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Weak ferromagnetism in antiferromagnets: α-Fe_2O_3 and La_2CuO_4

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The problem of weak ferromagnetism in antiferromagnets due to canting of magnetic moments is treated using Green's function technique. At first the eigenvalues and eigenfunctions of the electronic Hamiltonian corresponding to collinear magnetic configuration are calculated which are then used to determine the first and the second variations of the total energy as a function of the magnetic moments canting angle. Spin-orbit coupling is taken into account via perturbation theory. The results of calculations are used to determine an effective spin Hamiltonian. This Hamiltonian can be mapped on the conventional spin Hamiltonian that allows one to determine parameters of isotropic and anisotropic (Dzyaloshinskii-Moriya) exchange interactions. The method is applied to the typical antiferromagnets with weak ferromagnetism α-Fe_2O_3 and La_2CuO_4. The obtained values of the magnetic moments canting angles are in good agreement with previous theoretical results and are in reasonable agreement with experimental data.

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The Heisenberg Hamiltonian is the basis of most theoretical investigations of the transition metal compounds magnetism.[1–3] The essential part of these investigation is determination of exchange interaction parameters J_{ij}. It can be done in a phenomenological way by fitting those parameters to reproduce experimental data (temperature dependence of magnetic susceptibility and magnon dispersion curves obtained in inelastic neutron-scattering measurements).[4] However, much more physically appealing is to obtain them in *ab initio* calculations. In most cases it was done via calculated total energy values for different magnetic moments configurations. Mapping on Heisenberg Hamiltonian gave a system of linear equations for J_{ij} (for example, see Ref. 5). This procedure becomes inconvenient for the systems with a large number of long-range competing exchange interactions as in $(VO)_2P_2O_7$, NaV_2O_5, $Cu_2Te_2O_5X_2$ (X=Br,Cl), etc.[6]

In 1987 Lichtenstein *et al.*[7] proposed the calculation method that does not use total energy differences. They determined exchange interaction parameters via calculation of second variation of total energy $\delta^2 E$ for small deviation of magnetic moments from the collinear magnetic configuration. The expression for this second variation was derived analytically and required for its evaluation calculation of the integral over the product of the one-electron Green functions. Then this method was successfully applied to the various transition metal compounds.[8–11]

The combination of low symmetry and spin-orbit coupling was shown by Dzyaloshinskii[12] and Moriya[13] to give rise to anisotropic exchange coupling. Moriya has shown how the processes involving an additional virtual transition due to spin-orbit coupling can cause an anisotropic exchange interaction as a correction to the isotropic Anderson superexchange term and introduced the new term in the spin Hamiltonian which is the Dzyaloshinskii-Moriya interaction (DM). Solovyev *et al.*[14] has shown that the Dzyaloshinskii-Moriya interaction parameters can be calculated using perturbation theory and Green's function technique and described the canting of magnetic moments of $LaMnO_3$. Recently, Katsnelson, and Lichtenstein[15] have derived the general expression for Dzyaloshinskii-Moriya interaction term in the LDA++ approach.

This paper is devoted to the problem of first-principles theoretical description of weak ferromagnetism in antiferromagnets, specifically to the task of calculations of weak ferromagnetic moment value and direction of spin canting. For this we consider the first and second variations of the total energy of the system at small deviation of magnetic moments from collinear configuration with spin-orbit coupling introduced as a perturbation using Green's function technique. We show that there is an additional on-site term that was not taken into account in previous work,[14] which gives significant contribution to weak ferromagnetic moment. Based on the results of our calculations we propose an effective single site Hamiltonian. This Hamiltonian is sufficient for solving the problem of spin canting, but it can also be rewritten to the conventional form containing isotropic and anisotropic exchange interaction terms. We have applied our method to weak ferromagnetism in α-Fe_2O_3, the classical system which was used by Moriya in his pioneering work,[13] and in antiferromagnetic cuprate La_2CuO_4 in the low-temperature orthorhombic phase, estimated ferromagnetic moments values on the metallic ions in these compounds and determined the plane of spin canting. It is interesting to note that there is another possible source of noncollinearity arising from isotropic exchange interaction, which is the result of lattice frustration (for instance, triangular and pyrochlore lattices). Magnetic ions sublattices for both α-Fe_2O_3 and La_2CuO_4 are not frustrated, therefore spin-orbit coupling is the only possible source of spin noncollinearity in these systems.

Briefly, this paper is organized as follows. In Sec. I we describe the method for calculation of spin Hamiltonian parameters which are responsible for the magnetic moments canting. Section II contains the results of our calculations for α-Fe_2O_3 and La_2CuO_4 crystals. In Sec. III we discuss and briefly summarize our results.

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I. METHOD

According to Andersen's "local force theorem,"[16–18] the total energy variation δE under the small perturbation from the ground state coincides with the sum of one-particle energy changes for the occupied states at the fixed ground state potential. In the first order for the perturbations of the charge and spin densities one can find the following relation:[7]

$$\delta E = \int_{-\infty}^{E_F} d\epsilon\, \epsilon\, \delta n(\epsilon) = E_F \delta z - \int_{-\infty}^{E_F} d\epsilon\, \delta N(\epsilon) = - \int_{-\infty}^{E_F} d\epsilon\, \delta N(\epsilon), \qquad (1)$$

where $n(\epsilon)=dN/d\epsilon$ is the density of the electron state, $N(\epsilon)$ is the integrated density of the electron state, and E_F is the Fermi energy. In the case of magnetic excitation the change of total number of electrons δz is equal to zero. The Green function G is formally expressed in the usual way $G=(\epsilon - H)^{-1}$. One can express density of states and integrated density of states via Green function G:

$$n(\epsilon) = -\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{Sp}\,G(\epsilon) \qquad (2)$$

and

$$N(\epsilon) = -\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{Sp}\,\ln(\epsilon - H). \qquad (3)$$

Then the variation of integrated density of states is given by

$$\delta N(\epsilon) = \frac{1}{\pi}\,\mathrm{Im}\,\mathrm{Sp}[\delta H G]. \qquad (4)$$

Therefore the first and the second variations of total energy of the system take the following forms:

$$\delta E = -\frac{1}{\pi}\int_{-\infty}^{E_F} d\epsilon\,\mathrm{Im}\,\mathrm{Sp}(\delta H G) \qquad (5)$$

and

$$\delta^2 E = -\frac{1}{\pi}\int_{-\infty}^{E_F} d\epsilon\,\mathrm{Im}\,\mathrm{Sp}(\delta^2 H G + \delta H G\,\delta H G). \qquad (6)$$

Operator of spin rotation on the site j by the angle $|\vec{\delta\phi}|$ around direction $\vec{n}=\vec{\delta\phi}/|\vec{\delta\phi}|$ is given by

$$\hat{U} = e^{(1/2)i\vec{\delta\phi}\hat{\vec{\sigma}}}, \qquad (7)$$

where $\hat{\vec{\sigma}}=(\hat{\sigma}_x,\hat{\sigma}_y,\hat{\sigma}_z)$ are Pauli matrices. For small $|\vec{\delta\phi}|$ values we can expand the spin rotation operator in the following way:

$$\hat{U} = 1 + 1/2 i\vec{\delta\phi}\hat{\vec{\sigma}} - 1/8(\vec{\delta\phi}\hat{\vec{\sigma}})^2. \qquad (8)$$

New Hamiltonian of the system after rotation of the spin on j site around direction $\vec{n}$ by the angle $|\vec{\delta\phi}|$ results in the formula

$$\hat{\tilde{H}} = \hat{U}^{\dagger}\hat{H}\hat{U}. \qquad (9)$$

The first variation over the angle of rotation is expressed in the following form:

$$\delta\hat{H} = 1/2 i\vec{\delta\phi}[\hat{H},\hat{\vec{\sigma}}]. \qquad (10)$$

In the basis $|ilm\sigma\rangle$ (i denotes the site, l the orbital quantum number, m the magnetic quantum number, and σ the spin index) the Hamiltonian matrix takes the form $H^{\sigma\sigma'}_{ilm,jlm'} = \langle ilm\sigma|\hat{H}|jlm'\sigma'\rangle$. For simplicity, we drop the indexes of orbital and magnetic quantum numbers and leave spin and site indexes below. We assume that without spin-orbit interaction the ground state corresponds to the collinear magnetic configuration at which all spin moments lie along the z axis. Therefore the Hamiltonian matrix $H^{\sigma\sigma'}_{ij}$ is diagonal in the spin subspace

$$H_{ij} = \begin{pmatrix} \mathbf{H}^{\uparrow}_{ij} & 0 \\ 0 & \mathbf{H}^{\downarrow}_{ij} \end{pmatrix}.$$

One can rewrite the first variation of Hamiltonian Eq. (10) in the following form:

$$\delta H_{jj} = i\,\delta\phi^x_j \begin{pmatrix} 0 & \dfrac{\Delta_j}{2} \\ -\dfrac{\Delta_j}{2} & 0 \end{pmatrix} + \delta\phi^y_j \begin{pmatrix} 0 & \dfrac{\Delta_j}{2} \\ \dfrac{\Delta_j}{2} & 0 \end{pmatrix}, \qquad (11)$$

where $\Delta_j = \mathbf{H}^{\uparrow}_{jj} - \mathbf{H}^{\downarrow}_{jj}$. It is easy to show that the second variation of Hamiltonian is given by

$$\delta^2 H_{jj} = \delta^2\phi^x_j \begin{pmatrix} -\dfrac{\Delta_j}{2} & 0 \\ 0 & \dfrac{\Delta_j}{2} \end{pmatrix} + \delta^2\phi^y_j \begin{pmatrix} -\dfrac{\Delta_j}{2} & 0 \\ 0 & \dfrac{\Delta_j}{2} \end{pmatrix}. \qquad (12)$$

The rotation of spin moment around z axis does not change the energy of the system, therefore there is no term with $\delta\phi^z$ in Eqs. (11) and (12).

Then we take into account the spin-orbit coupling via perturbation theory. The Green function between ith and jth sites in the first order of perturbation theory with respect to the spin-orbit coupling can be written as

$$\tilde{G}_{ij} = G_{ij} + \sum_k G_{ik} H^{\mathrm{SO}}_k G_{kj}, \qquad (13)$$

where $H^{\mathrm{SO}}_k = \lambda_k \vec{L}\vec{S}$, k denotes site, G^{ij} is Green function of system with collinear magnetic configuration, and λ_k is spin-orbit coupling constant. The first variation of total energy Eq. (5) takes the form

$$\delta E = -\frac{1}{\pi}\sum_i \int_{-\infty}^{E_F} d\epsilon\,\mathrm{Im}\,\mathrm{Sp}\left(\delta H_i G_{ii} + \sum_k \delta H_i G_{ik} H^{\mathrm{SO}}_k G_{ki}\right). \qquad (14)$$

The first term in Eq. (14) is equal to zero. The second term can be expressed as the following sum:

$$\delta E = \sum_i A_i^x \delta\phi_i^x + A_i^y \delta\phi_i^y, \tag{15}$$

where

$$A_i^x = \sum_k B_{ik}^x = -\frac{1}{2\pi}\int_{-\infty}^{E_F} d\epsilon \,\mathrm{Re} \sum_k (\Delta_i G_{ik}^{\downarrow} H_{k\downarrow\uparrow}^{\mathrm{SO}} G_{ki}^{\uparrow} - \Delta_i G_{ik}^{\uparrow} H_{k\uparrow\downarrow}^{\mathrm{SO}} G_{ki}^{\downarrow}) \tag{16}$$

and

$$A_i^y = \sum_k B_{ik}^y = -\frac{1}{2\pi}\int_{-\infty}^{E_F} d\epsilon \,\mathrm{Im} \sum_k (\Delta_i G_{ik}^{\downarrow} H_{k\downarrow\uparrow}^{\mathrm{SO}} G_{ki}^{\uparrow} + \Delta_i G_{ik}^{\uparrow} H_{k\uparrow\downarrow}^{\mathrm{SO}} G_{ki}^{\downarrow}). \tag{17}$$

We consider the situation when all spins lie along the z axis and therefore the rotation around it does not change the energy of the system. In order to find A_i^z component of the magnetic torque vector $\vec{A}_i$, we change the coordinate system in the following way $(x,y,z) \rightarrow (z,y,-x)$ (rotation around the y axis):

$$\widetilde{H}^{\mathrm{SO}} = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} H_{\uparrow\uparrow}^{\mathrm{SO}} & H_{\uparrow\downarrow}^{\mathrm{SO}} \\ H_{\downarrow\uparrow}^{\mathrm{SO}} & H_{\downarrow\downarrow}^{\mathrm{SO}} \end{pmatrix}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}. \tag{18}$$

Therefore A_i^x component in the new coordinate system is A_i^z in the old one:

$$A_i^z = \sum_{ik} B_{ik}^z = -\frac{1}{4\pi}\int_{-\infty}^{E_F} d\epsilon \,\mathrm{Re} \sum_k [\Delta_i G_{ik}^{\uparrow}(H_{k\uparrow\uparrow}^{\mathrm{SO}} - H_{k\downarrow\downarrow}^{\mathrm{SO}}) G_{ki}^{\downarrow} - \Delta_i G_{ik}^{\downarrow}(H_{k\uparrow\uparrow}^{\mathrm{SO}} - H_{k\downarrow\downarrow}^{\mathrm{SO}}) G_{ki}^{\uparrow}]. \tag{19}$$

In contrast to the first variation δE, the second variation of total energy $\delta^2 E$ over small deviations of magnetic moments from ground state collinear magnetic configuration has nonzero value without taking into account spin-orbit coupling:

$$\delta^2 E = -\frac{1}{\pi}\int_{-\infty}^{E_F} d\epsilon \,\mathrm{Im}\,\mathrm{Sp}\left(\frac{1}{2}\sum_i \delta^2 H_{ii} G_{ii} + \frac{1}{2}\sum_j \delta^2 H_{jj} G_{jj} + \sum_{ij} \delta H_i G_{ij} \delta H_j G_{ji}\right), \tag{20}$$

where

$$\mathrm{Sp}(\delta^2 H_{ii} G_{ii}) = 1/2\,\delta^2\phi_i^x \Delta_i (G_{ii}^{\downarrow} - G_{ii}^{\uparrow}) + 1/2\,\delta^2\phi_i^y \Delta_i (G_{ii}^{\downarrow} - G_{ii}^{\uparrow}) \tag{21}$$

and

$$\mathrm{Sp}(\delta H_i G_{ij} \delta H_j G_{ji}) = 1/2\,\delta\phi_i^x \delta\phi_j^x (\Delta_i G_{ij}^{\downarrow} \Delta_j G_{ji}^{\uparrow}) + 1/2\,\delta\phi_i^y \delta\phi_j^y (\Delta_i G_{ij}^{\downarrow} \Delta_j G_{ji}^{\uparrow}). \tag{22}$$

Using the condition $G_{ii}^{\uparrow} - G_{ii}^{\downarrow} = (G^{\uparrow}\Delta G^{\downarrow})_{ii} = \Sigma_j G_{ij}^{\uparrow} \Delta_j G_{ji}^{\downarrow}$ one can rewrite Eq. (20) in the following form:

$$\delta^2 E = \frac{1}{4\pi}\int_{-\infty}^{E_F} d\epsilon \,\mathrm{Im} \sum_{ij} (\Delta_i G_{ij}^{\downarrow} \Delta_j G_{ji}^{\uparrow}) \times [(\delta\phi_i^x - \delta\phi_j^x)^2 + (\delta\phi_i^y - \delta\phi_j^y)^2]. \tag{23}$$

One can see that Eq. (23) contains only x and y components of $\vec{\delta\phi}$. In order to include z component, one can use the same rotation of coordinate system as for the site magnetic torque vector $\vec{A}$, Eq. (18). Finally, we obtain the following function of the total energy over angle $\vec{\delta\phi}$:

$$\Delta E = \sum_i \vec{A}_i \delta\vec{\phi}_i + \frac{1}{2}\sum_{ij} J_{ij} |\delta\vec{\phi}_i - \delta\vec{\phi}_j|^2, \tag{24}$$

where

$$J_{ij} = \frac{1}{4\pi}\int_{-\infty}^{E_F} d\epsilon \,\mathrm{Im}(\Delta_i G_{ij}^{\downarrow} \Delta_j G_{ji}^{\uparrow}). \tag{25}$$

The aim of this paper is description of canted magnetism in transition metal compounds caused by spin-orbit coupling. For this we have used the expression (24) for the total energy as a function of canting angle. In order to solve the problem of the weak ferromagnetism in antiferromagnets we suppose that the crystal is an antiferromagnet containing two sublattices 1 and 2, with the same canting angle for the atoms belonging to the same sublattice. With this assumption Eq. (24) is reduced to the following form:

$$\Delta E = \vec{A}_1 \delta\vec{\phi}_1 + \vec{A}_2 \delta\vec{\phi}_2 + \sum_{j>1} J_{1j} |\delta\vec{\phi}_1 - \delta\vec{\phi}_2|^2. \tag{26}$$

Our results for α-Fe_2O_3 and La_2CuO_4 demonstrated that $\vec{A}_1 = -\vec{A}_2$ (torque vector has an opposite sign for the atoms belonging to the different sublattices). That gives

$$\Delta E = \vec{A}_1 (\delta\vec{\phi}_1 - \delta\vec{\phi}_2) + \sum_{j>1} J_{1j} |\delta\vec{\phi}_1 - \delta\vec{\phi}_2|^2. \tag{27}$$

If we further suppose that the deviations of magnetic moments from the average direction defined by $\delta\vec{\phi}_i$ have the same absolute value but different sign for both sublattices, then Eq. (27) takes the following form (we suppose that magnetic moments lie in the plane perpendicular to site magnetic torque vector $\vec{A}$ and canting occurs in the same plane):

$$\Delta E = 2\vec{A}_1 \delta\vec{\phi}_1 + 4\sum_{j>1} J_{1j} |\delta\vec{\phi}_1|^2. \tag{28}$$

Then we find the value of $|\delta\vec{\phi}_1|$ where ΔE has a minimum

$$|\delta\vec{\phi}_1| = \frac{|\vec{A}_1|}{4\sum_{j>1} J_{1j}}. \tag{29}$$

The next step is to establish connection between Eq. (24) and conventional spin Hamiltonian

$$H = H_{\mathrm{DM}} + H_{\mathrm{exch}} = \sum_{i \neq j} \vec{D}_{ij}[\vec{e}_i \times \vec{e}_j] + \sum_{i \neq j} J_{ij}\vec{e}_i\vec{e}_j, \tag{30}$$

where e_i is a unit vector in the direction of the ith site magnetization, J_{ij} is the exchange interaction, and $\vec{D}_{ij}$ is the Dzyaloshinskii-Moriya vector. One can rewrite the second term in Eq. (30) as $H_{\mathrm{exch}}=\Sigma_{ij}J_{ij}|\vec{e}_i||\vec{e}_j|\cos(\theta_{ij})$. In the limit of small canting angle values we can assume that $\cos(\theta_{ij})=1-|\delta\vec{\phi}_i-\delta\vec{\phi}_j|^2/2$ and exchange interaction energy for antiferromagnetic configuration has the form

$$\Delta H_{\mathrm{exch}} = \frac{1}{2}\sum_{ij} J_{ij}|\delta\vec{\phi}_i - \delta\vec{\phi}_j|^2. \tag{31}$$

Therefore in the limit of small $\delta\vec{\phi}$ we can directly map the second term of total energy variation Eq. (24) onto the second term in spin Hamiltonian (30).

The first term in Eq. (24) describes the deviation of the spin moment on the site i from the initial collinear spin configuration direction. We assume that this initial spin direction on the site i is defined by the direction of Weiss mean-field $\vec{H}_i^{\mathrm{WF}}=\Sigma_{j(\neq i)}J_{ij}\vec{e}_j$ (the corresponding unit vector is $\vec{e}_i^{\,0}=\vec{H}_i^{\mathrm{WF}}/|\vec{H}_i^{\mathrm{WF}}|$). Therefore we can map the first term in Eq. (24) on the spin Hamiltonian

$$H_{\mathrm{dev}} = \sum_i \vec{A}_i[\vec{e}_i^{\,0} \times \vec{e}_i] \tag{32}$$

describing the deviation of spin moments away from the direction $\vec{e}_i^{\,0}$ of external Weiss field. (We have used here the connection between rotation vector $\delta\vec{\phi}_i$ and the change of the magnetic moment unit vector $\delta\vec{e}_i=\vec{e}_i-\vec{e}_i^{\,0}$: $\delta\vec{e}_i=[\delta\vec{\phi}_i\times\vec{e}_i^{\,0}]$.) In order to demonstrate the connection between $\vec{A}_i$ and $\vec{D}_{ij}$ one can rewrite the Eq. (32) in the following form:

$$H_{\mathrm{dev}} = \frac{1}{2}\left(\sum_i \vec{A}_i\left[\frac{\vec{H}_i^{\mathrm{WF}}}{|\vec{H}_i^{\mathrm{WF}}|} \times \vec{e}_i\right] + \sum_j \vec{A}_j\left[\frac{\vec{H}_j^{\mathrm{WF}}}{|\vec{H}_j^{\mathrm{WF}}|} \times \vec{e}_j\right]\right). \tag{33}$$

Using our definition of $\vec{H}_i^{\mathrm{WF}}$ we obtain

$$H_{\mathrm{dev}} = \frac{1}{2}\left(\sum_{ij} \frac{\vec{A}_i}{|\vec{H}_i^{\mathrm{WF}}|}J_{ij}[\vec{e}_j \times \vec{e}_i] + \sum_{ij} \frac{\vec{A}_j}{|\vec{H}_j^{\mathrm{WF}}|}J_{ij}[\vec{e}_i \times \vec{e}_j]\right). \tag{34}$$

This gives us the following expression for parameter $\vec{D}_{ij}$ of spin Hamiltonian (30):

$$\vec{D}_{ij} = \frac{1}{2}J_{ij}\left(\frac{\vec{A}_j}{|\vec{H}_j^{\mathrm{WF}}|} - \frac{\vec{A}_i}{|\vec{H}_i^{\mathrm{WF}}|}\right). \tag{35}$$

Therefore the components of Dzyaloshinskii-Moriya interaction vector are given by

$$\begin{aligned} D_{ij}^x = {} & -\frac{1}{4\pi}J_{ij}\int_{-\infty}^{E_F} d\epsilon\,\mathrm{Re} \\ & \times\sum_k\left(\frac{\Delta_j G_{jk}^{\downarrow}H_{k\downarrow\uparrow}^{\mathrm{SO}}G_{kj}^{\uparrow} - \Delta_j G_{jk}^{\uparrow}H_{k\uparrow\downarrow}^{\mathrm{SO}}G_{kj}^{\downarrow}}{|\vec{H}_j^{\mathrm{WF}}|}\right. \\ & \left. - \frac{\Delta_i G_{ik}^{\downarrow}H_{k\downarrow\uparrow}^{\mathrm{SO}}G_{ki}^{\uparrow} - \Delta_i G_{ik}^{\uparrow}H_{k\uparrow\downarrow}^{\mathrm{SO}}G_{ki}^{\downarrow}}{|\vec{H}_i^{\mathrm{WF}}|}\right), \end{aligned} \tag{36}$$

$$\begin{aligned} D_{ij}^y = {} & -\frac{1}{4\pi}J_{ij}\int_{-\infty}^{E_F} d\epsilon\,\mathrm{Im} \\ & \times\sum_k\left(\frac{\Delta_j G_{jk}^{\downarrow}H_{k\downarrow\uparrow}^{\mathrm{SO}}G_{kj}^{\uparrow} + \Delta_j G_{jk}^{\uparrow}H_{k\uparrow\downarrow}^{\mathrm{SO}}G_{kj}^{\downarrow}}{|\vec{H}_j^{\mathrm{WF}}|}\right. \\ & \left. - \frac{\Delta_i G_{ik}^{\downarrow}H_{k\downarrow\uparrow}^{\mathrm{SO}}G_{ki}^{\uparrow} + \Delta_i G_{ik}^{\uparrow}H_{k\uparrow\downarrow}^{\mathrm{SO}}G_{ki}^{\downarrow}}{|\vec{H}_i^{\mathrm{WF}}|}\right), \end{aligned} \tag{37}$$

$$\begin{aligned} D_{ij}^z = {} & -\frac{1}{8\pi}J_{ij}\int_{-\infty}^{E_F} d\epsilon\,\mathrm{Re}\sum_k\left(\frac{\Delta_j G_{jk}^{\uparrow}(H_{k\uparrow\uparrow}^{\mathrm{SO}} - H_{k\downarrow\downarrow}^{\mathrm{SO}})G_{kj}^{\downarrow}}{|\vec{H}_j^{\mathrm{WF}}|}\right. \\ & - \frac{\Delta_j G_{jk}^{\downarrow}(H_{k\uparrow\uparrow}^{\mathrm{SO}} - H_{k\downarrow\downarrow}^{\mathrm{SO}})G_{kj}^{\uparrow}}{|\vec{H}_j^{\mathrm{WF}}|} - \frac{\Delta_i G_{ik}^{\uparrow}(H_{k\uparrow\uparrow}^{\mathrm{SO}} - H_{k\downarrow\downarrow}^{\mathrm{SO}})G_{ki}^{\downarrow}}{|\vec{H}_i^{\mathrm{WF}}|} \\ & \left. + \frac{\Delta_i G_{ik}^{\downarrow}(H_{k\uparrow\uparrow}^{\mathrm{SO}} - H_{k\downarrow\downarrow}^{\mathrm{SO}})G_{ki}^{\uparrow}}{|\vec{H}_i^{\mathrm{WF}}|}\right). \end{aligned} \tag{38}$$

We have obtained more general expression for the Dzyaloshinskii-Moriya interaction parameter in comparison with those presented in paper.[14] There are two kinds of contributions into magnetic torque vector $\vec{A}_i$: on-site interaction $\vec{B}_{ii}$ (absent in Ref. 14) and intersite interaction $\vec{B}_{ik}(i\neq k)$. We have found that on-site contribution in the magnetic torque $\vec{A}$, which was not considered before, plays an important role in weak ferromagnetism description.

We have applied the calculation scheme developed above to the typical antiferromagnets with weak ferromagnetism α-Fe_2O_3 and La_2CuO_4 in low-temperature orthorhombic phase. In order to calculate Green functions corresponding to the collinear spin configurations we used LDA+U approach[19] realized in LMTO method within the atomic sphere approximation.[20]

II. RESULTS

A. Fe_2O_3

Weak ferromagnetism or weak noncollinearity of essentially antiparallel magnetic moments was first observed in α-hematite α-Fe_2O_3.[21] The trigonal crystal of α-Fe_2O_3 has $R\bar{3}c$ space group. Depending on temperature α-hematite occurs in two different antiferromagnetic states: at $T<250$ K the spins are along the trigonal axis, and at $250\text{ K}<T<950$ K they lie in one of the vertical planes of symmetry making small angle of 1.1×10^{-3} with basal plane.[22,23] In the latter case the α-Fe_2O_3 has a net ferromagnetic moment.

TABLE I. Values of exchange interactions of Atom 2 with atoms which belong to different coordination spheres estimated in experiment (Ref. 30), calculated in present work using LSDA and LDA $+U$ approximations (in meV). The couplings with negative sign are ferromagnetic. The number in bracket denotes the corresponding coordination sphere presented in Fig. 1.

	Samuelsen *et al.* (Ref. 30)	LSDA	LDA$+U$
$J^{(1)}$	−3.076	9.905	8.576
$J^{(3')}$	−0.528	−5.71	−7.3
$J^{(1')}$	20.313	25.957	25.224
$J^{(4')}$ and $J^{(4'')}$	12.554	13.488	17.502
$J^{(3)}$	1.056	−0.497	−0.073

Dzyaloshinskii has shown that the spin superstructure gives rise to a nonvanishing antisymmetric spin coupling vector which is parallel to the trigonal axis. Moriya[13] gave phenomenological Dzyaloshinski's explanation a microscopic footing by means of Anderson's perturbation approach to magnetic superexchange.

Sandratskii *et al.*[24] have performed the calculation based on the local approximation to spin-density functional theory (LSDA) using the fully relativistic version of ASW method. In spite of the well-known problem of proper determination of the energy gap in semiconducting and insulating materials using the LSDA approximation, the authors[24] succeeded in describing a weak ferromagnetism. The obtained ferromagnetic moment of about $0.002\mu_B$ per Fe atom together with atomic moment of iron of $3.72\mu_B$ results in the canting angle of 0.53×10^{-3} which is two times smaller than experimental value. In the present study we treat the problem of weak ferromagnetism description in α-Fe_2O_3 using perturbation theory.

The electronic structure of α-hematite calculated using the standard LDA$+U$ approximation[19] with on-site Coulomb interaction parameters $U=5$ eV, $J_H=0.88$ eV, and structure data from Ref. 25 is in good agreement with previous theoretical calculations.[26] The Brillouin zone integration has been performed in the grid generated by using (6;6;6) divisions. We have obtained the magnetic moment of $4.1\mu_B$ per Fe atom. This value is a little smaller than those seen experimentally (4.6–$4.9\mu_B$ in Refs. 27 and 28). The energy gap value of 1.67 eV is also slightly underestimated comparing with experimental data (2.14 eV in Ref. 29).

The calculated isotropic exchange interactions and contributions in site magnetic torque $\vec{A}_2$ are presented in Tables I and II, respectively. The energy integration has been performed in the complex plane by using 800 energy points on the rectangular contour. The simplified crystal structure and the interaction paths are shown in Fig. 1. One can see that the values of exchange interaction parameters and spin-orbit torque terms are converged in sum over the neighbors. Even the contributions from fifth-nearest neighbors are negligibly small. The obtained interaction picture is more complicated than those Moriya examined in order to describe the weak ferromagnetism in α-hematite.[13] There are strong isotropic exchange interaction with the third and the fourth neighbors.

TABLE II. The different contributions in components of site magnetic torque of α-Fe_2O_3 obtained in LDA$+U$ calculation (in meV). The couplings with negative sign are ferromagnetic. d_{ij} is the distance between ith and jth atoms in a.u. $\vec{R}_{ij}$ is the radius vector from ith site to jth site in units of the lattice constant (5.49 a.u.).

(i,j)	d_{ij}	$\vec{R}_{ij}$	B^x_{ij}	B^y_{ij}	B^z_{ij}
(2,2)	0	(0;0;0)	0	0	0.162
(2,1)	5.45	(0;0;−0.99)	0	0	0.005
$(2,3')$	5.60	(−0.5;−0.86;0.20)	−0.036	0.015	0.001
$(2,3')$	5.60	(1;0;0.20)	0.032	0.023	0.001
$(2,3')$	5.60	(−0.5;0.86;0.20)	0.004	−0.038	0.001
$(2,1')$	6.36	(0.5;−0.86;−0.58)	0.071	0.019	−0.14
$(2,1')$	6.36	(−1;0;−0.58)	−0.052	0.052	−0.14
$(2,1')$	6.36	(0.5;0.86;−0.58)	−0.019	−0.071	−0.14
$(2,4')$	6.99	(0.5;−0.86;0.79)	0.168	0.063	0.101
$(2,4')$	6.99	(−1;0;0.79)	−0.139	0.115	0.101
$(2,4')$	6.99	(0.5;0.86;0.79)	−0.029	−0.178	0.101
$(2,4'')$	6.99	(−0.5;−0.86;−0.79)	0.128	0.094	0.076
$(2,4'')$	6.99	(1;0;−0.79)	0.017	−0.158	0.076
$(2,4'')$	6.99	(−0.5;0.86;−0.79)	−0.145	0.064	0.076
(2,4)	7.53	(0;0;−1.37)	0	0	0.001

This agrees well with experimental results[30] and theoretical predictions.[31] The mean-field value of Néel temperature obtained via exchange interactions[24] overestimates the experimental result of about two times. We restrict our consideration to comparing of LDA$+U$ exchange interactions with

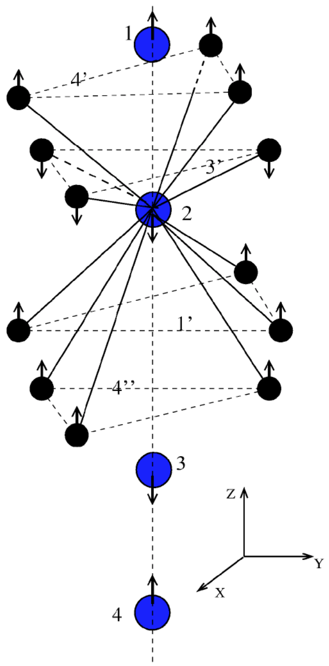

FIG. 1. (Color online) The crystal structure of α-Fe_2O_3. The large circles are Fe atoms which belong the smallest unit cell used in the LDA$+U$ calculations. The small circles are Fe atoms which surround atom 2. The arrows denote the magnetic configuration used in our calculations.

those deduced from inelastic neutron-scattering experiment.[30] Using the Green function method with RPA approximation[32] the authors of Ref. 30 obtained $T_N=1044$ K, which is in good agreement with experimental value varying from 947 to 969 K. Comparing our exchange interaction parameters obtained in LDA+U calculation with experimental values we observe good agreement for the largest magnetic interactions with the third and the fourth neighbors. There is disagreement between experiment and theory for interactions with the first and the second neighbors. While experimental exchange interaction J_{21} with the first neighbor is ferromagnetic, our results and results of other works[24,33] show that this interaction is antiferromagnetic in the ground state of α-Fe_2O_3.

The sum of the exchange interactions between atom 2 and its neighbors is given by $J_2=\Sigma_{i\neq 2}J_{2i}=189.26$ meV. We have also obtained the following components of site magnetic torque vector on the atom 2: $A_2^x=\Sigma_i B_{2i}^x=0$ eV, $A_2^y=\Sigma_i B_{2i}^y=0$ eV, and $A_2^z=\Sigma_i B_{2i}^z=0.282$ meV. One can see that on-site interaction B_{22}^z gives the main contribution in $\vec{A}_2$. The site magnetic torque of $\vec{A}_1$ has the following components $(0;0;-0.282)$, the same value but the opposite sign comparing with $\vec{A}_2$. The value of canting angle of $|\delta\vec{\phi}|=0.4\times10^{-3}$ calculated using Eq. (29) agrees well with previous theoretical results[24] (0.53×10^{-3}) and both are about two times smaller than experimental data $(1.1\times10^{-3}$ in Refs. 22 and 23). In order to compare our perturbation theory results with those which was obtained using the fully relativistic ASW method[24] we have calculated the canting angle within the LSDA approximation. The obtained canting angle value of 0.6×10^{-3} is in good agreement with both our LDA+U result and result of Sandratskii paper.[24]

It is easy to show that in the case when all spins lie along the z axis there is no canting of the spin moments. On the other hand, if direction of Weiss field is perpendicular to the z axis, the canting exists and the system has weak ferromagnetic moment. This picture fully agrees with experimental and theoretical data.[13,22,23]

B. La_2CuO_4

In the case of the cuprates Dzyaloshinskii-Moriya interaction is the leading source of anisotropy, since single-ion anisotropy does not occur due to $S=\frac{1}{2}$ nature of the spins on the Cu^{2+} sites. The experimental data[34,35] demonstrate that in case of low-temperature orthorhombic phase the spins do not lie exactly in the Cu—O planes, but are canted out of the plane by small angle of 0.17°. Coffey and co-workers[36] made complete examination of the anisotropic exchange interaction in orthorhombic phase based on a symmetry consideration. They assumed rotation axis of the CuO_6 as a direction of antisymmetric exchange interaction and obtained that the spins are canted in plane which is perpendicular to Dzyaloshinskii-Moriya vector.

The first attempt at a microscopic calculation of the Dzyaloshinskii-Moriya anisotropy for La_2CuO_4 in the low-temperature orthorhombic and tetragonal phases was made by Coffey, Rice, and Zhang.[37] They have examined the Dzyaloshinskii-Moriya interaction patterns on an antiferromagnetically ordered state and shown conditions for arising of weak ferromagnetism. Then the authors of Refs. 38–40 have demonstrated that the higher order terms with respect to spin-orbit coupling are also important to describe magnetic properties of La_2CuO_4. Here we present an *ab-initio* investigation of canted magnetism of La_2CuO_4 and concentrate only on the first order spin-orbit coupling terms.

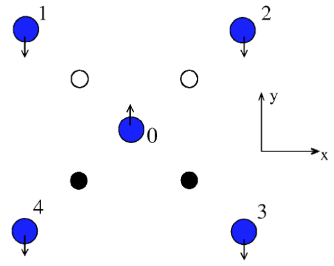

FIG. 2. (Color online) The schematic crystal structure of La_2CuO_4 in the low-temperature orthorhombic phase. The open circles are oxygen atoms which are tilted up out of the Cu plane, the black circles are oxygen atoms tilted down out the Cu plane. The big circles are copper atoms. The arrows denote the magnetic configuration used in LDA+U calculations with spin moments lie along the z axis.

We have performed the LDA+U calculations for La_2CuO_4 in the low-temperature orthorhombic phase using structural data for Nd doped La_2CuO_4,[41] with on-site Coulomb interaction parameters $U=10$ eV, $J_H=1$ eV (the same as used in Ref. 42). The Brillouin zone integration has been performed in the grid generated by using (6;6;6) divisions. The schematic structure of Cu—O layer of La_2CuO_4 in low-temperature orthorhombic phase is presented in Fig. 2.

The experimental value of the energy gap is reported to be about 2 eV (Ref. 43). Our gap value of 1.94 eV is in good agreement with experimental data. The calculated magnetic

TABLE III. Isotropic exchange interactions of atom 0 with neighbors and components of different contributions in site magnetic torque $\vec{A}_0$ (in meV). $\vec{R}_{0j}$ is radius vector from 0th site to jth site in units of the lattice constant (10.14 a.u.).

$\vec{R}_{0j}$	J_{0j}	B_{0j}^x	B_{0j}^y	B_{0j}^z
(0;0;0)	0	0.101	0	0
(−0.49;0.5;0)	14.576	0.020	−0.032	−0.005
(0.49;0.5;0)	14.576	0.020	0.032	0.005
(0.49;−0.5;0)	14.576	0.020	−0.032	−0.005
(−0.49;−0.5;0)	14.576	0.020	0.032	0.005
(0;1;0)	−2.071	0.002	0	0
(0;−1;0)	−2.071	0.002	0	0
(−0.98;0;0)	−1.943	−0.007	0	0
(0.98;0;0)	−1.943	−0.007	0	0
(−0.49;0;1.22)	0	0	0	0
(−0.49;0;−1.22)	0	0	0	0
(0.49;0;1.22)	0	0	0	0
(0.49;0;−1.22)	0	0	0	0

moment value on Cu atom is $0.61\mu_B$, which also agrees well with experiment.[44]

We have performed calculations of the isotropic exchange interactions and different contributions to site magnetic torque components (Table III) using the energy integration in the complex plane with 700 energy points on the rectangular contour. One can see that the exchange interaction parameters and the spin-orbit torque terms are converged in sum over the distance (R_{ij}). The obtained values of exchange interaction parameters are in good agreement with results of previous calculations for low-temperature tetragonal phase[42] and experimental estimations.[34] The sum of the isotropic exchange interaction terms and components of site magnetic torque are given by $J_0=\Sigma_{i\neq 0} \; J_{0i}=58.304$ meV, $A_0^x=0.171$ meV, $A_0^y=0$ meV, and $A_0^z=0$ eV. We obtained that $\vec{A}_2=(-0.171;0;0)$, again of the same value but the opposite sign comparing with $\vec{A}_0$. It means that the system has net ferromagnetic moment if spins lie in the plane which is perpendicular to x axis (axis of rotation of oxygen octahedra). This fully agrees with results of previous theoretical works.[34,36,37] The obtained value of canting angle $|\vec{\delta\phi}|=0.7\times 10^{-3}$ is about three times smaller than those experimentally observed $2.2-2.9\times 10^{-3}$ (Refs. 34 and 35).

III. CONCLUSION

We present method for calculation of spin Hamiltonian parameters responsible for magnetic moments canting. The effective Hamiltonian for canted magnetism is proposed. We show that the parameters of this model Hamiltonian can be obtained from first-principles calculations. Using the developed method we describe the weak ferromagnetism in α-Fe_2O_3 and La_2CuO_4. It is shown that on-site contribution $\vec{B}_{ii}$ in site magnetic torque $\vec{A}_i$ plays the crucial role for net ferromagnetic moment of α-Fe_2O_3 and La_2CuO_4 in low-temperature orthorhombic phase. Finally we can conclude that the obtained values of the magnetic moments canting angles are in good agreement with previous theoretical results and are in reasonable agreement with experimental data.

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