PHYSICAL REVIEW B **81**, 193402 (2010)

Recovery of the half-metallicity of an $Fe_3O_4(100)$ surface by atomic hydrogen adsorption

M. Kurahashi,[1] X. Sun,[2] and Y. Yamauchi[1]
[1]*National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*
[2]*University of Science and Technology of China, Hefei, Anhui 230026, China*
(Received 2 November 2009; published 5 May 2010)

We report experimental evidence that hydrogen termination largely enhances the spin polarization of an $Fe_3O_4(100)$ surface. An *in situ* prepared $Fe_3O_4(100)/MgO(100)$ film surface was exposed to atomic hydrogen and its surface spin polarization (P) was monitored with a spin-polarized metastable helium-atom beam under external magnetic fields of 0–5 T. The spin asymmetry at the high-energy cutoff, which reflects P at the Fermi level of the topmost surface, increased from $<5\%$ to $>50\%$ at 298 K by H adsorption. The enhancement in P was found to be consistent with the H-induced change in the surface electronic states predicted by a density-functional theory calculation.

DOI: 10.1103/PhysRevB.81.193402 PACS number(s): 79.20.Rf, 73.20.Hb, 75.70.−i

Fe_3O_4 has attracted much attention for its potential application to spintronics devices because bulk Fe_3O_4 is theoretically predicted to be half-metallic.[1,2] Similar to the cases for other half-metallic systems, however, we have to consider the effects of surface and interface states, materials stability, phonons, and electron-magnon interactions[2–4] when discussing its spin polarization (P) at finite temperatures. Actually, the tunneling magnetoresistance ratio[5] or the spin injection efficiency[6] obtained with an Fe_3O_4 electrode are not so high. The lower P at the Fe_3O_4 interfaces has been associated with the surface and interface effects, or the electron correlation in the bulk.[3] The P value at the interface, measured directly with spin-polarized photoemission spectroscopy (SPPES), has been reported to be $\sim -40\%$ at the Fermi level (E_F) for an Fe_3O_4/Al_2O_3 interface.[7] P_{E_F} of clean Fe_3O_4 surfaces has also been investigated intensively with SPPES. It has been reported that P_{E_F} is $\sim -80\%$ for the (111) surface[8,9] while that for the (100) surface is much lower [-55%,[9,10] -40%[11]]. Pentcheva *et al.*,[12] based on the density-functional theory (DFT) calculation, have mentioned that the low P_{E_F} at the $Fe_3O_4(100)$ surface may be associated with the hybridization between the oxygen surface states and the Fe $d_{x^2-y^2}$ states. Following their calculation, it may be reasonable to expect that the modification of the oxygen surface states enables us to improve P_{E_F} largely.

In the present study, we have observed that the adsorption of atomic hydrogen largely recovers P_{E_F} of an $Fe_3O_4(100)$ surface. The present experiments were partially motivated by the fact that the hydrogen termination tends to eliminate the surface dangling bonds as is well known for Si(111).[13] In the case of an Fe_3O_4 surface, hydrogen is expected to be bonded with the surface oxygen atom,[14] the electronic states of which affect P_{E_F} largely. In this paper, we will present an experimental evidence that the adsorption of atomic hydrogen drastically increases P_{E_F} of an $Fe_3O_4(100)$ surface. The results will be discussed on the basis of a DFT calculation, which predicts a drastic increase in P_{E_F} by the hydrogen termination.

Experiments have been conducted with an apparatus that combines the spin-polarized metastable helium (He^*) beam with a 5 T superconducting magnet.[15] Since He^* de-excites on the vacuum side of the topmost surface and ejects surface electrons, we can obtain information on the spin polarization of the topmost surface by monitoring the energy distribution of the ejected electrons.[15–20] Because the measurements were conducted under high magnetic fields in this study, the He^* spin dependence in the electron yield was measured with the sample current method.[15,16] P_{E_F} of the topmost surface can be estimated in the following way. Since He^* decays via the resonance ionization followed by Auger neutralization (AN) on the present surfaces, the kinetic energy (E_{kin}) of the ejected electrons is given by $E_{kin}=E_{eff}-E_1-E_2-2\phi$.[15–21] Here, E_{eff} is the effective ionization energy of He, E_1, E_2 is the binding energy of two electrons involved in AN, and ϕ is the surface work function. In AN, the electron that fills the $He^+ 1s$ hole must have a spin opposite to the He^+ ion while both spins are allowed for the second electron ejected from the surface.[19,20] The sample current measured at the sample voltage V_S, to which electrons with $E_{kin} \geq eV_S$ contribute, is written as

$$I_{\uparrow(\downarrow)}(V_S) \propto \int_0^{e(V_{max}-V_S)} dE \int_0^{E} dE' |H_{fi}|^2 \rho_{\downarrow(\uparrow)}(E-E')[\rho_\uparrow(E') + \rho_\downarrow(E')],$$

where $I_\uparrow(I_\downarrow)$ is the sample current for the He^* spin magnetic moment parallel (antiparallel) to the magnetic field. H_{fi} is the transition matrix element and $\rho_{\uparrow(\downarrow)}(E')$ is the spin density at an energy E', which is graduated from E_F. eV_{max} is equal to the maximum E_{kin} which occurs when AN involves two electrons at E_F. When $V_S \approx V_{max}$, $I_{\uparrow(\downarrow)}(V_S)$ can be approximated without integral, i.e., $I_{\uparrow(\downarrow)}(V_S) \propto \rho_{\downarrow(\uparrow)}(0)[\rho_\uparrow(0)+\rho_\downarrow(0)]$. If the spin asymmetry A is defined as

$$A(V_S) = \frac{I_\uparrow(V_S) - I_\downarrow(V_S)}{I_\uparrow(V_S) + I_\downarrow(V_S)},$$

we obtain $A(V_S) \approx -P_{E_F}$. The measurement of $I(V_S)$ at around V_{max} would therefore enable us to evaluate P_{E_F} of the topmost surface. We note the following as to the sample current measurement at around V_{max}. The primary beam contains a fractional amount of He I photons (21.2 eV) although most of them are removed by an on-axis beam stop.[15] In the spectra shown below, the photon contribution has been subtracted

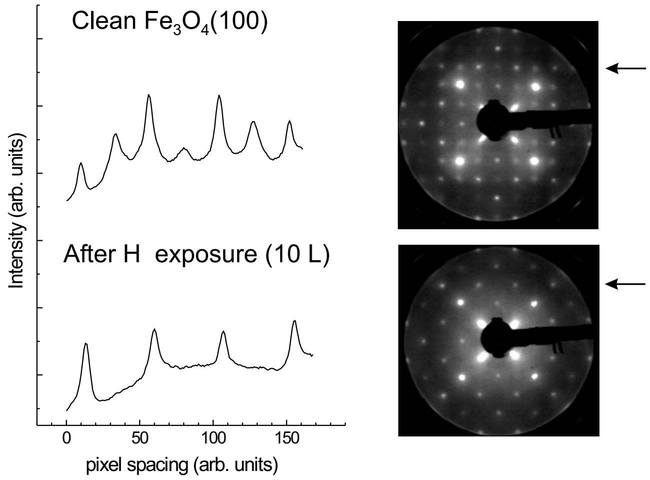

FIG. 1. The LEED pattern and intensity line scans for clean and H-adsorbed Fe_3O_4 surfaces measured at the beam energy of 107 eV.

by quenching the He* atoms in He gas introduced to the second chamber of the beam source.[15]

The MgO(100) substrate was cleaned by annealing at 973 K for 15 min under O_2 atmosphere of $P_{O_2} \sim 3\times 10^{-4}$ Pa. This completely removed the carbon contamination as has been checked by Auger electron spectroscopy (AES) measurement with a cylindrical mirror analyzer. No other impurities were found within the detection limit of AES. A 20-nm-thick Fe_3O_4 film was grown on the MgO(100) substrate at 550 K by evaporating Fe under $P_{O_2} \sim 3\times 10^{-4}$ Pa with the deposition rate of 0.1 nm/min. The AES spectrum measured for the film agreed well with that reported for Fe_3O_4.[22] A low-energy electron diffraction (LEED) pattern corresponding to $(\sqrt{2}\times\sqrt{2})R45°$ reconstruction (Fig. 1), which agrees well with that of previous reports,[10,11] was observed. A homemade atomic hydrogen source utilizing the thermal dissociation of H_2 on a heated tungsten filament was employed for the H-adsorption experiments. Since the absolute exposure of H has not been calibrated, the total background pressure multiplied by the treatment time was used as a relative measure for the H exposure. As has been reported previously,[14] the Fe_3O_4 surface was found to be quite inert against the H_2 gas.

Figure 2 shows the spin asymmetry A measured at 298 K as a function of the magnetic field (H) applied perpendicular to the surface. A reflects the surface magnetization perpendicular to the surface because the local magnetic field direction gives the quantization axis for the He* atom.[15] A increases linearly with H until 0.8 T and gradually at 1–5 T, reflecting the in-plane easy magnetization axis. This is also consistent with the fact that the saturation magnetization of Fe_3O_4 is about 0.9 T. The hydrogen-adsorbed surface, as will be discussed below, shows a much higher asymmetry while the shape of the $A(H)$ curve is similar to that for the clean surface. This would be because the $A(H)$ curve basically follows the magnetization of the Fe_3O_4 film. The gradual increase in the magnetization at higher fields has been attributed to the presence of the antiphase boundaries.[23–25] We fitted the data at 1–5 T to the formula $A=A_S(1-b/H^n)$ following Ref. 24 and obtained $n=0.65-0.85$. The value is similar to that for the $Fe_3O_4(100)/MgO(100)$ film with a similar thickness (50 nm, $n\sim 0.7$),[24] suggesting the same origin for the gradual increase in the $A(H)$ curve.

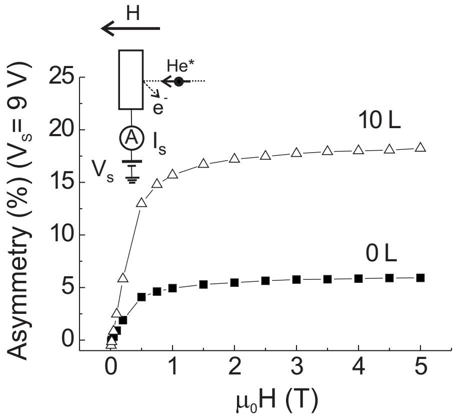

FIG. 2. The magnetic field (H) dependence in the spin asymmetry A measured for clean (0 L) and hydrogen-adsorbed (10 L) $Fe_3O_4(100)$ surfaces. The measurements were conducted at V_S =9 V and at 298 K. The H direction is perpendicular to the surface.

Figure 3 shows the V_S dependence of the sample current and its spin asymmetry A measured at 5 T and at 298 K. It is shown that, for the clean surface, the difference in $I(V_S)$ between the two spin configurations is small at around V_{max}, indicating that P_{E_F} is low for the clean $Fe_3O_4(100)$ surface. Furthermore, A at 1–2 eV below V_{max} is even higher than at V_{max}. This is consistent with the local density of states (LDOS) of the surface Fe atom calculated for the relaxed $Fe_3O_4(100)$ surface,[10] which shows a higher negative spin polarization at $-0.2\sim-0.7$ eV than at E_F. Tobin *et al.*,[11]

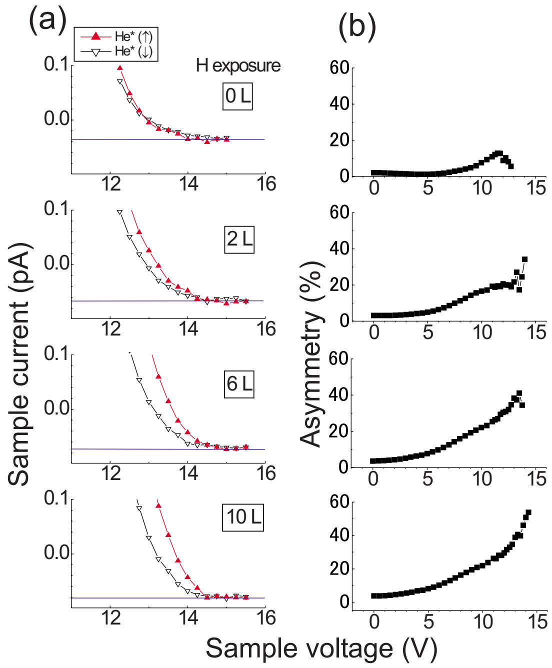

FIG. 3. (Color online) (a) The sample voltage dependence of the sample current measured with spin up and down He* at 5 T and at 298 K after various atomic hydrogen exposures. (b) Spin asymmetries corresponding to (a).

based on the SPPES measurements with different photoelectron detection angles, have proposed that P_{E_F} of the top surface region of $Fe_3O_4(100)$ would be very small, which may be consistent with the present result. In contrast, the hydrogen adsorption largely increases the difference in $I(V_S)$ between the two spin configurations. It is clear that $A > 50\%$ at around V_{max} at 10 L, indicating that the hydrogen adsorption drastically increases P_{E_F} of the topmost surface. A still increases with V_S at >14 V, but $I(V_S)$ is so low that it is difficult to correctly deduce the A values at >14 V. The A value at 14 V should therefore be considered as a lower bound for P_{E_F}. We note that the $I(V_S)$ curve is overlapped with a negative background. Because the background intensity was found to be almost constant at >15 V, it might be due to the desorption of positive ions induced by He* de-excitation.[26]

The LEED pattern of the $Fe_3O_4(100)$ surface was changed by the H adsorption (Fig. 1). The LEED spots corresponding to the $(\sqrt{2}\times\sqrt{2})R45°$ reconstruction were disappeared by the H adsorption. This LEED pattern change was found to correlate with the spin-polarization change mentioned above. We note that annealing the H-adsorbed surface at 550 K under $P_{O_2} \sim 3\times10^{-4}$ Pa recovers the $(\sqrt{2}\times\sqrt{2})R45°$ LEED pattern and the spin polarization of the clean Fe_3O_4 surface, indicating that the oxygen treatment removes the adsorbed H atoms.

To understand the mechanism of the H-induced enhancement of P_{E_F}, we have conducted a DFT calculation using the Vienna *ab initio* simulation program.[27] The surface was represented by a nine-layer slab with a vacuum region of 16.8 Å. The projector-augmented wave method for the electron-ion interaction and the generalized gradient approximation (GGA) for the exchange-correlation functional were used with an energy cutoff of 520 eV. There are two possible origins for the enhancement of P_{E_F}. One is the H-induced change in the chemical bonding and the other is the disappearance of the reconstruction. To discuss the former effect qualitatively, we calculated the LDOS of the surface atoms for an H-adsorbed ideal $Fe_3O_4(100)$ surface with only H position optimized. We used the ideal B-terminated $Fe_3O_4(100)$ substrate because the B termination has been shown to be most stable.[12] Oxygen atoms with and without subsurface Fe(A) neighbor are present on the surface (see the inset of Fig. 4), but the adsorption onto the latter (O1 site) is much more favorable because the calculated adsorption energy for O1 is by 0.6 eV higher than that for O2. We therefore compare the experimental results with the LDOS calculated for the O1 site adsorption.

Figure 4 shows the LDOS of the Fe(B) and O1 atoms of the clean and H-adsorbed surfaces. It is shown that the H adsorption onto the O1 site greatly enhances P_{E_F} of the Fe(B) atom. This is closely related to the oxygen p_x, p_y states locating at around E_F and having the spin-up character. As noted in Ref. 12, these states hybridize with the d states of the surface Fe(B) atom, reducing P_{E_F} of the clean surface. It is, however, shown in Fig. 4(b) that these states are shifted downward from E_F by the H termination and no longer contribute to the LDOS at E_F. In addition, the unoccupied states with the spin-down character shift downward and become dominant at E_F. These would be the main cause of the polarization enhancement. We have also confirmed that the LDOS at the adsorbed H atoms is negligibly low at E_F.

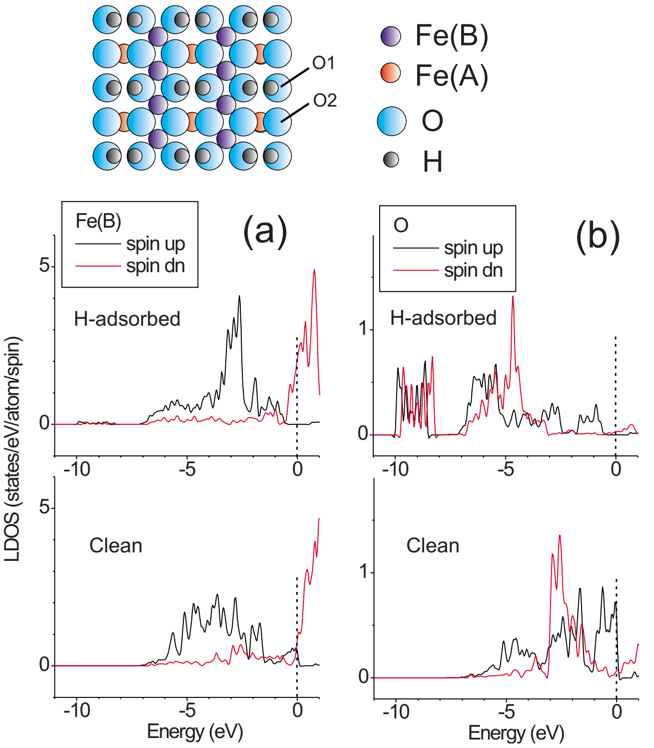

FIG. 4. (Color online) The LDOS of Fe(B) and O1 atoms calculated for clean (below) and H-adsorbed (above) $Fe_3O_4(100)$ surfaces.

Calculations including the on-site Coulomb interaction (U) term for treating the electron-correlation effects have been proved to be successful in giving a reasonably good explanation of experimental optical spectra of Fe_3O_4.[28] To see the effects of the electron correlation on the present phenomenon, we also conducted the calculation with the GGA $+U$ method. The Coulomb (U) and exchange (J) parameters of ~5 eV and ~1 eV, respectively, have been used previously.[28–30] In this study, we used $J=0.89$ eV following the recent calculation of Fe_3O_4 surface[29] and computed LDOS with various U values at 0–5 eV. We have found that the shape of the surface LDOS depends on the U value, but the following trends were commonly observed whichever U value we used. By hydrogen adsorption, (1) the spin-up LDOS of the surface O1 atom is decreased at around E_F and (2) the unoccupied spin-down bands shift downward and become partially filled. The enhancement in P_{E_F}, which is consistent with these H-induced changes, would therefore be expected to appear even if the electron-correlation effects are properly treated. We also note that the present calculation is for the Fe_3O_4 surface having a structure observed above the Verwey temperature while no temperature effect is included. The above discussions are therefore based on the assumption that the hydrogen-induced effects would not depend on the temperature.

The disappearance of the reconstruction observed by LEED would not contribute largely to the enhancement in

P_{E_F}. The difference in the Fe(B) LDOS between the ideal and reconstructed Fe_3O_4(100) surfaces, which has been calculated by Fonin *et al.*,[10] is much smaller than the change in the LDOS by the H adsorption. Therefore, although a close correlation has been observed between the LEED pattern and P_{E_F}, the enhancement in P_{E_F} would mainly come from the H-induced change in the chemical bonding.

The present phenomenon would be important in spintronics application for the following two points. First, the H-terminated Fe_3O_4 surface, although stacking an insulator layer on it with the hydrogen atoms kept at the interface might be difficult, could be utilized in the field of organic spintronics. Because of its much higher P_{E_F} at the topmost surface, it must be a much better spin injector to adsorbed functional molecules than a clean Fe_3O_4 surface. The fact that the H-terminated Fe_3O_4 surface is much more inert than clean Fe, Co, and Ni surfaces would be advantageous in device fabrication. Second, the present phenomenon implies that we can improve P_{E_F} at the Fe_3O_4 interface if we realize the environment similar to that obtained with the hydrogen termination. A higher interface P_{E_F} might be obtained if the interface atom, similar to atomic hydrogen, can remove the depolarizing oxygen $2p$ states and donates some electronic charge to the Fe(B) spin-down bands.

In summary, we have shown that hydrogen adsorption improves the spin polarization of the topmost Fe_3O_4 surface drastically. The present study suggests that the surface modification and the *in situ* observation of the surface spin polarization would be effective for designing an interface having a high spin polarization.

---

[1] Z. Zhang and S. Satpathy, Phys. Rev. B **44**, 13319 (1991).

[2] P. A. Dowben and R. Skomski, J. Appl. Phys. **95**, 7453 (2004).

[3] M. I. Katsnelson, V. Y. Irkhin, L. Chioncel, A. I. Lichtenstein, and R. A. de Groot, Rev. Mod. Phys. **80**, 315 (2008).

[4] R. Skomski, J. Phys.: Condens. Matter **19**, 315202 (2007).

[5] T. Kado, Appl. Phys. Lett. **92**, 092502 (2008).

[6] T. Taniyama, T. Mori, K. Watanabe, E. Wada, M. Itoh, and H. Yanagihara, J. Appl. Phys. **103**, 07D705 (2008).

[7] A. M. Bataille, A. Tagliaferri, S. Gota, C. de Nadai, J.-B. Moussy, M.-J. Guittet, K. Bouzehouane, F. Petroff, M. Gautier-Soyer, and N. B. Brookes, Phys. Rev. B **73**, 172201 (2006).

[8] Y. S. Dedkov, U. Rüdiger, and G. Güntherodt, Phys. Rev. B **65**, 064417 (2002).

[9] M. Fonin, Y. S. Dedkov, R. Pentcheva, U. Rüdiger, and G. Güntherodt, J. Phys.: Condens. Matter **20**, 142201 (2008).

[10] M. Fonin, R. Pentcheva, Y. S. Dedkov, M. Sperlich, D. V. Vyalikh, M. Scheffler, U. Rüdiger, and G. Güntherodt, Phys. Rev. B **72**, 104436 (2005).

[11] J. G. Tobin, S. A. Morton, S. W. Yu, G. D. Waddill, I. K. Schuller, and S. A. Chambers, J. Phys.: Condens. Matter **19**, 315218 (2007).

[12] R. Pentcheva, F. Wendler, H. L. Meyerheim, W. Moritz, N. Jedrecy, and M. Scheffler, Phys. Rev. Lett. **94**, 126101 (2005).

[13] M. Schlüter and M. L. Cohen, Phys. Rev. B **17**, 716 (1978).

[14] W. Huang and W. Ranke, Surf. Sci. **600**, 793 (2006).

[15] M. Kurahashi and Y. Yamauchi, Rev. Sci. Instrum. **79**, 073902 (2008); M. Kurahashi, S. Entani, and Y. Yamauchi, Appl. Phys. Lett. **93**, 132505 (2008).

[16] M. Kurahashi, T. Suzuki, and Y. Yamauchi, Appl. Phys. Lett. **85**, 2869 (2004).

[17] M. Onellion, M. W. Hart, F. B. Dunning, and G. K. Walters, Phys. Rev. Lett. **52**, 380 (1984).

[18] M. Getzlaff, D. Egert, P. Rappolt, M. Wilhelm, H. Steidl, G. Baum, and W. Raith, Surf. Sci. **331-333**, 1404 (1995).

[19] M. Salvietti, R. Moroni, P. Ferro, M. Canepa, and L. Mattera, Phys. Rev. B **54**, 14758 (1996).

[20] S. Förster, G. Baum, M. Müller, and H. Steidl, Phys. Rev. B **66**, 134427 (2002).

[21] W. Sesselmann, B. Woratschek, J. Küppers, G. Ertl, and H. Haberland, Phys. Rev. B **35**, 1547 (1987).

[22] S. K. Arora, H. C. Wu, R. J. Choudhary, I. V. Shvets, O. N. Mryasov, H. Yao, and W. Y. Ching, Phys. Rev. B **77**, 134443 (2008).

[23] D. T. Margulies, F. T. Parker, F. E. Spada, R. S. Goldman, J. Li, R. Sinclair, and A. E. Berkowitz, Phys. Rev. B **53**, 9175 (1996).

[24] D. T. Margulies, F. T. Parker, M. L. Rudee, F. E. Spada, J. N. Chapman, P. R. Aitchison, and A. E. Berkowitz, Phys. Rev. Lett. **79**, 5162 (1997).

[25] A. M. Bataille, L. Ponson, S. Gota, L. Barbier, D. Bonamy, M. Gautier-Soyer, C. Gatel, and E. Snoeck, Phys. Rev. B **74**, 155438 (2006).

[26] M. Kurahashi and Y. Yamauchi, Phys. Rev. Lett. **84**, 4725 (2000).

[27] G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996); Comput. Mater. Sci. **6**, 15 (1996).

[28] I. Leonov, A. N. Yaresko, V. N. Antonov, and V. I. Anisimov, Phys. Rev. B **74**, 165117 (2006); V. N. Antonov, B. N. Harmon, V. P. Antropov, A. Y. Perlov, and A. N. Yaresko, *ibid.* **64**, 134410 (2001).

[29] Z. Łodziana, Phys. Rev. Lett. **99**, 206402 (2007).

[30] H. Pinto and S. Elliott, J. Phys.: Condens. Matter **18**, 10427 (2006).