Spin current and magneto-electric effect in non-collinear magnets

Hosho Katsura,1 Naoto Nagaosa,1,2,3 and Alexander V. Balatsky4

1Department of Applied Physics, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
2CERC, AIST Tsukuba Central 4, Tsukuba 305-8562, Japan
3CREST, Japan Science and Technology Agency (JST)
4Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545 USA

A new microscopic mechanism of the magneto-electric (ME) effect based on the spin supercurrent is theoretically presented for non-collinear magnets. The close analogy between the superconductors (charge current) and magnets (spin current) is drawn to derive the distribution of the spin supercurrent and the resultant electric polarization. Application to the spiral spin structure is discussed.

PACS numbers: 75.80.+q, 71.70.Ej, 77.80.-e

The interplay between the magnetism and ferroelectricity is an old issue since the first prediction of the magneto-ferroelectric (ME) effect by Curie[1]. Later the phenomenological theory of ME effect was developed by Landau[2] and Dzyaloshinskii[3]. There they symmetry consideration is essential to classify the all possible ME tensors depending on the magnetic point group. Especially the time-reversal (T) and spatial inversion (I) are the key symmetries to the ME effect. For example, the linear ME effect corresponding to the term $\alpha_{ij}M_iP_j$ ($P$:polarization, $M$:magnetization) is allowed only when both $T$- and $I$-symmetries are broken. However, on the other hand, the microscopic quantum theory of ME effect has not yet been fully developed although several scenarios for particular materials such as Cr$_2$O$_3$ have been proposed[4,5]. For this particular material, the change of the anisotropy energy, exchange, and $g$-value due to the electric field have been proposed for the origin of the parallel ME effect. The transverse ME effect, on the other hand, can not be explained by these mechanisms.

A new microscopic mechanism of the magneto-electric (ME) effect based on the spin supercurrent is drawn to derive the distribution of the spin supercurrent and the resultant electric polarization. The ME effect and spin current are directly related. The spin current $j_s$ has attracted revived interests recently in the context of spintronics in semiconductors. In contrast to the charge current, it is $T$-even even since the spin polarization is also reversed together with the direction. Therefore from the viewpoint of pure symmetry, $j_s$ belongs to the same class as the electric polarization $P$, and it is natural to expect the coupling between these two. In fact, the electric field induced dissipationless spin current driven by the Berry phase curvature has been proposed for the semiconductors[10]. In magnets, the spin current is analogous to the superfluid current, i.e., spin supercurrent, associated with the spin rigidity[11]. In this paper, we present a new mechanism for the ME effect due to the spin supercurrent with the non-collinear spin structure such as the spiral state[12,13]. The idea is that the spin supercurrent is induced between the two spins with generic non-parallel configurations, which induces the electric polarization. This is the dual effect to DM interaction[6,7] and/or Aharonov-Casher effect[14]. The vector potential coupled to the spin current is the vector product of electric field/electric polarization and the direction of the bond connecting the two spins[17]. This allows one to develop a microscopic theory of the electric field induced DM interaction[8]. Applications to the spiral magnetic structure are also discussed.

Let us first review the analogy of the magnetically ordered state to the superconducting state. The key to understand the superconductivity is the canonical conjugate relation between the charge $n$ and the Josephson phase $\varphi$, i.e., $[n_i, \varphi_j] = i\delta_{ij}$, where $i, j$ are the indices for the site. Similar relation exists in the quantum spin operators as $[S^z_i, \theta_j] = i\delta_{ij}$, where $S^z$ is the $z$-component of the spin operator while $\theta$ is the angle of the vector $(S^x, S^y)$ measured from the $x$-axis. This makes the link between XY spin model and that of superconductivity. The Hamiltonian for XY model reads

$$H_{XY} = -\sum_{<ij>} \frac{J_{zij}}{2} (S^+_i S^-_j + S^-_i S^+_j)$$ (1)

and the spin supercurrent $j^s_{ij}$ defined so as to satisfy $i\partial S^z_i / \partial t = (1/i\hbar)[S^z_i, H] = -\sum_j j^s_{ij}$ is given by

$$j^s_{ij} = i J_{zij} (S^+_i S^-_j - S^-_i S^+_j)$$ (2)

Putting $(S^x_j, S^y_j) = S(\cos \theta_j, \sin \theta_j)$, We obtain

$$j^s_{ij} = J_{zij} S^z_i S^z_j \sin(\theta_i - \theta_j)$$ (3)

where $J_{z} S^z$ corresponds to the spin stiffness, i.e., rigidity. Equation (3) is analogous to the Josephson equation.

To go further with this analogy, the next question is “what is the vector potential $A_s$ coupled to the
spin supercurrent?”. The answer to this question can be found in the Aharonov-Casher (AC) effect \cite{14} and Dzyaloshinskii-Moriya (DM) interaction \cite{6,7}. The conventional DM interaction is given by

$$H_{DM} = \sum_{ij} \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j).$$  \hspace{1cm} (4)$$

When the DM vector $\mathbf{D}_{ij} = D_{ij} \hat{e}_z$, the total Hamiltonian $H_{total} = H_{XY} + H_{DM}$ with $H_{XY}$ in eq. (1) is written as

$$H_{total} = -\sum_{ij} \sqrt{J_{ij}} (e^{-iA_{ij}} S_i^+ S_j^- + e^{iA_{ij}} S_i^+ S_j^-)$$ \hspace{1cm} (5)$$

where $\sqrt{J_{ij}} e^{iA_{ij}} = J_{ij} + iD_{ij}$. Therefore the DM vector $\mathbf{D}$ acts as the vector potential or gauge field to the spin current. It is well known that the DM interaction exists only when the DM interaction is broken at the middle point between the two spins. Therefore when the crystal structure has the inversion symmetry, the external electric field $\mathbf{E}$ induces the DM interaction. Namely $\mathbf{D}_{ij} \propto \mathbf{E} \times \mathbf{e}_{ij}$, where $\mathbf{e}_{ij}$ is the unit vector connecting the two sites $i$ and $j$. This form is identical to the Aharonov-Casher (AC) effect, where the Lorentz transformation of the electric field induces the magnetic field in the moving frame which interacts with the spin moment. However the magnitude of the coupling constant for AC effect is extremely small in vacuum since it contains the rest mass of the electron $mc^2 \approx 5 \times 10^8 eV$ in the denominator. The situation is different for the DM interaction in solids, i.e., the electrons are trapped in the strong potential of the atoms with large momentum distribution leading to the enhanced spin-orbit interaction. Therefore the gauge potential $A_{ij}$ could be (a fraction) of the order of unity, e.g. $A_{ij} \sim 2\pi$ as seen below.

To illustrate this, consider the electron energy levels in the ligand field of 3d-transition metal \cite{14}. In the octahedral ligand field, the d-orbitals are split into $e_g$ orbitals and $t_{2g}$ orbitals. The $t_{2g}$ orbitals, i.e., $d_{xy}$, $d_{yz}$, and $d_{zx}$, have energy lower than $e_g$ orbitals. If we take account of the spin degree of freedom, there is 6-fold degeneracy in $t_{2g}$ energy level. Due to the on-site spin-orbit interaction, however, this degeneracy is lifted and we have two groups of spin-orbit coupled states, labeled $\Gamma_7$ and $\Gamma_8$. The 2-fold degenerate states, i.e., $\Gamma_7$ and $\Gamma_8$, are given by

$$|a\rangle = \frac{1}{\sqrt{3}}(|d_{xy,\uparrow}| + |d_{xy,\downarrow}| + i|d_{zx,\downarrow}|),$$ \hspace{1cm} (6)$$

and

$$|b\rangle = \frac{1}{\sqrt{3}}(|d_{xy,\downarrow}| - |d_{yz,\uparrow}| + i|d_{zx,\uparrow}|),$$ \hspace{1cm} (7)$$

respectively, where the quantization axis of spin is taken to be the $z$ axis. For the sake of simplicity, we consider the above two states alone. However, our method is valid for more general cases and one can easily generalize it to any other spin-orbit strongly coupled situation.

We consider the case where the inversion symmetry exists at the middle point of the two magnetic ions, and the generic non-collinear magnetic ordering is realized by the competing exchange interactions $J$’s and/or by the symmetry breaking due to the spin-orbit interaction. Here the magnetic moment at $j$-th site points to the unit vector $\mathbf{e}_j = (\cos \phi_j, \sin \phi_j, \sin \theta_j, \cos \theta_j)$. The mean field Hamiltonian applied to the Josephson model is given by (we take the unit where $\hbar = 1$ hereafter): $H = -U \sum_j \mathbf{e}_j \cdot \mathbf{S}_j$, where $U$ is energy of Coulomb repulsion. For each site $j$, we restrict the Hilbert space to the 2-dimensional one spanned by the above two states, and the effective Hamiltonian is reduced to the $2 \times 2$ matrix

$$-\frac{U}{3} \left[ \begin{array}{ccc} -\cos \theta & \sin \theta e^{-i\phi} & \\
\sin \theta e^{i\phi} & \cos \theta \end{array} \right].$$ \hspace{1cm} (8)$$

We diagonalize this Hamiltonian matrix to obtain eigenstates $|P\rangle, |AP\rangle$ as

$$|P\rangle = \sin \frac{\theta}{2} |a\rangle + e^{i\phi} \cos \frac{\theta}{2} |b\rangle,$$

$$|AP\rangle = \cos \frac{\theta}{2} |a\rangle - e^{i\phi} \sin \frac{\theta}{2} |b\rangle.$$ \hspace{1cm} (9)$$

Here $|P\rangle$ and $|AP\rangle$ means the spin state parallel and anti-parallel to the unit vector $\mathbf{e}$, and the corresponding eigenvalues are $-\frac{U}{3}$ and $\frac{U}{3}$, respectively. For convenience, we define the coefficients $A^\sigma$ and $B^\sigma$ and abbreviate the above two states as, $|P\rangle = \sum_{\sigma} A^\sigma |d_{\sigma}\rangle$, $|AP\rangle = \sum_{\sigma} B^\sigma |d_{\sigma}\rangle$, where $\sigma = xy, yz, zx$. From now on, we focus on the three atom model as shown in Fig.1, which represents the bond between the two transition metal ions M1, M2 through the oxygen atom O. We take the hole picture below, where the oxygen orbitals are empty. We assume the generic case of $\mathbf{e}_1$ and $\mathbf{e}_2$ including the non-collinear configuration. Each site has two states, i.e., $|P\rangle$ and $|AP\rangle$, mentioned above. So we define $|P\rangle_j$ and $|AP\rangle_j$ ($j = 1, 2$) corresponding to the magnetic order on each site. Because of the existence of the oxygen atom, there are hopping processes between the M site and the O site. The transfer integrals between the $d$- and $p$-orbitals can be found in the Slater-Koster tables \cite{17,18}, and the hopping Hamiltonian is given as follows:

$$H_t = H_t^{1-m} + H_t^{m-1} + H_t^{2-m} + H_t^{m-2},$$

$$H_t^{1-m} = +V \sum_{\sigma} \langle p_{y,\sigma}^{\dagger} d_{z,\sigma}^{(1)} \rangle + \langle p_{z,\sigma}^{\dagger} d_{z,\sigma}^{(1)} \rangle = (H_t^{m-1})^\dagger,$$

$$H_t^{2-m} = -V \sum_{\sigma} \langle p_{y,\sigma}^{\dagger} d_{y,\sigma}^{(2)} \rangle + \langle p_{z,\sigma}^{\dagger} d_{z,\sigma}^{(2)} \rangle = (H_t^{m-2})^\dagger,$$
where \( V(>0) \) is the transfer integral and the superscript \( j \) denotes the corresponding site number. Let us now treat the above Hamiltonian perturbatively in \( V \). The eight bases we must prepare for this problem are \( |P\rangle_{j}, |AP\rangle_{j}, (j = 1, 2) \), and \( \tilde{p}_{i, \sigma}, (i = y, z, \sigma = \uparrow, \downarrow) \). Using the second-order perturbation theory, the four lowest lying states and corresponding perturbed energies are obtained as follows:

\[
|1\rangle = \frac{\alpha e^{-i \frac{\Delta\phi}{2}}}{\sqrt{2} |\alpha|} \left( |P\rangle_{1} + \frac{V}{\Delta} \sum_{\sigma} (A^{x, \sigma}_{(1)} |p_{y, \sigma}\rangle + A^{z, \sigma}_{(1)} |p_{z, \sigma}\rangle) \right) + \frac{1}{\sqrt{2}} \left( |P\rangle_{2} - \frac{V}{\Delta} \sum_{\sigma} (A^{x, \sigma}_{(2)} |p_{y, \sigma}\rangle + A^{z, \sigma}_{(2)} |p_{z, \sigma}\rangle) \right),
\]

with \( E_{1} = -\frac{4}{3} V^{2}(1 + |\alpha|) \),

\[
|2\rangle = -\frac{\alpha e^{-i \frac{\Delta\phi}{2}}}{\sqrt{2} |\alpha|} \left( |P\rangle_{1} + \frac{V}{\Delta} \sum_{\sigma} (A^{y, \sigma}_{(1)} |p_{y, \sigma}\rangle + A^{z, \sigma}_{(1)} |p_{z, \sigma}\rangle) \right) + \frac{1}{\sqrt{2}} \left( |P\rangle_{2} - \frac{V}{\Delta} \sum_{\sigma} (A^{y, \sigma}_{(2)} |p_{y, \sigma}\rangle + A^{z, \sigma}_{(2)} |p_{z, \sigma}\rangle) \right),
\]

with \( E_{2} = -\frac{4}{3} V^{2}(1 - |\alpha|) \), and two other higher energy states. Here \( \Delta(>0) \) is the energy difference between the p-orbitals and \( |P\rangle_{j}, \Delta \phi = \phi_{1} - \phi_{2}, \) and we have introduced the complex number \( \alpha = \frac{4}{3} \cos \frac{\Delta \phi}{2} e^{-i \frac{\Delta\phi}{2}} + \sin \frac{\Delta \phi}{2} e^{i \frac{\Delta\phi}{2}} \). Before calculating the expected value of the polarization, it is useful to note that only the following matrix elements are non-zero from the shapes of d- and p-orbitals:

\[
I = \int d^{3} \vec{r} \vec{e}_{j}^{(j)}(\vec{r}) \vec{p} \vec{r}, \quad (j = 1, 2),
\]

and its cyclic permutations. The integral \( I \) is approximately estimated as

\[
I \approx \frac{16}{3} Z_{O}^{5/2} Z_{M}^{7/2} \left( \frac{Z_{O} + Z_{M}}{2} \right)^{-6} a_{0},
\]

where \( a_{0} \) is the Bohr radius and \( Z_{O}/Z_{M} \) is the atomic number of O/M. We can easily check the above results by expanding wavefunctions in terms of lattice constant \( a \). So let us now calculate the expected value of polarization in the following two cases.

**Double-exchange interaction**— First, we consider the situation where only one hole is present. In this case, this hole is put into the ground state, determined by the above second order perturbation theory, and the expected value of polarization, \( \langle 1 | e | 1 \rangle / \langle 1 | 1 \rangle \), is given by

\[
\vec{P} \approx \frac{e V}{3 \Delta} \vec{e}_{12} \times (\vec{e}_{1} \times \vec{e}_{2})
\]

(10)

where \( \vec{e}_{12} \) is the unit vector parallel to the direction of the bond from site M1 to site M2, and \( \vec{e}_{12} \) is the angle between the two vectors \( \vec{e}_{1} \) and \( \vec{e}_{2} \), i.e., \( \vec{e}_{1} \cdot \vec{e}_{2} = \cos \theta_{12} \). Spin current \( \vec{J}_{s} \) is approximately given by \( \vec{J}_{s} \sim (V^{2}/\Delta) a_{0} (\vec{e}_{1} \times \vec{e}_{2}) / \cos \theta_{12} \), and eq. (10) can be rewritten as \( \vec{P} \sim (eV) \vec{e}_{12} \times \vec{J}_{s} \). Therefore the spin current is essential to the electric polarization.

**Superexchange interaction**— Next we consider the case of two holes. From a viewpoint of Hartree-Fock approximation, two holes are put into the ground state \( |1\rangle \) and the second low-lying state \( |2\rangle \), and the expected value of the polarization is given by the following form similar to (10):

\[
\vec{P} \approx \frac{-4e}{9 V \Delta} J \vec{e}_{12} \times (\vec{e}_{1} \times \vec{e}_{2}).
\]

(11)

In this case, we must pay attention to the difference of the normalization factor between the two perturbed states, i.e., \( \langle 1 | 1 \rangle^{-1} \approx 1 - 2(V^{2}/\Delta)^{2}(1 - |\alpha|) \) and \( \langle 2 | 2 \rangle^{-1} \approx 1 - \frac{2}{3}(V^{2}/\Delta)^{2}(1 + |\alpha|) \). Of course there are many other terms but this term mainly contributes. As the above result is order of \( (V/\Delta)^{3} \), one may think that the polarization is too small to observe. By using the superexchange interaction \( J \), i.e., \( J \approx V^{4}/(U \Delta^{2}) \), however, (11) can be rewritten as

\[
\vec{P} \approx \frac{-4e}{9 V \Delta} J \vec{e}_{12} \times (\vec{e}_{1} \times \vec{e}_{2}).
\]

(12)

Again this equation can be interpreted in terms of the spin current \( \vec{J}_{s} \) as \( \vec{P} \sim (eU/V \Delta) \vec{e}_{12} \times \vec{J}_{s} \). Therefore the magnitude is not too small on the ground that the ratio of \( U \) to \( \Delta \) is by no means small practically.

For more general models, the magnitude of the electric polarization induced by the spin current would differ from those obtained in the present model, and depends
the spin current $\vec{j}_x$ is along the $z$-direction, and the electric polarization $\vec{P}$ is along the $y$-direction for each site. Therefore the total uniform polarization is finite along the $y$-direction. Note that even when the spiral wavenumber $\vec{q}$ is incommensurate with the lattice periodicity, the uniform polarization, i.e., the ferroelectricity, is realized. When the spins are in the $yz$-plane (Fig. 2(c)), i.e., $\alpha = \pi/2$, both $\vec{e}_{jj+1}$ and $\vec{j}_x$ are in the $x$-direction and their vector product is zero. Therefore we do not expect any electric polarization induced in this case. Figure 2(d) shows the “conical” spin structure, where the finite $x$-component of the spin is induced starting from the structure in Fig. 2(c), i.e., $\alpha = \pi/2$, $0 < \beta < \pi/2$. In this case, the finite $S_x$ component at each site produces the rotating polarization, but these cancel out to zero uniform electric polarization.

Now consider the effect of the external electric field $E_y$ along the $y$-direction on the generic spiral configuration. This field induces uniform magnetization (per site), estimated as $\vec{m}_x \propto E_y \sin^2 \beta \cos \beta \sin \alpha \cos \sin q_j$ and $\vec{m}_y \propto E_y \sin^2 \beta \cos \beta \sin \alpha (a + b \cos \alpha)$ (a, b: constants). This dependence is consistent with the group theoretical consideration and the experiments on ZnCr$_2$Se$_4$ (Figures 6 and 7 of ref. 8).

Acknowledgements This work was supported by NAREGI and Grant-in-Aids for Scientific Research from MEXT, and US DOE LDRD at Los Alamos.

References

[1] P. Curie, J. Physique 3e series, 3, 393 (1894)
[2] L. D. Landau and E. Lifshitz, Electrodynamics of Continuous Media (Butterworth-Heinemann, Oxford, 2002) p. 176
[3] I. E. Dzialoshinskii, Sov. Phys.—JETP. 10, 628 (1960)
[4] M. Date, J. Kanamori, and Y. Tachiki, J. Phys. Soc. Jpn. 16, 2589 (1961)
[5] G. T. Rado and V. J. Folen, J. Appl. Phys. 33, 1126 (1962)
[6] I. Dzyaloshinskii, J. Phys. Chem. Solids 4, 241 (1958)
[7] T. Moriya, Phys. Rev. Lett. 4, 228 (1960); T. Moriya, Phys. Rev. 120, 91 (1960)
[8] K. Shiratori and E. Kita, J. Phys. Soc. Jpn. 48, 1443 (1980).
[9] Y.F. Popov et al., JETP. 87, 146 (1998)
[10] S. Murakami, N. Nagaosa, and S. C. Zhang, Science 301(5638), 1348 (2003); J. Sinova et al., Phys. Rev. Lett. 92, 126603 (2004).
[11] J. Konig, M. C. Bonsager, and A. H. MacDonald, Phys. Rev. Lett. 87, 187202 (2001); G. Tatara and N. Garcia, Phys. Rev. Lett. 91, 076806 (2003).
[12] A. Yoshimori, J. Phys. Soc. Jpn. 14, 807 (1959)
[13] T. Nagamiya, in Solid State Physics, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press, New York and London, 1967) Vol. 20, p.305
[14] Y. Aharonov and A. Casher, Phys. Rev. Lett. 53, 319 (1984)
[15] F. Meier and D. Loss, Phys. Rev. Lett. 90, 167204 (2003)
[16] H.Kamimura, S.Sugano, and Y.Tanabe, Multiplets of Transition-Metal Ions in Crystals (Academic Press, New York, 1970)
[17] J.C.Slater and G.F.Koster, Phys. Rev. 94, 1498 (1954)
[18] W. A. Harrison, Elementary Electronic Structure (World Scientific, Singapore, 1999) p.546
[19] P. W. Anderson and H. Hasegawa, Phys. Rev. 100, 675 (1955)
[20] For a microscopic theory of the antisymmetric spin interaction in metal, see M. Kataoka, et al., J. Phys. Soc. Jpn. 53, 3624 (1984).
[21] P. W. Anderson, in Solid State Physics, edited by F. Seitz and D.Turnbull (Academic Press, New York, 1963) Vol.14, p.99