

Electric-Field-Induced Modification of the Magnon Energy, Exchange Interaction, and Curie Temperature of Transition-Metal Thin Films

M. Oba,¹ K. Nakamura,^{1,*} T. Akiyama,¹ T. Ito,¹ M. Weinert,² and A. J. Freeman³

¹Department of Physics Engineering, Mie University, Tsu, Mie 514-8507, Japan

²Department of Physics, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201, USA

³Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60208, USA

(Received 20 May 2014; revised manuscript received 4 December 2014; published 13 March 2015)

The electric-field-induced modification in the Curie temperature of prototypical transition-metal thin films with the perpendicular magnetic easy axis, a freestanding Fe(001) monolayer and a Co monolayer on Pt(111), is investigated by first-principles calculations of spin-spiral structures in an external electric field (E field). An applied E field is found to modify the magnon (spin-spiral formation) energy; the change arises from the E -field-induced screening charge density in the spin-spiral states due to p - d hybridizations. The Heisenberg exchange parameters obtained from the magnon energy suggest an E -field-induced modification of the Curie temperature, which is demonstrated via Monte Carlo simulations that take the magnetocrystalline anisotropy into account.

DOI: 10.1103/PhysRevLett.114.107202

PACS numbers: 75.70.Ak, 71.20.Be, 73.20.At

Electric-field-induced magnetism in itinerant transition metals has shown promise as a potential approach offering a new pathway to control magnetism at the nanoscale with ultralow-energy power consumption. It was originally reported that the coercivity of thin films of FePt and FePd was reversibly varied by the application of a voltage [1]. Later, the magnetocrystalline anisotropy (MCA) of the 3d transition-metal thin films with MgO interfaces was successfully controlled by a voltage [2–6], thus opening a new avenue towards MgO-based magnetic tunnel junction electronics [6]. It is now agreed that a change in the screening charge density due to the electric field (E field), which causes a small change in band structures around the Fermi energy (E_F), gives rise to the modification of the MCA energy [7–10].

A continuing challenge is an E -field control of the Curie temperature T_C of ferromagnets [11–18]. In diluted ferromagnetic semiconductors such as (Ga,Mn)As and (In,Mn)As, a modification in the carrier density by an applied voltage leads to a change in the T_C [11–13], but with the serious shortcoming that T_C is inevitably less than room temperature. Recently, a small change (~ 12 K) in the T_C with an applied gate voltage was reported experimentally for metal thin Co films (4 Å) [15] where the T_C is around 300–330 K. Further, the very large E field created by the electrolytic double layer formed by a polymer film containing an ionic liquid enhances the change in T_C up to about 100 K [16]. Similar behavior was also suggested for metal thin Fe films from electrolytic double layer experiments [17].

Theoretically, an E -field-induced T_C modification at metal surfaces was proposed based on the surface critical phenomena [19] and the change in the number of electrons N , but the experimental observations for Co/Pt(111)

[15,16] that an increase of N (by a positive E field) tends to increase T_C was the opposite of theoretical prediction [20]. In films with two-dimensional character, a change in the MCA with the perpendicular magnetic easy axis may further drive the T_C modification [21,22]. However, a quantitative understanding of the underlying physics and the mechanism of the E -field-induced T_C modification is still lacking, which hinders a search for other promising thin film candidates.

Here, we demonstrate an E -field-induced T_C modification from first-principles calculations for prototypical transition-metal thin films with perpendicular magnetic easy axis, a freestanding Fe monolayer and a Co monolayer on Pt(111). The results predict that an applied E field modifies the magnon (spin-spiral formation) energy compared to the zero-field value, leading to modification of the Heisenberg exchange parameters.

Calculations were performed using the full-potential linearized augmented plane wave (FLAPW) method [23–25] that treats a film geometry by including fully the additional (nonperiodic) vacuum regions outside of a single slab. This geometry allows the inclusion of an E field along the surface normal with proper boundary conditions [8,26]. For treating spin-spiral structures in an E field, the generalized Bloch theorem [27,28] is introduced into the FLAPW method [29,30]. Self-consistent calculations were carried out in the scalar relativistic approximation based on the local spin density approximation [31] for the freestanding Fe monolayer and the generalized gradient approximation [32] for the Co/Pt. LAPW functions with a cutoff of $|\mathbf{k} + \mathbf{G}| \leq 3.9$ a.u., muffin-tin sphere radii of 2.2 a.u. for the Fe and Co atoms and 2.4 a.u. for the Pt atom, and an angular momentum cutoff of $\ell = 8$ were used. The spin-orbit coupling (SOC), needed to obtain the MCA in an

E field, was included using the second variation method. The uses of 8100 and 3600 special \mathbf{k} points in the full two-dimensional Brillouin zone (BZ) for the freestanding Fe monolayer and the Co/Pt(111), respectively, were confirmed to suppress numerical fluctuations in the spin-spiral formation energy.

For simplicity in discussion, we first present the freestanding Fe monolayer with an in-plane lattice constant of MgO(001) in E fields of 0 and 1 V/Å. The applied E fields, defined at a vacuum region far enough from the surfaces, may be near the maximum expected fields attainable before the dielectric breakdown of high- κ gate insulators in devices [18] such as MgO (dielectric constant is 9.8) and HfO (20). The calculated magnon (spin-spiral formation) energy $E(\mathbf{q})$ relative to the antiferromagnetic state as a function of the spiral wave vector \mathbf{q} along high-symmetry directions is shown in Fig. 1. In zero field, the $E(\mathbf{q})$ in the neighborhood of $\bar{\Gamma}$ increases approximately proportional to the square of \mathbf{q} , characteristic of a ferromagnet. We confirmed that there is almost no change in the magnetic moments ($\sim 3.2\mu_B$) as \mathbf{q} varies. When an E field is applied, $E(\mathbf{q})$ shows the same trend as in zero field, but an E -field-induced modification in $E(\mathbf{q})$ is observed; e.g., along $\bar{\Gamma}$ to \bar{M} , $E(\mathbf{q})$ is modified by a few meV/atom compared to zero field.

The density of states (DOS) for the spin-spiral states with \mathbf{q} along $\bar{\Gamma}$ to \bar{M} illustrate the E -field-induced modification of the band structures, as shown in Fig. 2(a). In zero field, the DOS at $\bar{\Gamma}$ has a wide bandwidth due to its itinerant ferromagnetic behavior. When \mathbf{q} increases, however, the

bandwidth gradually narrows, since the electron hopping to the neighboring atoms, where the spin-up and -down states do not mix, is suppressed due to the spin-spiral rotation. When an E field is applied, two small pseudogaps below and above the E_F (arrows in the figure) appear at $\bar{\Gamma}$, originating from the screening charge density in the E field, as pointed out previously [8]. An important trend can be further discerned: the pseudogaps have a noticeable variation with respect to \mathbf{q} , and tend to disappear when \mathbf{q} is close to \bar{M} . Thus, the screening charge density behaves differently depending on \mathbf{q} , leading to the modification in the magnon dispersion (cf. Fig. 1).

To get a clearer understanding of such screening behavior, the partial DOS projected onto the p_z and d_{z^2} orbitals is presented in Figs. 2(b) and 2(c). In zero field, the p_z and d_{z^2} states at $\bar{\Gamma}$ extend widely above and below E_F . However, the application of an E field causes a p - d hybridization that induces the pseudogap above E_F . The pseudogap below E_F in Fig. 2(a) was confirmed to arise mainly from $p_{x,y}$ - $d_{xz,yz}$ hybridization. As pointed out previously [8], an E field at an atomic site is described by the Y_0^1 spherical harmonic, which couples orbitals with ℓ and $\ell \pm 1$ (e.g., p and d orbitals) and the same magnetic quantum number m . Indeed, the p_z ($m = 0$) orbitals couple to the d_{z^2} states, inducing an energy gap. Similarly, the $p_{x,y}$ ($m = \pm 1$) orbitals couple to the $d_{xz,yz}$ states. As \mathbf{q} moves away from

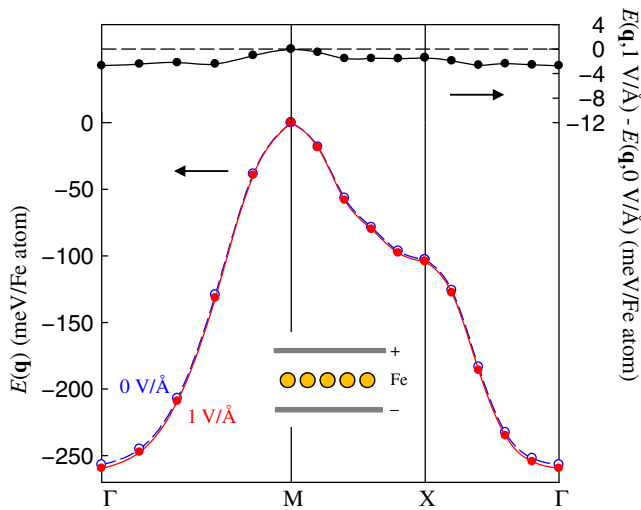


FIG. 1 (color online). Calculated magnon (spin-spiral formation) energy $E(\mathbf{q})$ in E fields of 0 and 1 V/Å for a freestanding Fe monolayer as a function of the spiral wave vector \mathbf{q} . The reference energy ($E = 0$) is set to the value at \bar{M} [$\mathbf{q} = (0.5, 0.5)$] corresponding to an antiferromagnetic state, and open (blue) and solid (red) circles represent results at 0 and 1 V/Å, respectively. The top of the figure shows the energy difference energy between 0 and 1 V/Å. The inset shows a model of the monolayer in an E field.

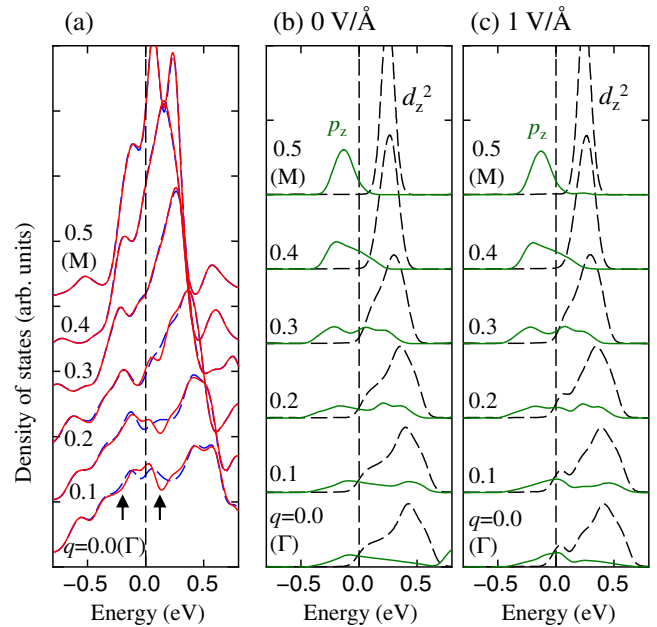


FIG. 2 (color online). (a) Calculated DOS of a freestanding Fe monolayer at the spin wave vector $\mathbf{q}(q, q)$ from $\bar{\Gamma}$ [$\mathbf{q} = (0, 0)$] to \bar{M} [(0.5, 0.5)]. Broken (blue) and solid (red) lines represent the DOS in 0 and 1 V/Å of E field, respectively, and the Fermi energy is set to zero. Arrows indicate pseudogaps induced by the E field. (b),(c) Partial DOS projected to the p_z (green solid lines) and d_{z^2} (black broken lines) orbitals in 0 and 1 V/Å; the p_z DOS is magnified by 40 times with respect to the d_{z^2} DOS.

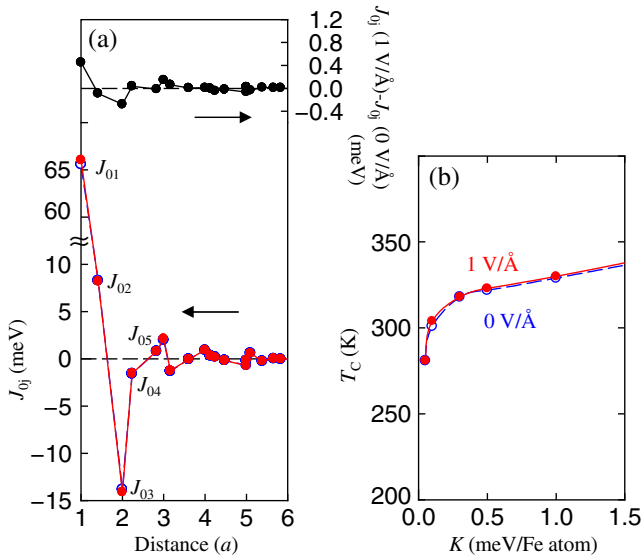


FIG. 3 (color online). (a) Calculated exchange parameters, J_{0i} , for a freestanding Fe monolayer obtained from back Fourier transforming the magnon energy, where the top curve shows the difference between 0 and 1 V/Å. (b) Curie Temperature T_C as a function of the magnetocrystalline anisotropy parameter K obtained by Monte Carlo simulations. Open (blue) and solid (red) circles indicate results for E fields of 0 and 1 V/Å, respectively.

$\bar{\Gamma}$, the bandwidths of the p and d orbitals narrow, and the p states shift down in energy below E_F while the d states shift up above E_F , decreasing the p - d hybridization.

The exchange parameters for 0 and 1 V/Å within the classical Heisenberg model, $\mathcal{H} = \sum_{i<j} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j$, obtained by back Fourier transforming the magnon energy [33,34], are shown in Fig. 3(a). [The J_{ij} are extracted from the $E(\mathbf{q})$ given on a uniform 10×10 \mathbf{q} points in the first BZ.] In zero field, the nearest-neighbor exchange parameter (J_{01}) has a positive value, which stabilizes parallel alignment between the nearest-neighbor atomic moments; for the third neighbors (J_{03}), an antiparallel coupling is favorable. When an E field is applied, J_{01} increases by 0.5 meV compared to that in zero field, which enhances the ordering of the parallel magnetic moment alignment, but for the third nearest neighbors, the J_{03} decreases by 0.3 meV, which tends to favor the antiparallel alignment. The difference in the integrated exchange interaction energy, $\sum_j J_{0j}(1 \text{ V/Å}) - \sum_j J_{0j}(0 \text{ V/Å})$, is 1.5 meV, which suggests that the applied E field increases T_C by 11 K within mean-field theory.

The Heisenberg exchange parameters are, however, unsatisfactory for a 2D ferromagnet such as the present Fe monolayer, since according to the Mermin-Wagner theorem [35] the isotropic Heisenberg ferromagnet cannot order above zero temperature. A perpendicular MCA, however, is known to stabilize long-range ferromagnetic order at finite temperatures by introducing an anisotropy-induced gap at the bottom of the spin wave

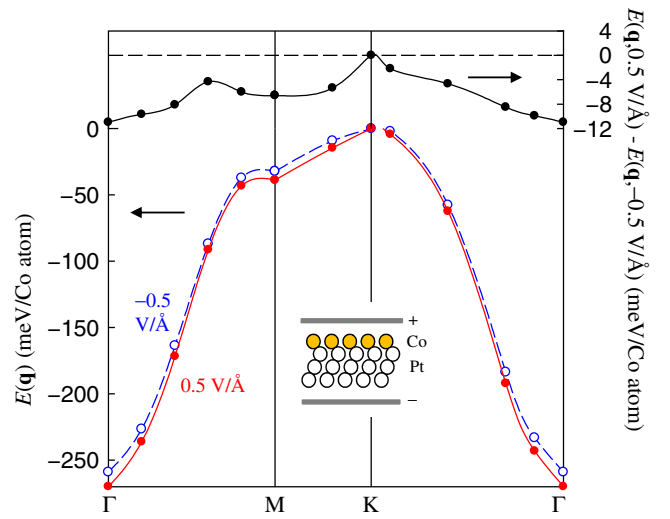


FIG. 4 (color online). Calculated magnon (spin-spiral formation) energy $E(\mathbf{q})$ in E fields of -0.5 and 0.5 V/Å for a Co monolayer on Pt(111) as a function of the spiral wave vector \mathbf{q} . The reference energy ($E = 0$) is set to the value at $\bar{\mathbf{K}}$ corresponding to an antiferromagnetic state, and open (blue) and solid (red) circles represent results at -0.5 and 0.5 V/Å, respectively. Top curve shows the energy difference between -0.5 and 0.5 V/Å. The inset shows a model of the Co monolayer on Pt(111) in a positive E field.

spectrum [21,22]. Since calculations with SOC are restricted to commensurate spin-spiral states [29], we simply included the MCA energy, $\mathcal{H}_{\text{MCA}} = \sum_i K \mathbf{e}_{z,i}^2$, where K is a MCA parameter, in Monte Carlo simulations [36] with a 70×70 square-lattice cell to estimate T_C . As shown in Fig. 3(b), T_C varies significantly with K , with T_C decreasing to zero as K approaches zero, in agreement with the Mermin-Wagner theorem [35], while the modification of T_C due to the change in the exchange interaction is small. Since K of the freestanding Fe monolayer changes from 0.2 meV/atom to almost zero when an E field of 1 V/Å is applied [8], the T_C modification is governed by the change in the MCA, where T_C decreases when K decreases.

We now consider a Co monolayer on Pt(111) in E fields of -0.5 and 0.5 V/Å. The Pt(111) was modeled by a three-atomic-layer slab and the Co atoms are located on hcp sites of the Pt(111) surface, as shown in the inset in Fig. 4, as in calculations for Co adsorption on the Pt(111) surface [37]. The Co and top Pt layers were allowed to fully relax using the atomic forces while the lower two Pt layers are fixed in the positions to the calculated bulk value. Almost no relaxation caused by the E fields is observed, the distance between the Co and top Pt layers were altered by less than 0.2% for both E fields compared to that in the zero field.

The calculated $E(\mathbf{q})$ is presented in Fig. 4, where $E(\mathbf{q})$ shows ferromagnetic characteristics. Although $E(\mathbf{q})$ in both E fields have the same trend with variations of \mathbf{q} , the E -field-induced modification is clearly observed due to the different screening behavior of the charge density in

the spiral wave states, as seen in the freestanding Fe monolayer. The energy difference between the ferromagnetic ($\bar{\Gamma}$) and antiferromagnetic (\bar{K}) states increases by 11.0 meV/Co atom when the applied E field is varied from -0.5 to 0.5 V/Å; this stabilizes the ferromagnetic ordering and so increases the exchange interaction of the J_{01} and J_{03} by 1.1 and 0.8 meV, respectively, as shown in Fig. 5(a). The difference in the integrated exchange interaction energy, $\sum_j J_{0j}(0.5 \text{ V/Å}) - \sum_j J_{0j}(-0.5 \text{ V/Å})$, is 10.3 meV, which suggests that the positive E field increases T_C compared to that in a negative field by 80 K in mean-field theory.

The MCA energy, as calculated using the FLAPW method with SOC, results in $K = 0.50$ and 0.10 meV/Co atom for -0.5 and 0.5 V/Å, respectively, where the magnetization energetically favors orienting along the perpendicular direction. The positive (negative) E field decreases (increases) the MCA energy, in agreement with experiments [38]. As discussed for the freestanding Fe monolayer, if T_C is governed by the MCA, T_C will decrease when the positive E field is applied, but this trend is the opposite of experimental observations [15,16].

Taking K into account, Monte Carlo simulations with a 70×70 triangular-lattice cell were carried out. The magnetization M/M_S , as a function of the temperature T , is shown in Fig. 5(b). The results clearly demonstrate that T_C for positive E fields is higher than that in negative fields, by about 20 K, in agreement with experiments [15]. The

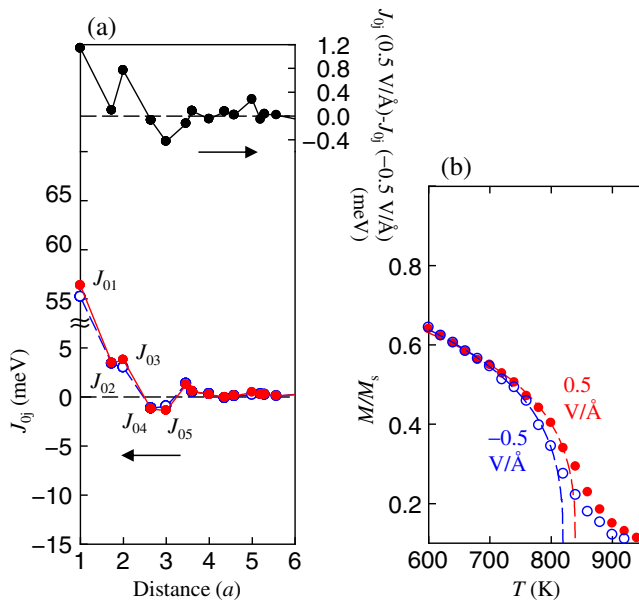


FIG. 5 (color online). (a) Calculated exchange parameters J_{0i} for a Co monolayer on Pt(111) in E fields of -0.5 and 0.5 V/Å; the top curve shows the difference between both E fields. (b) Magnetization M/M_S as a function of the temperature T obtained from Monte Carlo simulations. Open (blue) and solid (red) circles indicate results for -0.5 and 0.5 V/Å, respectively.

calculated critical exponent is about 0.26 for both E fields; the value gets roughly closer to the experimental one [15]. The quantitative discrepancy to the experimental T_C of ~ 320 K [15,16] may be attributed to the simplicity in the present model, e.g., an ideal interface without defects such as interatomic mixing and roughness, but these effects will not alter the conclusions regarding the E -field dependence.

Finally, we comment on the relationship between a change in the number of electrons (N) and the modification of T_C . In the present calculations, the positive E field (0.5 V/Å) increases N of the Co atom by 3.8×10^{-3} electrons compared to that in the negative E field (-0.5 V/Å), as would naturally be expected. However, the number of d electrons decreases by 1.1×10^{-3} electrons while the sp electrons increase by 4.5×10^{-3} electrons, since the later electrons predominately contribute the screening of the E field. The relation between the number of d electrons and T_C behaves like the Slater-Pauling curve for $3d$ magnetic alloys [20], where the valence d electrons decrease as T_C increases.

In summary, we investigated the electric-field modification of T_C of a freestanding Fe monolayer and a Co monolayer on Pt(111) based on first-principles calculations that treat spin-spiral structures in an applied E field. Our results predict that the calculated magnon (spin-spiral formation) energy in the presence of the E field is modified by more than several meV compared to zero field. The Heisenberg exchange parameters obtained from the calculated magnon energies suggest that T_C will be modified by an E field, a conclusion supported by Monte Carlo simulations that take the MCA into account.

We thank Professor T. Oguchi and Professor K. Sano for fruitful discussions. Work at Mie University was supported by a Grant-in-Aid for Scientific Research No. 20540334 from the Japan Society for the Promotion of Science, and the Cooperative Research Program of “Network Joint Research Center for Materials and Devices.” Computations were performed at Center for Computational Materials Science, Institute for Materials Research, Tohoku University, and Supercomputer Center, Institute for Solid State Physics, University of Tokyo. Work at Northwestern University was supported by the U.S. Department of Energy Grant No. DE-FG02-05ER45372. Work at University of Wisconsin-Milwaukee was supported by NSF Grant No. DMR-1335215.

*kohji@phen.mie-u.ac.jp

- [1] M. Weisheit, S. Fähler, A. Marty, Y. Souche, C. Poinshignon, and D. Givord, *Science* **315**, 349 (2007).
- [2] T. Maruyama, K. Ohta, T. Nozaki, T. Shinjo, M. Shiraishi, S. Mizukami, Y. Ando, and Y. Suzuki, *Nat. Nanotechnol.* **4**, 158 (2009).

- [3] K. Ohta, T. Maruyama, T. Nozaki, M. Shiraishi, T. Shinjo, Y. Suzuki, S.-S. Ha, C.-Y. You, and W. van Roy, *Appl. Phys. Lett.* **94**, 032501 (2009).
- [4] Y. Shita, T. Maruyama, T. Nozaki, T. Shinjo, M. Shiraishi, and Y. Suzuki, *Appl. Phys. Express* **2**, 063001 (2009).
- [5] M. Endo, S. Kanai, S. Ikeda, F. Matsukura, and H. Ohno, *Appl. Phys. Lett.* **96**, 212503 (2010).
- [6] W.-G. Wang, M. Li, S. Hageman, and C. L. Chien, *Nat. Mater.* **11**, 64 (2012).
- [7] C.-G. Duan, J. P. Velev, R. F. Sabirianov, Z. Zhu, J. Chu, S. S. Jaswal, and E. Y. Tsymlal, *Phys. Rev. Lett.* **101**, 137201 (2008).
- [8] K. Nakamura, R. Shimabukuro, Y. Fujiwara, T. Akiyama, T. Ito, and A. J. Freeman, *Phys. Rev. Lett.* **102**, 187201 (2009).
- [9] M. Tsujikawa and T. Oda, *Phys. Rev. Lett.* **102**, 247203 (2009).
- [10] K. Nakamura, T. Akiyama, T. Ito, M. Weinert, and A. J. Freeman, *Phys. Rev. B* **81**, 220409 (2010).
- [11] H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl, Y. Ohno, and K. Ohtani, *Nature (London)* **408**, 944 (2000).
- [12] H. Boukari, P. Kossacki, M. Bertolini, D. Ferrand, J. Cibert, S. Tatarenko, A. Wasiela, J. A. Gaj, and T. Dietl, *Phys. Rev. Lett.* **88**, 207204 (2002).
- [13] D. Chiba, F. Matsukura, and H. Ohno, *Appl. Phys. Lett.* **89**, 162505 (2006).
- [14] Y. Yamada, K. Ueno, T. Fukumura, H. T. Yuan, H. Shimotani, Y. Iwasa, L. Gu, S. Tsukimoto, Y. Ikuhara, and M. Kawasaki, *Science* **332**, 1065 (2011).
- [15] D. Chiba, S. Fukami, K. Shimamura, N. Ishiwata, K. Kobayashi, and T. Ono, *Nat. Mater.* **10**, 853 (2011).
- [16] K. Shimamura, D. Chiba, S. Ono, S. Fukami, N. Ishiwata, M. Kawaguchi, K. Kobayashi, and T. Ono, *Appl. Phys. Lett.* **100**, 122402 (2012).
- [17] M. Kawaguchi, K. Shimamura, S. Ono, S. Fukami, F. Matsukura, H. Ohno, D. Chiba, and T. Ono, *Appl. Phys. Express* **5**, 063007 (2012).
- [18] D. Chiba and T. Ono, *J. Phys. D* **46**, 213001 (2013).
- [19] I. V. Ovchinnikov and K. L. Wang, *Phys. Rev. B* **79**, 020402 (R) (2009).
- [20] C. Takahashi, M. Ogura, and H. Akai, *J. Phys. Condens. Matter* **19**, 365233 (2007).
- [21] P. Bruno, *Phys. Rev. B* **43**, 6015 (1991).
- [22] L. M. Sandratskii, E. Sasioglu, and P. Bruno, *Phys. Rev. B* **73**, 014430 (2006).
- [23] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, *Phys. Rev. B* **24**, 864 (1981).
- [24] M. Weinert, E. Wimmer, and A. J. Freeman, *Phys. Rev. B* **26**, 4571 (1982).
- [25] K. Nakamura, T. Ito, A. J. Freeman, L. Zhong, and J. Fernandez-de-Castro, *Phys. Rev. B* **67**, 014420 (2003).
- [26] M. Weinert, G. Schneider, R. Podloucky, and J. Redinger, *J. Phys. Condens. Matter* **21**, 084201 (2009).
- [27] C. Herring, in *Magnetism*, edited by G. Rado and H. Suhl (Academic, New York, 1966).
- [28] L. M. Sandratskii, *Adv. Phys.* **47**, 91 (1998).
- [29] K. Nakamura, N. Mizuno, T. Akiyama, T. Ito, and A. J. Freeman, *J. Appl. Phys.* **99**, 08N501 (2006).
- [30] K. Nakamura, T. Akiyama, T. Ito, and A. J. Freeman, *J. Appl. Phys.* **105**, 07C304 (2009).
- [31] U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).
- [32] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [33] S. V. Halilov, H. Eschrig, A. Y. Perlov, and P. M. Oppeneer, *Phys. Rev. B* **58**, 293 (1998).
- [34] L. M. Sandratskii and P. Bruno, *Phys. Rev. B* **66**, 134435 (2002).
- [35] N. D. Mermin and H. Wagner, *Phys. Rev. Lett.* **17**, 1133 (1966).
- [36] D. P. Landau and K. Binder, *A Guide to Monte Carlo Simulations in Statistical Physics* (Cambridge University Press, Cambridge, England, 2000).
- [37] P. Blonski and J. Hafner, *J. Phys. Condens. Matter* **21**, 426001 (2009).
- [38] K. Yamada, K. Kakizaki, K. Shimamura, M. Kawaguchi, S. Fukami, N. Ishiwata, D. Chiba, and T. Ono, *Appl. Phys. Express* **6**, 073004 (2013).