observed [16,17] increase of the Curie temperature of the ferromagnetic phase above $x = 0.4$.

As one can see from Fig. 1, in the region of the FM phase ($x > 0.4$) there exists a strong 2nd NN AFM interaction, which significantly reduces the value of the Curie temperature. On the other hand, as the concentration of V increases, there are two competing effects: i)

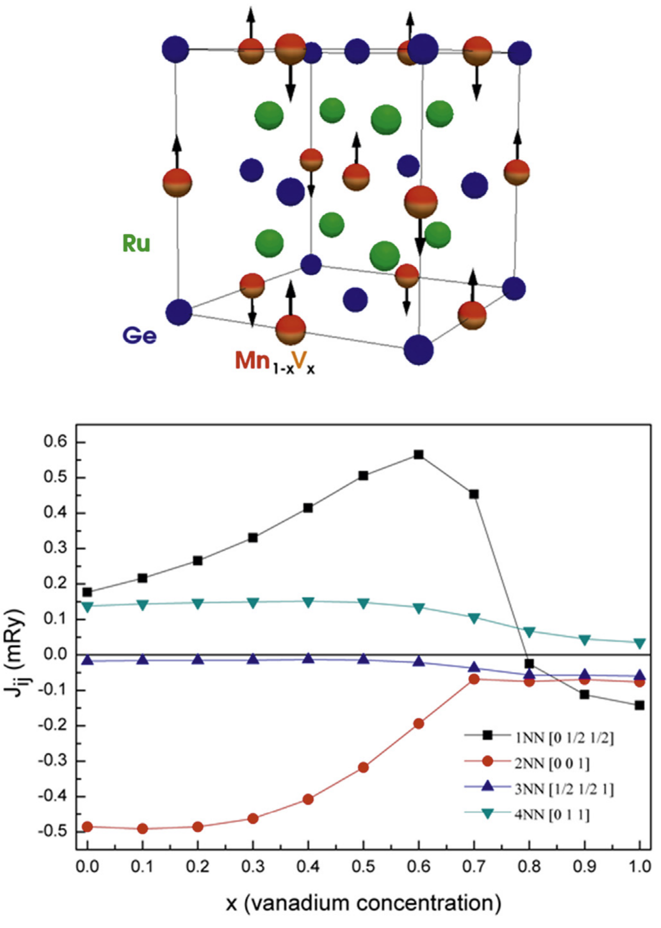

Fig. 1. Upper panel: The crystal structure and antiferromagnetic ground state of $Ru_2(Mn_{1-x}V_x)Ge$ alloys. Lower panel: Calculated Mn–Mn exchange interactions in $Ru_2(Mn_{1-x}V_x)Ge$ alloys as a function of the vanadium concentration *x*. The interactions are shown only for the first four nearest neighbor shells.

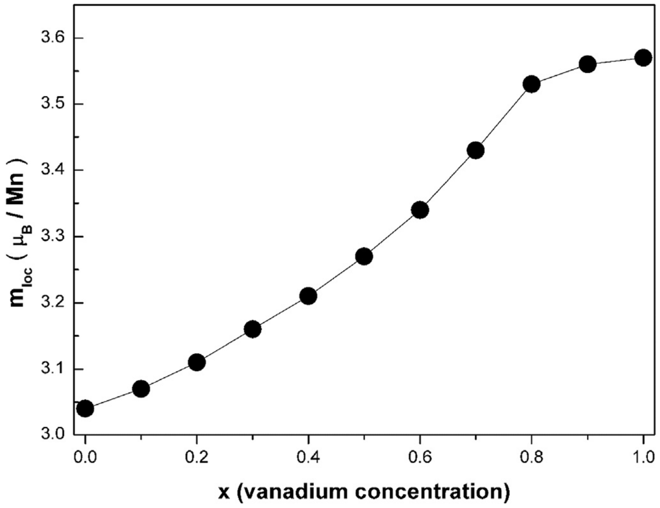

Fig. 2. Calculated local Mn moments in the paramagnetic DLM state of $Ru_2(Mn_{1-x}V_x)$ Ge alloys as a function of the vanadium concentration *x*.

the non-magnetic substitutions reduce the number of the magnetic sites which should lead to a reduction of the magnetic ordering temperature; ii) The 1st NN FM interactions are increasing and the frustrated 2nd NN AFM interactions are decreasing in magnitude, thus favoring an increase of the Curie temperature. The experimentally observed maximum of the Curie temperature in the region near $x = 0.6$ is the consequence of the competition of these two effects. Note also that starting from $x = 0.6$ the 1st NN coupling sharply decreases in magnitude with increasing V concentration. As a result the system is expected to show a very low ordering temperature or even lose the magnetic order at any temperature and to develop a spin glass like state for V concentrations more than $x = 0.8$ (dilute magnetic regime). Indeed such a behavior has been observed in experiment [17].

In Fig. 3 we present the ordering temperatures and low temperature total magnetization obtained from Monte-Carlo (MC) simulations on the chemically disordered fcc Mn sublattice with the ab-initio derived exchange interactions from Fig. 1. The results of the MC simulations are indeed fully in accordance with the conclusions outlined above. The MC simulations numerically predict the onset of a ferromagnetic ground state for V concentrations above $x = 0.4$, and a maximum of the Curie temperature in the region between $x = 0.4$ and $x = 0.6$. We note that the total magnetization per unit cell in the ferromagnetic state continuously decreases (in accordance with experiment) with increasing vanadium concentration since there is less Mn in the system, whereas the Curie temperature behaves non-monotonously due to the complexity of the exchange interactions as described above. We thus see that the ab-initio calculated exchange interactions together with the numerical model of chemical and magnetic disorder correctly describe the magnetic properties of $Ru_2(Mn_{1-x}V_x)$Ge alloys upon vanadium alloying found experimentally [16,17]. However, our calculations slightly overestimate the magnetic ordering temperatures (by about 20%) and the occurrence of the FM-AFM transition is shifted towards higher V concentrations. The reason for that is probably the presence of a considerable amount of anti-site disorder in the Mn–Ge sublattices in the real alloy $Ru_2(Mn_{1-x}V_x)$Ge (see Ref. [17] for a careful discussion of this effect on the Néel temperature in the stoichiometric Ru_2MnX series). We restrain ourselves from the analysis of this effect here since to our best knowledge there is no reliable experimental information on the Mn–Ge disorder for $Ru_2(Mn_{1-x}V_x)$Ge alloys.

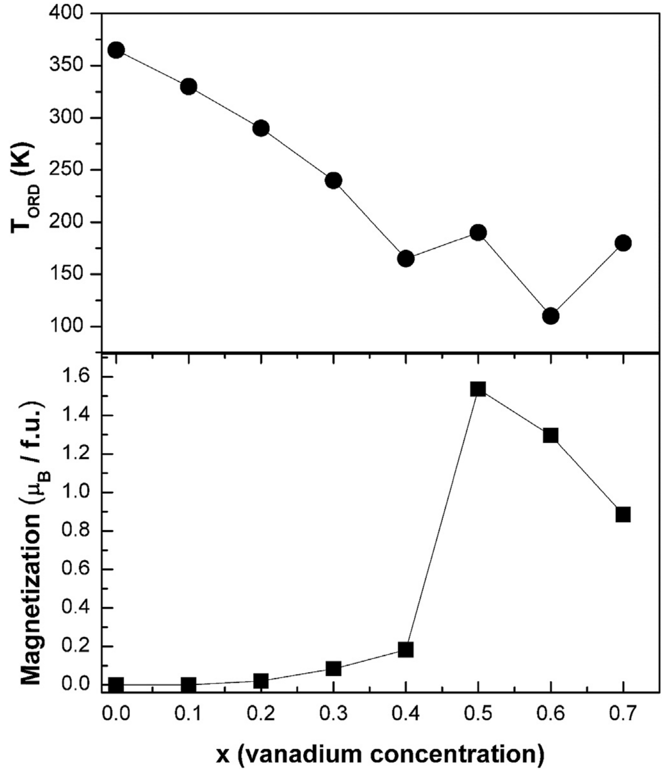

Fig. 3. Magnetic ordering temperatures of $Ru_2(Mn_{1-x}V_x)$Ge alloys obtained from Monte-Carlo simulations on the disordered Mn sublattice (upper panel) and the total magnetization at low temperature (lower panel).

3. Conclusions

In order to explain the complex magnetic phenomena of $Ru_2(Mn_{1-x}V_x)$Ge alloys found experimentally we performed a combined study in terms of state-of-the-art ab initio calculations and subsequent Monte-Carlo simulations. The exchange interactions calculated in the framework of the magnetic force theorem and the ab-initio electronic structure obtained for the disordered alloys provide a very good description of the evolution of magnetism when substituting V for Mn. In particular, the AFM-FM transition is explained as the consequence of increasing direct 1st NN ferromagnetic exchange interaction. Further increase of the V concentration beyond the critical value for the onset of the FM state simultaneously leads to an increase of 1st NN FM and a decrease of indirect AFM exchange mediated by the *p*-states of Ge. The latter effect provides the mechanism for the observed maximum of the Curie temperature at intermediate vanadium concentrations. The subtle effects underlying the rich magnetic phase diagram of $Ru_2(Mn_{1-x}V_x)$Ge alloys make this system a perfect case for further experimental investigation of the magnetic exchange mechanism in full Heusler alloys. For instance, as pointed out above, the role of the partial disorder between the magnetic transition metal (Mn) and *p*-element Ge might be particularly interesting for experimental and theoretical exploitation.

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References

[1] S. Polesya, S. Mankovsky, D. Ködderitzsch, J. Minár, H. Ebert, Phys. Rev. B 93 (2016) 024423.
[2] S. Maat, J.-U. Thiele, E.E. Fullerton, Phys. Rev. B 72 (2005) 214432.
[3] J.B. Staunton, R. Banerjee, M. dos Santos Dias, A. Deak, L. Szunyogh, Phys. Rev. B 89 (2014) 054427.
[4] J. Kudrnovský, V. Drchal, I. Turek, Phys. Rev. B 91 (2015) 014435.
[5] W. Pepperhoff, M. Acet, Constitution and Magnetism of Iron and its Alloys, Springer-Verlag, Berlin, 2001.
[6] P.A. Herpin, P. Meriel, J. Phys. Radium 22 (1961) 337.
[7] J.K. Glasbrenner, K.M. Bussmann, I.I. Mazin, Phys. Rev. B 90 (2014) 144421.
[8] J.K. Glasbrenner, Phys. Rev. B 93 (2016) 184402.
[9] A. Handstein, K. Nenkov, U.K. Rößler, K.-H. Müller, J. Appl. Phys. 87 (2000) 5789.
[10] L. Udvardi, S. Khmelevskyi, L. Szunyogh, P. Mohn, P. Weinberger, Phys. Rev. B 73 (2006) 104446.
[11] B. Wu, H. Yuan, A. Kuang, H. Chen, Y. Feng, Comp. Mat. Sci. 78 (2013) 123.
[12] X.Y. Wu, J. Zhang, H.K. Yuan, A.L. Kuang, H. Chen, Phys. Stat. sol.(b) 247 (2010) 945.
[13] M. Acet, E. Duman, E.F. Wassermann, L. Maosa, A. Planes, J. Appl. Phys. 92 (2002) 3867.
[14] E. Simon, J. Gy Vida, S. Khmelevskyi, L. Szunyogh, Phys. Rev. B 92 (2015) 054438.
[15] I. Galanakis, E. Şaşıoğlu, Appl. Phys. Lett. 98 (2011) 102514.
[16] S. Mizusaki, A. Douzono, T. Ohnishi, Y. Nagata, T.C. Ozawa, H. Samata, Y. Noro, J. Phys. Conf. Ser 200 (2010) 052017.
[17] S. Mizusaki, T. Ohnishi, A. Douzono, M. Hirose, Y. Nagata, M. Itou, Y. Sakurai,

T.C. Ozawa, H. Samata, Y. Noro, J. Phys. Condens. Matter 24 (2012) 255601.
[18] S. Khmelevskyi, E. Simon, L. Szunyogh, Phys. Rev. B 91 (2015) 094432.
[19] T. Graf, J. Winterlik, L. Müchler, G.H. Fecher, C. Felser, S.S.P. Parkin, in: K.H.J. Buschow (Ed.), Handbook of Magnetic Materials, Elsevier, North-Holland, 2013, p. 1. V. 23.
[20] K.R.A. Ziebeck, K.-U. Neumann, Heusler alloys, in: H.R.J. Wijn, Landolt Bornstein (Eds.), New Series, Group III, Vol. 32CSpringer, Berlin, 2001, 64–314.
[21] T. Graf, S.S.P. Parkin, C. Felser, IEEE Trans. Magn. 47 (2011) 367.
[22] Y. Kurtulus, R. Dronkowski, G. Samolyuk, V.P. Antropov, Phys. Rev. B 71 (2005) 014425.
[23] I.A. Abrikosov, H.L. Skriver, Phys. Rev. B 47 (1993) 16532.
[24] A.V. Ruban, H.L. Skriver, Comp. Mater. Sci. 15 (1999) 199.
[25] B.L. Gyorffy, A.J. Pindor, J. Staunton, G.M. Stocks, H. Winter, J. Phys. F. Mater. Phys. 15 (1985) 1337.
[26] A.I. Liechtenstein, M.I. Katsnelson, V.P. Antropov, V.A. Gubanov, J. Magn. Magn. Mater 67 (1987) 65.
[27] A.V. Ruban, S.I. Simak, S. Shallcross, H. Skriver, Phys. Rev. B 67 (2003) 214302.
[28] S. Khmelevskyi, P. Mohn, Appl. Phys. Lett. 93 (2008) 162503.
[29] S. Khmelevskyi, P. Mohn, J. Phys. Condens. Matter 24 (2012) 016001.
[30] S. Khmelevskyi, A.V. Ruban, P. Mohn, Phys. Rev. B 93 (2016) 184404.
[31] T. Kanomata, M. Kikuchi, H. Yamauchi, J. Alloys Comp. 414 (2006) 1.
[32] S. Ishida, S. Kashiwagi, S. Fujii, S. Asano, Phys. B 210 (1995) 140.
[33] J.L. Moran-Lopez, R. Rodriiguez-Alba, F. Aguilera-Granja, J. Magn. Magn. Mater 131 (1994) 417.
[34] E. Şaşıoğlu, L. Sandratskii, P. Bruno, I. Galanakis, Phys. Rev. B 72 (2005) 184415.