Electronic structures and magnetocrystalline anisotropy energies of ordered $Co_{1-x}Ni_x$ alloys: a first principles study*

Zhang Sha(张 莎), Pang Hua(庞 华)†, Fang Yang(方 阳), and Li Fa-Shen(李发伸)

Institute of Applied Magnetics, Lanzhou University, Lanzhou 730000, *China*

(Received 17 May 2010; revised manuscript received 18 June 2010)

The electronic structures and magnetocrystalline anisotropy (MA) of ordered hexagonal close-packed (hcp) $Co_{1-x}Ni_x$ alloys are studied using the full-potential linear-augmented-plane-wave (FLAPW) method with generalized gradient approximation (GGA). Great changes of magnetocrystalline anisotropy energy (MAE) are gained with different Ni compositions. Also, in-plane magnetocrystalline anisotropy is obtained for $Co_{15}Ni$ in which the Snoek's limit is exceeded. It is found that the changes of the symmetry of the crystal field on Ni induce small variations in band structures around the Fermi level under different compositions, which plays an important role in modulating the magnetization direction, where the hybridization between Co-3d and Ni-3d orbits is of special importance in deciding the magnetocrystalline anisotropy of itinerant states. The rigid-band model is inapplicable to explain the evolution of magnetocrystalline anisotropy energy with Ni composition, and it is also inadequate to predict the magnetocrystalline anisotropy energy through the anisotropy of the orbital magnetic moment.

Keywords: first principles, anisotropy, electronic structures

PACC: 7115M, 7530G, 7125

1. Introduction

Transition metals and alloys are widely used magnetic materials and their electronic structures remain a subject of discussion.[1] Several theoretical models have been proposed, such as the rigid-band model and the virtual-bound-state model. The former makes no distinction between the different constituents of the alloy and attributes a common band to all electrons,[1,2] while the later assumes screening of the host electrons at the site of the impurity.[1] However, neither of these two limiting models can fully describe the actual situation. And till now, no mechanism is universal for understanding the electronic structures of transition-metal alloys, which activates further research interests in itinerant states and related properties.

The MA is one of the ground-state properties and is highly related to the band structures.[3,4] Nowadays research interests are focused on modulating the direction and stiffness of the magnetization.[5−7] There have been many studies on the physical origin of MA in transition-metal alloys and the modulations of MA in these materials by doping, alloying and low-dimensional magnetism.[7−11] To the best of our knowledge, there are few reports about the electronic structures of hcp $Co_{1-x}Ni_x$ ($x < 0.25$) alloys, though the face-centered cubic (fcc) CoNi alloys have been extensively investigated.[12,13] In K. Hara's report,[14] the MA of hcp $Co_{1-x}Ni_x$ alloys changes with the Ni composition and the easy magnetization direction turns into the basal plane in some composition range. In this work, the first principles calculations of the electronic structures and the MAE of ordered hcp $Co_{1-x}Ni_x$ alloys are systematically studied. Investigation is focused on the mechanism of spin-reorientation in hcp $Co_{1-x}Ni_x$ alloys with changing Ni composition.

2. Computational method

All calculations performed in this work were based on the density-functional theory (DFT) using the FLAPW method, while the GGA was employed for the exchange–correlation potential.[3] The band states and the core-level states were treated with scalar-relativistic effects and fully relativistic effects, respectively. The muffin-tin (MT) radii $R_{\rm MT}$ were chosen to be 2.2 a.u. for Co as well as Ni. The potential and

*Project supported by the National Natural Science Foundation of China (Grant Nos. 10774061 and 10975066).

†Corresponding author. E-mail: hpang@lzu.edu.cn

© 2010 Chinese Physical Society and IOP Publishing Ltd

the charge density in the MT-spheres were expanded in the spherical harmonics with $l_{\max} = 10$.[3,15] The plane-wave cutoff parameter $R_{\mathrm{MT}}K_{\max}$ was 7.0 and the magnitude of the largest vector $G_{\max}$ was 12.0.

The hcp Co was built and the c axis was set as the z axis of Cartesian coordinates. Then the volume and lattice parameters were optimized. Based on the optimized parameters, the model systems of Co_3Ni, Co_7Ni, $Co_{15}Ni$ and $Co_{31}Ni$, corresponding to $x = 0.25$, 0.125, 0.0625, 0.03125, respectively, were founded according to the standard super-cell approach. There are several possible structures for each system, from which the one with the lowest energy was selected. Usually, the structure with optimized energy also has the highest symmetry. Then, the volume and lattice parameters of the selected structures were optimized and the atomic positions in each system were fully relaxed until the force on each atom was smaller than 5.0 mRy/a.u. The optimized lattice parameters are displayed in Fig. 1(a). As the MAE is crucially dependent on the details of the Brillouin zone (BZ) integration,[3,16,17] it is important to insure the convergence of the MAE with respect to the number of k-points. We tested the number of k-points for each model system and found that 24000, 8000, 5000, 800 and 400 k-points are enough for Co, Co_3Ni, Co_7Ni, $Co_{15}Ni$ and $Co_{31}Ni$ systems, respectively.

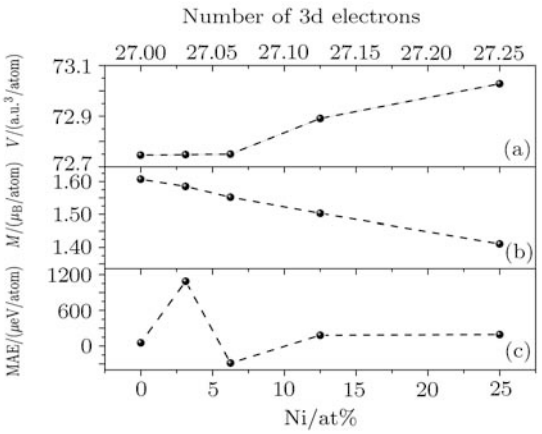


Fig. 1. The equilibrium volume (a), the spin moment in MT-sphere (b) and the MAE per atom (c) plotted as the functions of Ni content (bottom scale) or the average number of 3d electrons per atom (top scale).

There are two well-known approaches to calculate the MAE from first principles calculation.[4,6,10,18] One is to calculate the difference in total energies between two different magnetization directions.[6,15] The other is based on the force theorem, from which the change in total energy upon inclusion of the spin–orbit (SO) coupling is given by the change in the single-particle eigenvalues.[4] According to this theorem, one can start from the same converged density without SO coupling, and then perform a one step iterative including SO coupling for the two different magnetization directions n_1 and n_2. MAE is defined as: $\Delta E_1 \approx \sum_i^{\mathrm{occ}} \varepsilon_i(n_1) - \sum_i^{\mathrm{occ}} \varepsilon_i(n_2)$,[4] where ε_i denotes the eigenvalue, and the sum runs through all occupied states. The MAE in $Co_{15}Ni$ system was calculated using both methods. The results give the same direction of the easy axis and the same order of magnitude of MAE. Therefore the force theorem was employed to calculate the MAE in this work except for the pure Co system. Considering that magnetization in the basal-plane will lower the symmetry of the structure, we chose the same lowest symmetry group for all calculations including SO coupling to eliminate systematic errors.

3. Results and discussion

3.1. Magnetic moment

The main results of the present calculations are listed in Fig. 1, where the equilibrium volume, the spin moment in MT-sphere and the MAE per atom is plotted as the functions of composition (bottom scale) or the average number of 3d electrons per atom (top scale). Obviously, the variation of the lattice constant with composition is nonlinear. But the average magnetic moment obtained at the theoretical equilibrium volume does follow a linear variation with composition. This observation represents the experimental results in trend,[14] and also matches the prediction of Slater–Pauling curve that the moment decreases linearly with increasing average d occupation for the latter transition-metal alloys.[19] Thereby, the energy band-filling effects play a dominate role in deciding the magnetic moment.

To further understand the electronic structures, we calculated the total electronic densities of states (DOS) and the Ni-DOS for all systems. As shown in Fig. 2, the majority spin states are fully occupied and the DOS profiles for all systems are very similar to each other. For minority spin, the addition of Ni shifts the states to lower energies compared with pure Co. This observation explains the decreasing trend of the moment with band-filling and implies that the

rigid-band model is adequate in describing the magnetic moment of ordered hcp $Co_{1-x}Ni_x$ alloys.

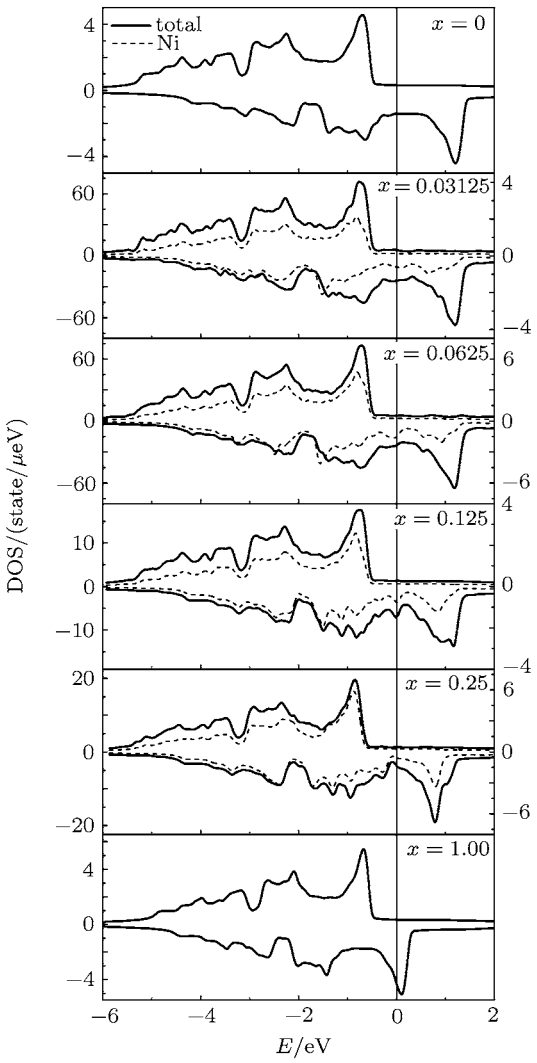


Fig. 2. Total DOSs and Ni-DOSs for hcp $Co_{1-x}Ni_x$ alloys. The positive direction stands for the majority spin states, while the negative direction stands for the minority spin states. The Fermi level is indicated with a vertical line.

It is found that the profiles of the total DOS are quite similar to that of the Ni for all systems, which means strong sharing of electrons by Co and Ni constituents. The local magnetic moment supports this suggestion. In the present hcp $Co_{1-x}Ni_x$ models, where sphere sizes for Co and Ni are equal, we find the local magnetic moment remains about constant for Ni, whereas it increases for Co. And the moment of Co seems related to the distance to Ni. For example, the moments are about 1.69 μB/atom, 1.68 μB/atom and 1.67 μB/atom for the first, second and third neighbours of Ni in $Co_{31}Ni$ system, respectively.

Compared with the case of pure Co, the DOS profiles of minority spin states change slightly, especially around the Fermi level (E_f) in hcp $Co_{1-x}Ni_x$ alloys. What is more, the features of the Ni-DOS well represent those of the total DOS around the E_f, implying that the electronic distribution of Ni attributes to the observation. Actually, the local environment of Ni changes with different compositions. For example, the space groups of $Co_{15}Ni$ and $Co_{31}Ni$ are F_{mm2} and C_{mcm}, respectively, quite different from the hexagonal P_{6mmm} of pure Co. The decreasing in the symmetry of the local environments of the dopant induces slight variations of DOS around E_f, which is found to be crucial in determining the MA of these systems, as discussed below.

3.2. MAE

MA is a property close related to the details of the band structures, especially those near the Fermi energy.[4] In the present paper, MAE is calculated as: $\Delta E_1 \approx \sum_i^{occ} \varepsilon_i^{[1100]} - \sum_i^{occ} \varepsilon_i^{[0001]}$, thus systems with negative ΔE_1 have in-plane MA while those with positive ΔE_1 have uniaxial MA. The MAE for each model system is shown in Fig. 1(c). Obviously, the composition of Ni greatly affects the magnetization direction in hcp $Co_{1-x}Ni_x$ alloys. For pure Co, the calculated MAE 56 μeV/atom agrees well with the experiments.[15,20] When the system diluted doped with Ni, such as $Co_{31}Ni$, it shows much enhanced uniaxial anisotropy. When the percentage of Ni increased to 6.25%, the magnetization turns to the basal plane. With further increasing of the Ni content, the easy axis turns back to the c axis and the values of MAE tend to be steady. Both Co_3Ni and Co_7Ni belong to this situation. The calculated variation trend of MAE with Ni composition is consistent with the experimental reports.[14]

To see how well the dependence of MAE on Ni composition fits the prediction of rigid-band model, we calculated the MAE of each model system as a function of band filling q (number of valence electrons), and the results are shown in Fig. 3, where $\Delta q = 0$ corresponds to the Fermi level. Clearly, the evolutions of MAE with Δq are quite different for the four model systems, indicating that the MAE cannot be expected by simply shifting the band filling in hcp $Co_{1-x}Ni_x$ alloys. This observation strongly supports that small variations in the minority spin states induce large variations in MAE because the MAE is highly sensitive to the details of the band structures near the Fermi level.

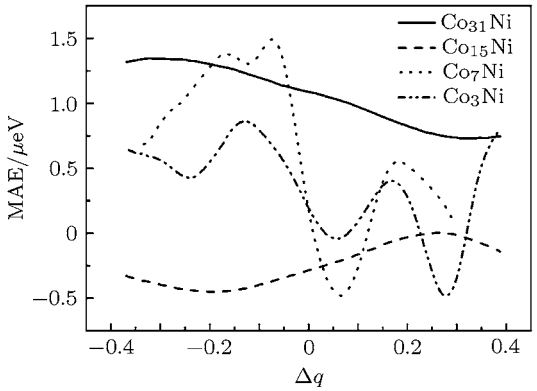


Fig. 3. Dependence of total MAE on band filling Δq in hcp $Co_{1-x}Ni_x$ alloys, where the Fermi energy corresponds to $\Delta q = 0$.

In transition metal alloys, the microscopic origin of MA can be attributed to the SO interaction of 3d electrons from which the energy gain is proportional to the dot product of spin moment and orbital moment $\boldsymbol{S} \cdot \boldsymbol{L}$.[4,21,22] Bruno put forward that in the limit of strong exchange splitting, the MAE is proportional to the anisotropy of the orbital magnetic moment $\Delta M_l (= M_{l[1100]} - M_{l[0001]})$.[23] This relationship is proved to be quite successful in understanding the origin of MA in alloys with local band structures, such as 3d–4f compounds.[16,17,21] But the predicted MAE values according to this method disagree with the results from force theorem for all the present supercells. We suggest that the anisotropy in the spin moment and its correlation with the orbital moment should be taken into account in deciding MAE for materials with itinerate states. It is found that the hybridization between the Co-3d and Ni-3d states is of special importance in introducing MA in hcp $Co_{1-x}Ni_x$ alloys. For example, calculations of MAE with the SO coupling on Ni site switched off yield strongly reduced MAE in $Co_{31}Ni$, great enhanced MAE in Co_7Ni, and nearly zero MAE in $Co_{15}Ni$. Same thing happens for FePt and CoPt alloys.[9,23]

We then turn to the electronic structures of each system to understand the origin of MAE in hcp $Co_{1-x}Ni_x$ alloys. As discussed above, each supercell has distinct space group hence the symmetry of the crystal field on Ni is different, which results in slightly different spatial distributions of Ni-3d states. We count the electron occupation numbers of 3d orbits in the R_{MT} radii of Ni and its neighbour Co sites before SO coupling was included. With increasing composition, the occupation numbers of Ni-3d states decrease, indicating that Ni-3d states tend to be more delocalized in space, which benefits the interactions between neighbour atoms. Compared with $\mathrm{d}z^2$ and $\mathrm{d}x^2y^2 + \mathrm{d}xy$ orbits, the changes in the occupation of $\mathrm{d}xz + \mathrm{d}yz$ orbit are more pronounced for both Ni-3d states and Co-3d states. Further investigations reveal that the redistributions of the electronic structures are spatially staggered. Take the situation in $Co_{15}Ni$ as an example. Compared with $Co_{31}Ni$, the occupation number of Ni-$\mathrm{d}xz + \mathrm{d}yz$ states increases, while the occupation number of Co1-$\mathrm{d}xz + \mathrm{d}yz$ (Co1, Co2 are the first and second nearest neighbours of Ni, and so on.) states decreases. For Co2 site, the $\mathrm{d}xz + \mathrm{d}yz$ states are the most occupied. As to sites further away, the influence from the dopant is weak and the electronic structures gradually tend to those of the bulk Co. What is more, the redistribution of electrons is spin-polarized. For example, the decreasing numbers of the minority spin states overcome that of the majority states of Ni-3d electrons. In this manner, the electrons can minimize the Coulomb energy and further influence the magnetization.

We then try to clarify the atomic origin of the MAE. Following Ref. [9], the contribution from atom i can be approximated as: $\Delta E_i \approx E_i^{[1100]} - E_i^{[0001]}$, and $E_i^n = \int_{-\infty}^{E_{\mathrm{f}}} N_i^n(\varepsilon)\mathrm{d}\varepsilon$, where N_i is the atom projected number of states and E_{f} is the average Fermi energy of the two magnetization directions n. The results are listed in Table 1. The situation of the Co_3Ni is quite similar to that of the Co_7Ni and not shown here.

Table 1. The averaged atomic MAE of Ni and its near neighbour Co sites calculated from atomic MAE for each model system.

MAE/(meV/atom)	Co1	Co2	Co3	Co4	Co5	Ni
$Co_{31}Ni$	0.739	1.288	0.304	1.479		0.096
$Co_{15}Ni$	–1.343	–0.417	–0.595	1.057	0.691	–3.006
Co_7Ni	1.981	–2.867	4.807			0.672

The magnetization of Ni is along the c axis except that in $Co_{15}Ni$. The individual Co site contributions to the MA are different in the four model systems. In $Co_{31}Ni$, the average values of MAE are positive for all neighbour Co sites of Ni hence induce large uniaxial anisotropy. In $Co_{15}Ni$ alloy, the three nearest neighbour sites show negative values of MAE, among which the contribution from the Co1 site is the most. Though the fourth and the fifth neighbour sites provide un-neglectable positive MAE values, the total MAE of the system is negative. In Co_7Ni system, the Co1 site and Co3 site, which are in the same xy-plane without Ni, show positive MAE, while the Co2 site, which is in the plane with Ni, provides negative MAE. The same thing happens in Co_3Ni system, except that the average MAE value for each site is slightly different.

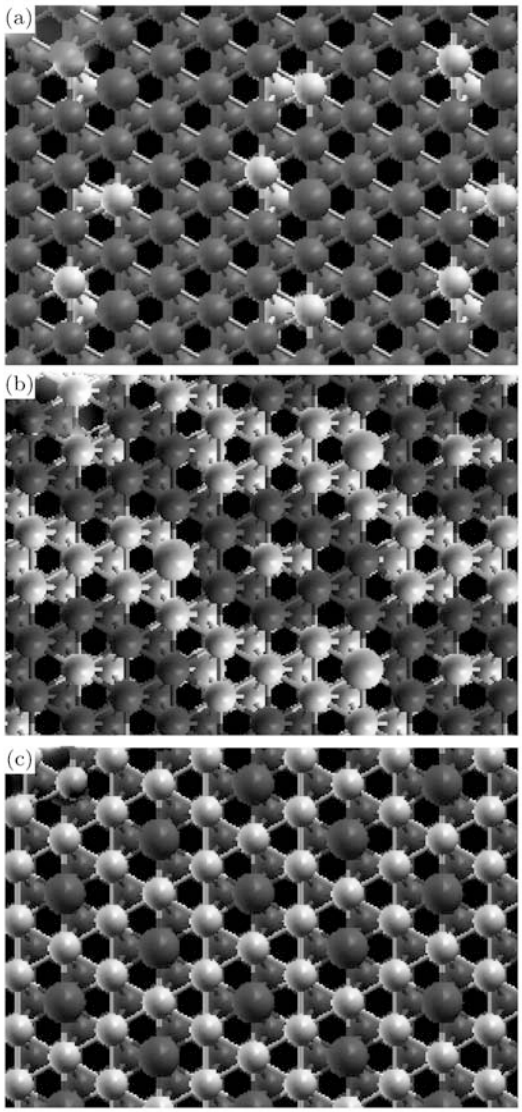


Fig. 4. The spatial distribution of atomic MAE for $Co_{31}Ni$ (a), $Co_{15}Ni$ (b) and Co_7Ni (c) model systems.

Based on the above discussion, we display the spatial distributions of atomic MAE, as shown in Fig. 4. To make it clear, more than one unit cell are depicted. The larger balls denote the Ni atoms while the smaller ones are Co atoms. Atoms with positive MAE values are dark grey, and those with negative MAE values are light grey. Clearly, the competition between these two kinds of atoms decides the magnetization direction of the supercell.

With increasing composition of Ni, the evolutions in the spatial distributions of the atomic MAE are quite interesting. For small composition, such as $Co_{31}Ni$, one Co1 atom and one of its first nearest neighbour of Co2 atom form a cluster with negative MAE. Since the dopant is far away from each other, the clusters are isolated and embeded in the Co matrix. The enhanced uniaxial MAE has also been found in FeCo and CoPt alloys with small content of Co.[5,11,17] From our observation, it seems that the existence of isolated clusters with negative MAE enhances the uniaxal anisotropy of the matrix Co atoms, hence results in large uniaxial MA in diluted doped hcp $Co_{1-x}Ni_x$ supercell. In $Co_{15}Ni$ system, the atoms with negative MAE increase and join together along the [1100] crystalline direction, for the nearest distance between the Ni atoms is across this direction. While the atoms with positive MAE distribute like connected circles stretched along the [1100] direction. In Co_7Ni, the Ni atoms are so close to each other that they correlate strongly. Now the atoms with different signs of MAE are layer-distributed, that is, the layers with Ni atom show negative MAE, while those without Ni atom show positive MAE.

To some extent, the evolutions of spatial distributions of atomic MAE with increasing Ni composition resemble the nucleation and grow up processes of first-order phase transitions. The clusters with negative MAE form around Ni site. With increasing composition, the clusters grow up, merge with each other and finally form layers intersected by the matrix atoms with positive MAE. Our observation suggests that the formation and correlation among the atoms with negative MAE decide the magnetization direction of the supercells where the hybridization between the Ni-3d and Co-3d states is dominant.

At the end of this report, we briefly discuss the possibility of $Co_{15}Ni$ as a potential magnetic material with high permeability at high frequencies. As discussed above, the $Co_{15}Ni$ system has in-plane anisotropy. According to the bi-anisotropy pic-

ture, for a bulk polycrystalline material with in-plane anisotropy, the static permeability μ_s and the ferromagnetic resonance frequency f_r fit the function[24]

$$(\mu_s - 1)f_r = \frac{\gamma}{2\pi} M_s \sqrt{\frac{H_{a1}}{H_{a2}}},$$

where M_s is the saturation magnetization, H_{a1} and H_{a2} are the effective anisotropy fields when the magnetization deviates from the easy axis in the hard plane and rotates in the easy plane, respectively.[25] We then calculated the MAE in the basal plane according to $\Delta E_2 \approx \sum_i^{occ} \varepsilon_i([1100]) - \sum_i^{occ} \varepsilon_i([1\bar{1}00])$. The calculated ΔE_2 is 17.98 μeV/atom, from which one obtains $\sqrt{H_{a1}/H_{a2}} = \sqrt{\Delta E_1/\Delta E_2} \approx 4$. Obviously, the value of $(\mu_s - 1)f_r$ is four times larger than $(\gamma/2\pi)M_s$, exceeds the Snoek's limit.[24,26]

4. Conclusions

This paper presents a first principles study on the electronic structures and MAE of ordered hcp $Co_{1-x}Ni_x$ alloys by FLAPW method. The DOS shows that the rigid-band model is adequate in describing the magnetic moment, but inapplicable to predicate the MAE of itinerant states in this system. Meanwhile, the MAE cannot be simply ascribed to the anisotropy of the orbital magnetic moment. Further investigations of the electronic structures indicate that, due to the changes of the symmetry of the crystal field on Ni with different compositions, the redistribution of 3d electrons, especially those close to the Fermi level, and the hybridization between Ni-3d and Co-3d states are dominant in deciding MA in hcp $Co_{1-x}Ni_x$ alloys. The evolutions of spatial distributions of atomic MAE with increasing Ni composition resemble the nucleation and grow up processes of first-order phase transitions. Yet further research is needed to determine whether this mechanism is applicable in other alloys with itinerant d states.

Acknowledgments

The computer resources were provided by Key Laboratory for Magnetism and Magnetic Materials, Ministry of Education, Lanzhou University, China.

References

[1] Hüfner S, Wertheim G K, Cohen R L and Wernick J H 1972 *Phys. Rev. Lett.* **28** 488
[2] Hsieh H H, Chang Y K, Pong W F, Pieh J Y, Tseng P K, Sham T K, Coulthard I, Naftel S J, Lee J F, Chung S C and Tsang K L 1998 *Phys. Rev.* B **57** 15204
[3] Zhu Q X, Pang H and Li F S 2009 *Chin. Phys.* B **18** 2953
[4] Steinbeck L, Richter M and Eschrig H 2001 *Phys. Rev.* B **63** 184431
[5] Wu D X, Zhang Q M, Liu J P, Yuan D W and Wu R Q 2008 *Phys. Rev. Lett.* **92** 052503
[6] Burkert T, Eriksson O, James P, Simak S I, Johansson B and Nordström L 2004 *Phys. Rev.* B **69** 104426
[7] Eastham D A, Denby P M, Harrison A, Kirkman I W and Whittaker A G 2002 *J. Phys.: Condens. Matter* **14** 605
[8] Kuo C C, Lin W C, Chuang S F and Lin M T 2005 *Surf. Sci.* **576** 76
[9] Burkert T, Eriksson O, Simak S I, Ruban A V, Sanyal B, Nordström L and Wills J M 2005 *Phys. Rev.* B **71** 134411
[10] Ravindran P, Kjekshus A, Fjellvåg H, James P, Nordström L, Johansson B and Eriksson O 2001 *Phys. Rev.* B **63** 144409
[11] Gambardella P, Rusponi S, Veronese M, Dhesi S S, Grazioli C, Dallmeyer A, Cabria I, Zeller R, Dederichs P H, Kern K, Carbone C and Brune H 2003 *Science* **300** 1130
[12] Aymard L, Dumont B and Viau G 1996 *J. Alloys Compd.* **242** 108
[13] Turek I and Záděák T 2010 *J. Phys.: Conference Series* **200** 052029
[14] Hara K, Itoh K, Kamiya M, Okamoto K, Hashimoto T and Fujiwara H 1991 *J. Magn. Magn. Mater.* **102** 247
[15] Trygg J, Johansson B, Eriksson O and Wills J M 1995 *Phys. Rev. Lett.* **75** 2871
[16] Enkovaara J, Ayuela A, Nordström L and Nieminen R M 2002 *Phys. Rev.* B **65** 134422
[17] Galanakis I, Alouani M and Dreyssé H 2000 *Phys. Rev.* B **62** 6475
[18] James P, Eriksson O, Hjortstam O, Johansson B and Nordström L 2000 *Phys. Rev. Lett.* **76** 915
[19] Kakehashi Y and Hosohata O 1988 *Journal de Physique Colloques* **49** C8-73
[20] Daalderop G H O, Kelly P J and Schuurmans M F H 1990 *Phys. Rev.* B **41** 11919
[21] Tung J C and Guo G Y 2007 *Phys. Rev.* B **76** 094413
[22] Mokrousov Y, Bihlmayer G, Heinze S and Blügel S 2006 *Phys. Rev. Lett.* **96** 147201
[23] Shick A B and Mryasov O N 2003 *Phys. Rev.* B **67** 172407
[24] Xue D S, Li F S, Fan X L and Wen F S 2008 *Chin. Phys. Lett.* **25** 4120
[25] Wen F S, Qiao L, Zhou D, Zuo W L, Yi H B and Li F S 2008 *Chin. Phys.* B **17** 2263
[26] Yang W F, Qiao L, Wei J Q, Zhang Z Q, Wang T and Li F S 2010 *J. Appl. Phys.* **107** 033913