Ab initio study of Heusler alloys Co$_2$XY (X=Cr, Mn, Fe; Y=Al,Ga) under high pressure

Swetarekha Ram [a] , Mudavath Rahul Chauhan [b] , Kunal Agarwal [c]
& V. Kanchana [a]

[a] Department of Physics, Indian Institute of Technology
Hyderabad, Ordnance Factory Campus, Yeddumailaram, Andhra
Pradesh 502205, India

[b] Department of Electrical Engineering, Indian Institute
of Technology Hyderabad, Ordnance Factory Campus,
Yeddumailaram, Andhra Pradesh 502205, India

[c] Department of Computer Science Engineering, Indian
Institute of Technology Hyderabad, Ordnance Factory Campus,
Yeddumailaram, Andhra Pradesh 502205, India

Available online: 07 Jul 2011

PLEASE SCROLL DOWN FOR ARTICLE

demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Ab initio study of Heusler alloys Co$_2$XY (X = Cr, Mn, Fe; Y = Al, Ga) under high pressure

Swetarekha Ram[a], Mudavath Rahul Chauhan[b], Kunal Agarwal[c] and
V. Kanchana[a]*

[a]*Department of Physics, Indian Institute of Technology Hyderabad, Ordnance Factory Campus, Yeddumailaram, Andhra Pradesh 502205, India;* [b]*Department of Electrical Engineering, Indian Institute of Technology Hyderabad, Ordnance Factory Campus, Yeddumailaram, Andhra Pradesh 502205, India;* [c]*Department of Computer Science Engineering, Indian Institute of Technology Hyderabad, Ordnance Factory Campus, Yeddumailaram, Andhra Pradesh 502205, India*

The structural, electronic, and magnetic properties of ferromagnetic Heusler alloys Co$_2$XY (X = Cr, Mn, Fe; Y = Al, Ga) have been investigated by means of the all-electron full-potential linearized augmented plane wave method within the generalized gradient approximation for the exchange and correlation potential. The main focus of this study is to elaborate the changes brought about in the electronic and the magnetic properties by applied pressure. The calculated total spin magnetic moments of all the compounds are found to be in good agreement with experiments. Out of these compounds, Co$_2$CrAl is found to be perfectly half-metallic (HM) and the other compounds are found to be nearly HM. Thus the HM to metal transition was observed at 75 GPa pressure for Co$_2$CrAl and the nearly half-metal to half-metal transition was observed at 40 GPa and 18 GPa for Co$_2$CrGa and Co$_2$MnAl, respectively, while no transition is observed in other compounds under investigation. It can be clearly seen that pressure affects the minority spin states rather than the majority states, leading to a slight reconstruction of the minority spin states with a shift in the Fermi level driving the above-mentioned transition.

1. Introduction

In the last decade, structural, electronic, and magnetic properties of Heusler alloys served as a prime focus for many experimental and theoretical studies [1–6]. Half-metallic ferromagnetism in this family of compounds was first introduced by de Groot et al. [7] and is characterized by the metallic electronic band structure for majority spins while the band structure for minority spins is semiconducting, indicating a high-spin polarization at Fermi level (E_F). These materials play an important role in various spin-dependent electronic applications such as

---

*Corresponding author. Email: kanchana@iith.ac.in

spintronics [8,9], giant magneto resistance [10], and spin injection to semiconductor [11–13]. The electronic and magnetic properties of these half and full Heusler alloys were studied extensively both experimentally and by *ab initio* techniques [14–16]. The electronic structure plays an important role in determining the magnetic properties of Heusler compounds and in particular for predicting the half-metallic ferromagnetism. Among the Heusler compounds, Co_2XY are promising materials for spintronics applications due to their wide band gap in the minority spins and are easy to be synthesized experimentally [17,18]. Co-based Heusler alloys were investigated theoretically using *ab initio* calculations and most of them are predicted to be half-metallic (HM) [14,17,19,20]. Magnetic and HM properties of the full Heusler alloys Co_2TiX (X = Al, Ga, Si, Ge, Sn, Sb) were carried out by Lee et al. [21], where in Co_2TiX (X = Al, Si, Ge, Sn) are shown to be half-metallic and ferromagnetic. Fermi surface and electronic structure of the Heusler alloy Co_2TiSn has been studied by Hickey et al. [22], where they claim this alloy not to be a half metal, which is quite different from the observations of Picozzi et al. [23]. Galanakis et al. also found the alloys Co_2TiSn and Co_2TiAl not to be HM. With the desire of finding new promising half metals, Co_2YSi series was also explored by many theoreticians [24,25]. Despite many investigation on Heusler alloys, looking at it from different perspectives, there are still many compounds which are yet to be explored with a deep insight, and forms the main part of this work. We present the electronic and magnetic properties of Co_2XY (X = Cr, Mn, Fe; Y = Al, Ga) and also study the pressure effect on the magnetic properties of these alloys. Until now, we are quite familiar and have observed the pressure-induced metallization in the non-magnetic insulator and semiconductor compounds rather than in HM ferromagnets. The same has been observed in Ba chalcogenides, Strontium halides [26,27], etc. However, there are no theoretical or experimental literature available explaining the stability of the HM behavior under pressure for these alloys. Quite recently, electronic structure of HM Co_2MnSi has been studied under pressure, which indicated a half-metal to metal transition occurring around 70 GPa [28]. In this work, we have also carried out the pressure effect on the magnetic properties of Co_2XY (X = Cr, Mn, Fe; Y = Al, Ga). The rest of this article is organized in the following way. Section 2 deals with computational method. Results and discussion are presented in Section 3. Finally, Section 4 concludes this article.

2. Crystal structure and computational details

Half-metallic ferromagnetic (HMF) Heusler compounds are ternary inter metallics with general formula X_2YZ, where X and Y are transition metals and Z is a main group element. These materials crystallize in $L2_1$ crystal structure (space group: 225 Fm-3m), which can be thought as a simple cubic lattice for Co atoms with X and Y atoms arranged at alternate body-centered positions. The X atoms are placed at (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4) positions. The Y and Z atoms are located on (0, 0, 0) and (1/2, 1/2, 1/2) positions, respectively. In this work the electronic structure and the basic ground state properties of the Heusler alloys are calculated using the full-potential linearized augmented plane-wave (FLAPW) method as implemented in WIEN2K [29,30] within the generalized gradient approximation (GGA) to the

Table 1. Calculated and experimental lattice parameter a (Å) and bulk modulus B (GPa) of Co_2XY compounds.

Compounds	Lattice parameter		$B_{calc.}$
	a_{expt}	$a_{calc.}$	
Co_2CrAl	5.73[a]	5.70	207.23
Co_2CrGa	5.81[a]	5.72	208.81
Co_2MnAl	5.75[a]	5.69	196.37
Co_2MnGa	5.77[a]	5.70	200.61
		5.73[b]	196[b]
Co_2FeAl	5.73[a]	5.69	215.87
		5.72[b]	
Co_2FeGa	5.74[a]	5.71	198.85

Notes: [a]Ref [19], [a]Experimental values for lattice parameter are taken from [19] and the additional references reported therein.
[b]Ref [38].

exchange-correlation potential according to the Perdew–Burke–Ernzerhof parameterization [31]. The muffin tin spheres were chosen as $R_{MT}^{Co} = R_{MT}^{Cr} = R_{MT}^{Mn} = R_{MT}^{Fe} = 2.05$ a.u., and $R_{MT}^{Al} = R_{MT}^{Ga} = 1.93$ a.u. The maximum l value in the expansion of the crystal potential and electron density within muffin-tin spheres is $l = 10$. The cut-off parameter is $RK_{MAX} = 7$ for the plane waves in a Fourier expansion of potential in the interstitial region. The Brillouin zone sampling was performed according to the Monkhorst–Pack scheme [32] and for k-space integration, a $(24 \times 24 \times 24)$ mesh was used resulting in $413\,k$ points of the irreducible part in the Brillouin zone.

3. Results and discussion

Spin-polarized total energies were calculated as a function of lattice constant for all the six bulk compounds Co_2XY (X = Cr, Mn, Fe; Y = Al, Ga) and were fitted to the Birch equation of state [33] to obtain the basic ground state properties. The calculated lattice constants, bulk modulus of all the six compounds are tabulated in Table 1. Comparing with the experiments, the minimum error in the lattice constant is 0.43% found for Co_2CrAl and the maximum is around 1.5% for Co_2CrGa.

3.1. *Electronic properties (band structure and density of states)*

Spin-polarized band structure within the GGA scheme for all the six Co_2XY (X = Cr, Mn, Fe; Y = Al, Ga) compounds were analyzed. The minority and majority spin-band structure of representative compounds Co_2CrAl, Co_2CrGa, and Co_2MnAl are shown in Figure 1. The lowest valence bands in both the majority and minority spin states are mainly due to the "s" electrons of Y(Al, Ga) atom that are well separated from the other states and remains unaffected by the exchange interaction between the two transition metals Co and X (Cr, Mn, Fe). The bands lying close to the Fermi level are the ones arising from the hybridization of Co "d" states and X
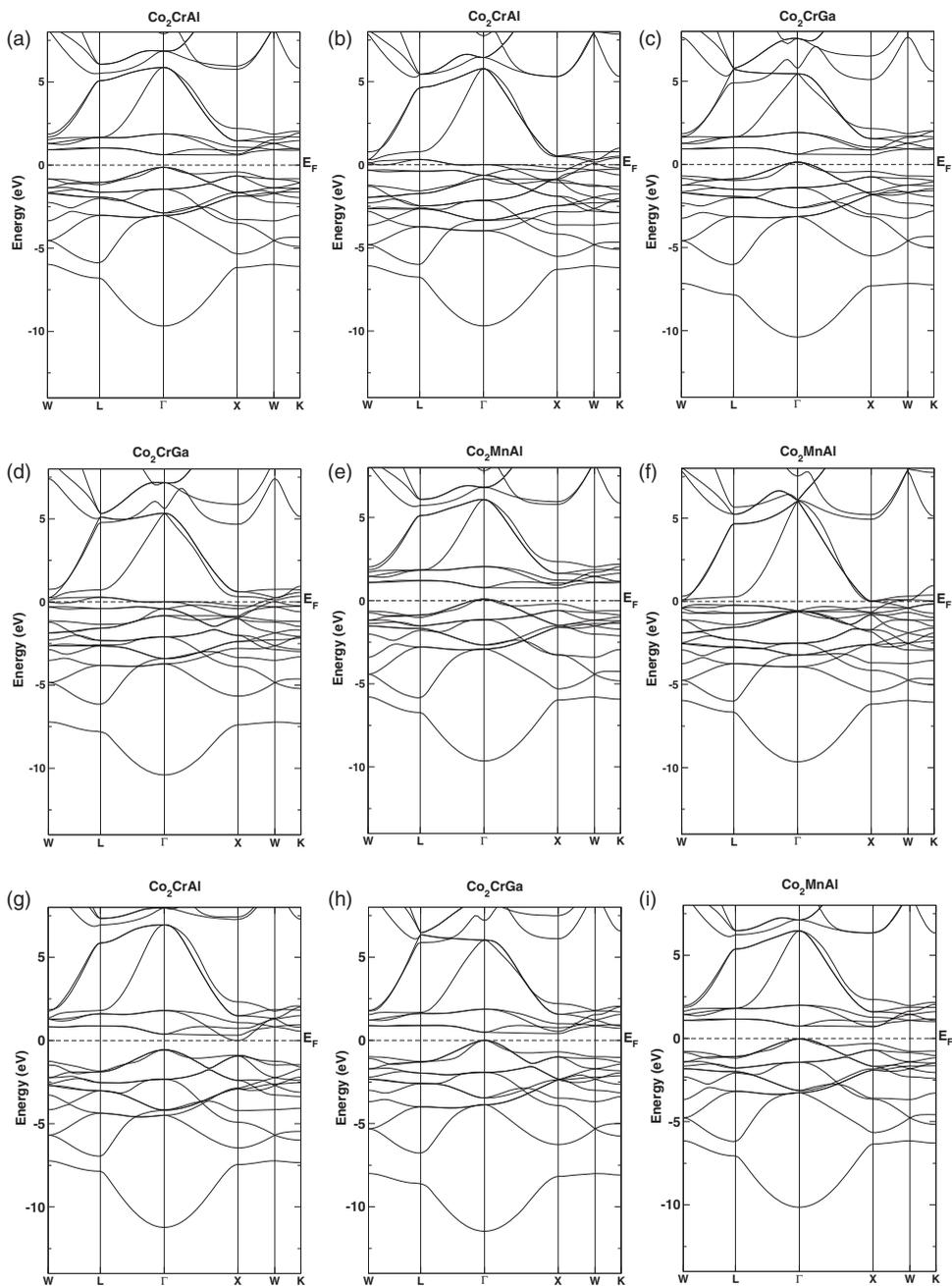
Figure 1. (a), (c), (e) minority spin-band structure for Co_2CrAl, Co_2CrGa, Co_2MnAl (b), (d), (f) majority spin-band structure for Co_2CrAl, Co_2CrGa, Co_2MnAl, (g) minority spin-band structure of Co_2CrAl at half-metal to metal transition, (h) minority spin-band structure of Co_2CrGa at nearly half-metal to half-metal transition and (i) minority spin-band structure of Co_2MnAl at nearly half-metal to half-metal transition.

Figure 2. Conduction band minimum (CB_{min}) and valence band maximum (VB_{max} of minority spin for Co_2XY ($X = Cr$, Mn, Fe; $Y = Al$, Ga) as a function of pressure.
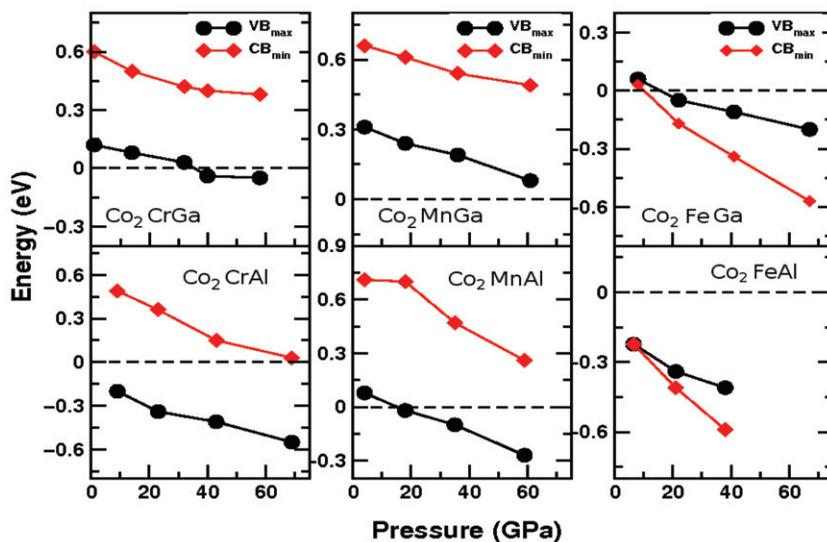
"d" states, including a small contribution from the "p" states of X atom. The majority spin-band structure is strongly metallic. In Co_2CrAl, the minority spin-band structure is such that, there is a gap at the E_F, leading to a HM behavior as shown in Figure 1a, and compares with the band structure calculation of Ming Zhang et al., who claim Co_2CrAl to be HM [34]. The rest of the compounds are found to be nearly half-metallic (NHM). It is interesting to note that under pressure there is a downward shift of conduction bands at "X-point" close to the Fermi level for minority spin, which leads to the metallic nature in Co_2CrAl as shown in Figure 1g. The pressure required to achieve this metallicity is predicted to be around 75 GPa for Co_2CrAl. A different transition from NHM to HM state is also visualized in Co_2CrGa and Co_2MnAl, around 40 GPa and 18 GPa, respectively, and this is mainly due to the downward shift of the VB_{max} at Γ-point under pressure, which is evident from Figures 1h and 1i. The rest of the compounds remain metallic at ambient and even at high pressure. The variation of VB_{max} and CB_{min} clearly shows the metallic nature of these compounds, as shown in Figure 2. Recently, a similar transition (from HM to Metal (M)) has been observed in Co_2MnSi at 70 GPa [28]. The important point is that overall shape of the band structure for both the majority and minority spin states do not change much with increasing pressure. The effect of pressure can be better understood with the electronic density of states. The total and the spin-resolved partial density of states of Co_2CrAl, Co_2CrGa, and Co_2MnAl at the transition (HM to metal in Co_2CrAl and NHM to HM in Co_2CrGa, and Co_2MnAl) is shown in Figure 3. The main contribution to the DOS comes from the 3d states of Co and X atoms. The HM nature in these compounds mainly results from the minority spin gap induced by the Co "d" states due to crystal field splitting. The calculated minority spin gap is found to be 0.17 eV in Co_2CrAl, in comparison with the 0.18 eV observed by Block et al. [35] and for Co_2CrGa and
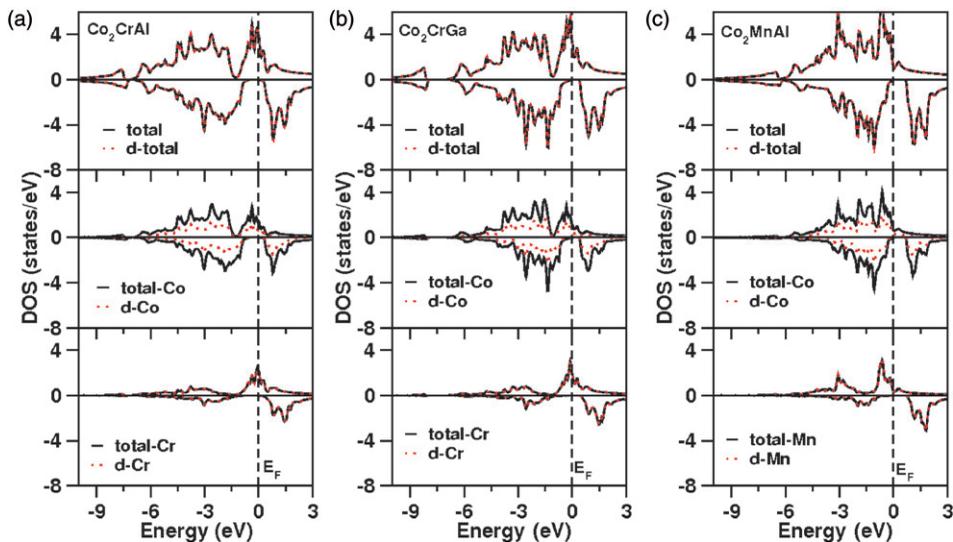
Figure 3. Density of states (DOS) of Co_2CrAl (a), Co_2CrGa (b), and Co_2MnAl (c) at equilibrium lattice constant.

Co_2MnAl it is $0.42\,eV$ and $1.9\,eV$, respectively. Under pressure there is a slight reconstruction of the minority spin states leading to the shift in the Fermi level, resulting in the above-mentioned transition. In Co_2FeAl the conduction band minimum is well below the Fermi level at ambient and upon compression, it still shifts downwards and no question of half-metallicity arises, as evident from Figure 2. Apart from analyzing the changes brought about by varying X (X = Cr, Mn, Fe), we also tried to change the main group element Al to Ga and we find HM nature in Co_2CrGa under pressure as mentioned above. But for Co_2MnGa, it is metallic till $87\,GPa$ and is again evident from Figure 2. In Co_2FeGa, though the conduction band minimum is above E_F, the valence band maximum has crossed the E_F and is positioned above the conduction minimum. So there is a simultaneous downward shift of valence band maximum and conduction band minimum upon compression and the conduction band minimum crosses the E_F and realizing half-metallicity in this compound is thus ruled out, which can be again seen in Figure 2.

3.2. *Pressure effect on the magnetic properties*

The calculated total magnetic moments of all the six compounds and the atom-specific magnetic moments are tabulated in Table 2, along with the experimental comparisons for the total magnetic moments. Our calculations show that Co_2CrAl has local magnetic moment of $0.82\,\mu_B$ on Co and $1.44\,\mu_B$ on Cr. The exchange interaction between the Co and Cr atoms are found to be ferromagnetic leading to a total magnetic moment of $3.0\,\mu_B$, at the experimental lattice constant ($a = 5.73\,\text{Å}$). The calculated moments of all the other compounds are also in good agreement with the experimental values and obey the Slater–Pauling rule [36,37], which scales with

Table 2. Calculated and experimental values of total and partial magnetic moments (in μ_B) of Co_2XY compounds.

Compounds	Total magnetic moment		Partial magnetic moment		
	Experiment	Calculated	Co	(X)	(Y)
Co_2CrAl	1.55[a]	3.00 3.00[b]	0.82	1.44	−0.038
Co_2CrGa	3.01[a]	3.028 3.05[b]	0.78	1.50	−0.029
Co_2MnAl	4.04[a]	4.03 4.04[b]	0.80 0.85	2.57	−0.045
Co_2MnGa	4.05[a]	4.11 4.12[b] 4.09[c]	0.79 0.76[c]	2.60 2.75[c]	−0.034 −0.08[c]
Co_2FeAl	4.96[a]	4.99 4.98[b] 5.00[c]	1.23 1.24[c]	2.74 2.78[c]	−0.038 −0.08[c]
Co_2FeGa	5.08[a]	5.02 5.02[b]	1.22	2.76	−0.028

Notes: [a]Experimental values for magnetic-moment are taken from [19] and the additional references reported therein.
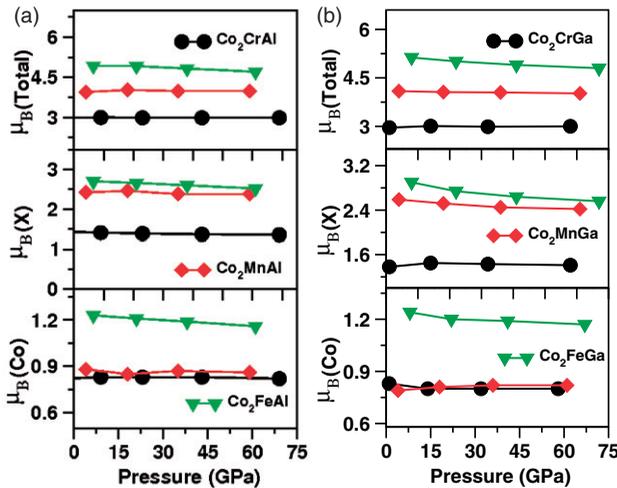[b]Ref [19].
[c]Ref [38]

Figure 4. (a) Variation of magnetic moment under pressure for Co_2X (Cr, Mn, Fe) Al and (b) for Co_2X(Cr, Mn, Fe) Ga.

the number of valence electrons. According to this rule $M_t = Z_t - 24$, where M_t is total magnetic moment in μ_B per unit cell and Z_t is total number of valence electrons per unit cell. As shown in Table 2, the non-integer magnetic moments observed in all these compounds leads to low-spin polarization at the Fermi level. The variation of total magnetic moment with pressure is plotted in Figure 4, along with the local

moments at Co and X site. It can be clearly seen that total magnetic moment decreases with pressure. It is also evident that the major contribution to the magnetic moment comes from the transition metal other than Co in all the six compounds. The magnetic moment of Y in all the compounds is found to increase under pressure. But the magnetic moment of Co increases for Co_2MnGa and it decreases for rest of the compounds under pressure. It can be seen that Co_2CrAl has an integer magnetic moment at ambient and both Co_2CrGa and Co_2MnAl has an integer magnetic moment after undergoing a transition from NHM state to HM state at around 40 and 18 GPa. Though the pressure required for the above-mentioned transition is in the range of 50–60 GPa or higher, not much changes occur in the band structure, which accounts for the structural stability of these $L2_1$ compounds.

4. Conclusions

The structural, electronic, and magnetic properties of Co_2XY (X = Cr, Mn, Fe; Y = Al, Ga) were studied by density functional calculations at ambient as well as at elevated pressures. The GGA calculated structural parameters are in good agreement with the experimental values. The half-metallicity is achieved for Co_2CrAl at ambient pressure, while for Co_2CrGa and Co_2MnAl the same is achieved at 40 GPa and 18 GPa, respectively. In the case of Co_2MnGa, it is metallic till 87 GPa ($V/V_0 = 0.76$). But for Co_2FeAl and Co_2FeGa the half-metallicity is not observed even at high pressures. The electronic structure of these system are largely determined by the hybridization of d-electronic states of Co and X (Cr, Mn, Fe). The general characteristics of energy band structure are maintained with increase in pressure, and there is a slight reconstruction of the minority spin states with a shift in the Fermi level driving the above-mentioned transition.

References

[1] W. Pickett, Phys. World 11 (1998) p.22.
[2] K. Endo, T. Phayama and R. Kitamura, J. Phys. Soc. Jpn. 19 (1964) p.1494.
[3] J. Dong, L. Chen, C. Palmstrom, R. James and S. McKernan, Appl. Phys. Lett. 75 (1999) p.1443.
[4] A.A. Ayuela, J. Enkovaana, K. Ullakko and R.E. Nieminen, J. Phys. Condens. Matter 11 (1999) p.2017.
[5] V. Godlevsky and K. Rabe, Phys. Rev. B 63 (2001) p.134407.
[6] A.A. Ayuela, J. Enkovaara and R. Nieminen, J. Phys. Condens. Matter 14 (2002) p.5325.
[7] R.A. deGroot, F.M. Muller, P.G. van Engen and K.H.J. Buschow, Phys. Rev. Lett. 50 (1983) p.2024.
[8] V.Yu. Irkhin and M.I. Katsnelson, Usp. Fiz. Nauk 164 (1994) p.705.
[9] I. Zutic, J. Fabian and S.D. Sarma, Rev. Mod. Phys. 76 (2004) p.323.
[10] B. Dieny, V.S. Speriosu, S.S.P. Parkin, B.A. Gurney, D.R. Wilhoit and D. Mauri, Phys. Rev. B 43 (1991) p.1297.
[11] G. Schmidt, D. Ferrand, L.W. Molenkamp, A.T. Filip and B.J. Van Wees, Phys. Rev. B 62 (2000) p.R4790.
[12] R. Fiederling, M. Keim, G. Reuscher, W. Ossan, G. Schmidt, A. Waag and L.W. Molenkamp, Nature (London) 402 (1999) p.787.

[13] Y. Ohno, D.K. Young, B. Beschoten, F. Matsukura, H. Ohno and D.D. Awschalom, Nature (London) 402 (1999) p.790.

[14] I. Galanakis, P.H. Dederichs and N. Papanikolaou, Phys. Rev. B 66 (2002) p.174429.

[15] I. Galanakis, P.H. Dederichs and N. Papanikolaou, Phys. Rev. B 66 (2002) p.134428.

[16] I. Galanakis and Ph. Mavopoulos, J. Phys. Condens. Matter 19 (2007) p.315213.

[17] P.J. Brown, K.U. Neumann, P.J. Webster and K.R.A. Ziebeck, J. Phys. Condens. Matter 12 (2000) p.1827.

[18] S. Wurmehl, G.H. Fecher, H.C. Kandpal, V. Ksenofentov, C. Felser, H.J. Lin and J. Morais, Phys. Rev. B 72 (2005) p.184434.

[19] H.C. Kandpal, G.H. Fecher and C. Felser, J. Phys. D Appl. Phys. 40 (2007) p.1507.

[20] T. Block, C. Felser, G. Jakob, J. Ensling, B. Muhling, P. Gutlich, V. Beaumont, F. Studer and R.J. Cava, J. Solid State Chem. 176 (2003) p.646.

[21] S.C. Lee, T.D. Lee, P. Blaha and K. Schwarz, J. Appl. Phys. 97 (2005) p.10c307.

[22] M.C. Hickey, A. Husmann, S.N. Holmes and G.A.C. Jones, J. Phys. Condens. Matter 18 (2006) p.2897.

[23] S. Picozzi, A. Continenza and A.J. Freeman, Phys. Rev. B 66 (2002) p.094421.

[24] X.-Q. Chen, R. Podloucky and P. Rogl, J. Appl. Phys. 100 (2006) p.113901.

[25] H.C. Kandpal, C. Felser and G.H. Fecher, J. Magn. Magn. Mater. 310 (2007) p.1626.

[26] S.T. Weir, Y.K. Vohra and A.L. Ruoff, Phys. Rev. B 35 (1987) p.874.

[27] V. Kanchana, G. Vaitheeswaran and M. Rajagopalan, J. Alloys. Compds. 359 (2003) p.66; V. Kanchana, G. Vaitheeswaran and M. Rajagopalan, Physica B 328 (2003) p.283.

[28] G. Gkoglu and O. Glseren, Eur. Phys. J. B 76 (2010) p.321.

[29] P. Blaha, K. Schwarz, P. Sorantin and S. Tricky, Comput. Phys. Commun. 59 (1990) p.399.

[30] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka and J. Luitz, WIEN2K, in *An Augmented plane Wave Plus Local Orbitals Program for Calculating Crystal Properties*, K. Schwarz, ed., Wien Technical University, Vienna, Austria, 2001.

[31] J.P. Perdew, K. Burke and M. Ernzernhof, Phys. Rev. Lett. 77 (1996) p.3865.

[32] H.J. Monkhorst and J.D. Pack, Phys. Rev. B 13 (1976) p.5188.

[33] F. Birch, J. Geophys. Res. 83 (1978) p.1257.

[34] M. Zhang, Z.H. Liu, H.N. Hu, G.D. Liu, Y.T. Cui, J.L. Chen, G.H. Wu, X.X. Zhang and G. Xiao, J. Magn. Magn. Mater. 277 (2004) p.130.

[35] T. Block, M.J. Carey, B.A. Gurney and O. Jepsen, Phys. Rev. B. 70 (2004) p.205114.

[36] J.C. Slater, Phys. Rev. 49 (1936) p.931.

[37] L. Pauling, Phys. Rev. 54 (1938) p.899.

[38] S.E. Kolkova, S.S. Kolkov and A.V. Subashiev, Comput. Mater. Sci. 36 (2006) p.249.