Effect of orbital symmetry on the anisotropic superexchange interaction

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Abstract. Employing the microscopic superexchange model incorporating the effect of spin–orbit interaction, we have investigated the Dzyaloshinsky–Moriya (DM) interaction in perovskite transition-metal (TM) oxides and explored the interplay between the DM interaction and the TM-3d orbital symmetry. For $d^3$ and $d^5$ systems with isotropic orbital symmetry, the DM vectors are well described by a simple symmetry analysis considering only the bond geometry. In contrast, the DM interaction for $d^4$ systems with anisotropic orbital symmetry shows slightly different behavior, which does not obey simple symmetry analysis. The direction as well as the strength of the DM vector varies depending on the occupied orbital shape. We have understood this behavior based on the orbital symmetry induced by local crystal field variation.

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1. Introduction

Spin–orbit (SO) interaction is the most interesting relativistic effect in condensed matter physics. In solids, it gives rise to strong interplay among electronic, structural and magnetic degrees of freedom and brings about intriguing physical phenomena in cooperation with other physical parameters such as the crystal field, Coulomb correlation and spin exchange interaction. Therefore, SO coupling becomes a key ingredient in various research subjects that gained recent interest: multiferroics [1], spintronics [2] and topological insulators [3].

In general, the SO interaction is suppressed in transition-metal (TM) oxides because the strong crystal field lifts the degeneracy of localized orbitals and causes the orbital angular momentum to be almost quenched. Nevertheless, the SO interaction can have considerable effects in the limit of second-order perturbation [4]. The conventional superexchange interaction is described by the isotropic Heisenberg-type interaction. However, considering the effects of SO coupling on the conventional superexchange theory, additional anisotropic magnetic interactions emerge, the so-called Dzyaloshinsky–Moriya (DM) interaction and the pseudodipolar interaction [5, 6]. Then the magnetic interaction between adjacent magnetic ions is given by

$$H_{ij} = J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + D_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j) + \mathbf{S}_i \cdot \mathbf{R}_{ij} \cdot \mathbf{S}_j,$$

where the first, second and third terms refer to the isotropic superexchange, DM interaction and pseudodipolar interaction, respectively, where $\mathbf{R}_{ij}$ is the $3 \times 3$ symmetric matrix. The anisotropic interactions are known to play a crucial role in the weak ferromagnetism in α-Fe$_2$O$_3$ [7, 8] and RFeO$_3$ ($R$ = rare-earth) [9, 10], the strong magnetoelectric effect in multiferroic materials such as TbMnO$_3$ [11, 12], the reversal magnetization in YVO$_3$ [13] and the electron spin resonance (ESR) behavior in KCuF$_3$ [14].

The antisymmetric DM vector $D_{ij}$ can be determined by using a simple symmetry analysis [5]. When two magnetic ions interact via an intervening oxygen ion and the system has mirror symmetry with respect to the plane which includes three ions (see figure 1), $D_{12}$ is known to be perpendicular to the mirror plane ($D_{12} \propto \hat{x}_1 \times \hat{x}_2$). This feature was confirmed by microscopic derivation [15]. Therefore, in most of the existing literature the DM interaction has been analyzed by employing symmetry analysis. However, in symmetry analysis, one important aspect has not been considered carefully. Namely, it is overlooked that the orbital shape of magnetic ions could break the mirror symmetry that the bond geometry has. This aspect is not serious when dealing with the systems with isotropic $A_{1g}$ symmetry, e.g. TM oxides with $d^3$, $d^5$ and $d^8$ configurations. But it becomes important when considering the systems with anisotropic orbital symmetry, e.g. TM oxides with $d^4$ and $d^9$ configurations. In fact, the previous microscopic derivation was performed only for systems with $A_{1g}$ symmetry [15]. Even though the DM interaction for a system with $E_g$ symmetry was studied in relation to the magnetic interaction in cuprate systems [16, 17], the role of the orbital effect was not considered seriously in the symmetric property of the DM interaction.

In this study, we investigate the relation between the DM interaction and orbital symmetry in perovskite oxides for various d-orbital occupations: (i) orbital quenched $d^3$ and $d^5$ systems and (ii) strong Jahn–Teller (JT) $d^4$ systems. Solving the microscopic model incorporating the SO coupling, we demonstrate that the DM vector shows quite different behavior depending

$^2$ The additional anisotropic exchange terms of nondipolar type appear for $S > \frac{1}{2}$ (see [23]).
on the relevant orbital degrees of freedom, even though the systems have the same structural details.

2. Microscopic model

Let us consider the $M$–$O$–$M$ cluster to investigate the effect of the SO interaction on the superexchange interaction of TM systems (see figure 1). Here, the magnetic interaction between adjacent magnetic ions is mediated by a corner-shared ligand oxygen, as in perovskite manganites. Let us assume that \{\(\hat{x}_i, \hat{y}_i, \hat{z}_i\) \(i = 1, 2\) are local coordinate axes, by which the orbital states of TMs are described easily due to a strong crystal field, and \(\hat{\delta}_i\) refers to their spin direction. The effective Hamiltonian of the $M$–$O$–$M$ cluster is given by

$$H = \sum_{i,\mu_i} \varepsilon_{\mu_i} n_{\mu_i} + \frac{U_d}{2} \sum_{\mu_i,\nu_i,\sigma_i,\sigma_i'} n_{\mu_i\sigma_i} n_{\nu_i\sigma_i'} - \frac{J_d}{2} \sum_{\mu_i,\nu_i,\sigma_i} n_{\mu_i\sigma_i} n_{\nu_i\sigma_i'}$$

$$+ \sum_p \varepsilon_p n_p + \frac{U_p}{2} \sum_{pp\sigma\sigma', pp\sigma\sigma' \neq pp\sigma'\sigma} n_{pa\sigma} n_{p'\sigma'} - \frac{J_p}{2} \sum_{pp\sigma, pp\sigma \neq pp'\sigma'} n_{pa\sigma} n_{p'\sigma'}$$

$$+ \sum_{\mu_i,\rho_i,\sigma_i} t_{\rho_i\sigma_i}^{\mu_i\rho_i} [d_{\mu_i\sigma_i}^\dagger c_{\rho_i} + \text{h.c.}] + \sum_{i,\mu_i,\nu_i,\sigma_i,\sigma_i'} \tilde{t}_{\rho_i\sigma_i}^{\mu_i\rho_i} d_{\mu_i\sigma_i}^\dagger d_{\nu_i\sigma_i'}. \quad (2)$$

Here, \(d_{\mu_i\sigma_i}^\dagger\) is the creation operator of $M$ 3d-electron with \(\mu_i\) orbital and \(\sigma_i\) spin states at $i$-site, and \(c_{\rho_i}\) is the annihilation operator of O 2p-electron with \(p\) orbital and \(\sigma\) spin states. Local orbital state \(\mu_i\) is determined by local crystal symmetry, and \(\sigma_i\) is an eigenvalue of $\mathbf{S} \cdot \hat{\delta}_i$; \(U\) and \(J\) are the Coulomb and the exchange interaction parameter, respectively.\(^3\) Let \(D^{ij}\) and

\(^3\) We have used a simple form of the Coulomb interaction parameter in our model. The real Coulomb integrals depend on interacting orbital pairs. But the orbital dependence would cause only a small modification in the calculated values of the parameters \(J\), \(D\) and \(R\). According to \([16]\), \(\Delta D\) is expected to be \(\frac{2U_d}{R^2} D\); that is, the strength of \(D\) is slightly modified by \(\Delta U_d\). Therefore, the present simple treatment is valid to describe the overall behavior of the antisymmetric superexchange interaction for perovskite oxides.
\(\Sigma^{(i)}\) be transformation matrices from the global to local coordinates for orbital and spin parts, respectively. Then the hopping integral \(t_{\sigma_i\sigma_j}^{\mu_i\mu_j}\) and the SO matrix \(\tilde{t}_{\sigma_i\sigma_j}^{\mu_i\nu_j}\) can be expressed as

\[
t_{\sigma_i\sigma_j}^{\mu_i\mu_j} = \sum_{\nu\sigma'} (D_{\mu_i\mu})^* (\Sigma^{(i)}_{\sigma_i\sigma'})^* \delta_{\sigma \sigma'} t_{\sigma_i\sigma_j}^{\mu_i\mu_j},
\]

\[
\tilde{t}_{\sigma_i\sigma_j}^{\mu_i\nu_j} = \sum_{\mu\nu\sigma'\sigma} (D_{\mu\mu})^* (\Sigma^{(i)}_{\sigma_i\sigma})^* D_{\nu\nu'}^* \Sigma^{(i)}_{\sigma_j\sigma'} \tilde{t}_{\sigma\sigma'}^{\mu\nu},
\]

where \(\mu, \nu \in \{|x\rangle, |y\rangle, |z\rangle, |3z^2 - r^2\rangle, |x^2 - y^2\rangle\}\) and \(\tilde{t}_{\sigma\sigma'}^{\mu\nu} = \frac{i}{2} \sum \lambda \langle L_{\lambda\mu}(\sigma_i)\rangle \langle \sigma_{\sigma'} \rangle\). Due to the strong on-site Coulomb interaction, the ground state of the cluster should be contributed mainly by an \(M(3d^\nu) - O(2p^6) - M(3d^\nu)\) configuration. Only the hopping \((H_t)\) and SO \((H_{SO})\) terms in equation (2) give rise to a virtual overlap with other configurations. For this reason, we have considered the restricted Hilbert space of the \(M - O - M\) cluster, whose states are made to overlap with the ground state of \(M(3d^\nu) - O(2p^6) - M(3d^\nu)\) configuration via off-diagonal elements of \(H_{SO}, H_t\) and \((H_t)^2\). This assumption was found to be adequate to explore the superexchange interaction of insulating TM oxides [20, 21]. By setting the Hamiltonian matrix and diagonalizing it [22], we have calculated the ground state energies of given spin directions \(E [\hat{s}_1, \hat{s}_2]\). Assuming that the energy difference between two cases, in which only one has opposite spin direction, is given by equation (1), we can estimate \(J_{ij}, D_{ij}\) and \(\tilde{R}_{ij}\) by the following relations:

\[
J_{12} = \frac{1}{3} \sum_{\alpha} [\bar{J}_{12}]_{\alpha\alpha},
\]

\[
[D_{12}]_{\alpha\beta} = \epsilon_{\alpha\beta\gamma} ([\bar{J}_{12}]_{\beta\gamma} - [\bar{J}_{12}]_{\gamma\beta})/2,
\]

\[
[\tilde{R}_{12}]_{\alpha\alpha} = [\bar{J}_{12}]_{\alpha\alpha} - J_{12},
\]

\[
[\tilde{R}_{12}]_{\alpha\beta} = ([\bar{J}_{12}]_{\alpha\beta} + [\bar{J}_{12}]_{\beta\alpha})/2 \quad (a \neq b),
\]

where \(2[\bar{J}_{12}]_{\alpha\beta} S^2 = E [\hat{s}_\alpha, \hat{s}_\beta] - E [\hat{s}_\alpha, -\hat{s}_\beta]\). In this way, the contribution of the single-ion anisotropy energy, even when it exists, will be canceled when considering the energy difference between the two cases. Even though the additional nondipolar terms of the double-ion anisotropy, which were neglected in equation (1), could cause some numerical error when evaluating \([\bar{J}_{12}]_{\alpha\beta}\), it was shown that the effects of those terms are rather small and become averaged out to be vanishing at zero temperature [23].

3. Magnetic interaction

According to the symmetry analysis, the DM vector for the \(M - O - M\) cluster in figure 1 is parallel to the normal vector \(\hat{n}\) \((D \propto \hat{x}_1 \times \hat{x}_2)\). However, we have to take into account the effect...
of surrounding oxygens\textsuperscript{4}. As shown in figure 1, the mirror symmetry via the $M$–O–$M$ plane could be broken when two octahedra rotate around the $\hat{x}_1$ and $\hat{x}_2$ axes with angles $\delta_1$ and $\delta_2$, respectively. Indeed, the orthorhombic perovskite has nonzero $\delta_{1(2)}$ between $\hat{n}$ and $\hat{z}_{1(2)}$. In the case of the ideal orthorhombic perovskite system, which is characterized by the tilting angle $\omega$ and the $M$–O distance, the angle $\delta_{1(2)}$ is given by $\delta_{1(2)} = \cos^{-1} \left[ \pm \sin \omega + 2\sqrt{3} \cos \omega \sqrt{3 \cos^2 \omega - 1} \right] / \left( 2 + 4 \cos^2 \omega \right)$ for the $M$–O–$M$ triad in the $ab$-plane, and $\delta_1 = \delta_2 = \pi/4$ for that along the $c$-axis\textsuperscript{5}. Hence, they are always nonzero except for $\omega = 0$.

In conventional magnetic insulators, the charge transfer energy $\Delta$ of O-2p to $M$-3d orbitals is much larger than the crystal field splitting $10Dq$ of $M$-3d orbitals, and so the dominant role of surrounding oxygens is to provide the electrostatic potential for local $M$-3d orbital states. It means that finite $\delta_i$'s correspond to the rotation of occupied d-orbitals via $\hat{x}_i$'s and the behavior of the DM interaction with respect to $\delta_i$'s should be strongly coupled to the orbital symmetry of d-orbitals of magnetic ions. When three $t_{2g}$ or two $e_g$ orbitals in the $O_h$ crystal field have the same occupation, the orbital shape of occupied d-orbitals is isotropic and, in this case, the magnetic interaction could be independent of finite $\delta_i$'s. In contrast, when the population of a specific orbital, which has an anisotropic shape, is larger than those of others, the broken symmetry of surrounding oxygens should play a crucial role. Thus, to study the relation between orbital occupations and the DM interaction, we have considered the orthorhombic perovskite oxides LaCrO$_3$ and LaFeO$_3$ for the former case and LaMnO$_3$ for the latter case.

3.1. $A_{1g}$ symmetry

Let us first consider systems that have an isotropic orbital shape. Typical examples are perovskite oxides whose TM ions have 3d$^3$, 3d$^5$ and 3d$^8$ configurations, such as Cr$^{3+}$, Fe$^{3+}$ and Ni$^{2+}$. Owing to a strong cubic crystal field and the Hund coupling, these systems have $t_{2g}^3$, $t_{2g}^3 e_{g}^2$ and $t_{2g}^3 t_{2g}^1 e_{g}^2$ orbital occupations, respectively, so as to have the stabilized $A_{1g}$ orbital symmetry. As mentioned above, the bond geometry plays a crucial role in determining the direction of the DM interaction. To demonstrate this scenario, we have adopted relevant physical parameters (table 1) for LaCrO$_3$ (3d$^3$) and LaFeO$_3$ (3d$^5$) and evaluated their DM interactions as a function of bond angle.

Figure 2 provides the obtained DM vectors for the ideal orthorhombic perovskite systems ($Pbnm$ space group) with d$^3$ and d$^5$ configurations. Because there are four different TM sites in orthorhombic perovskites, there are a few different types of $M$–O–$M$ bonds. According to [26], the DM interactions associated with different bonds are characterized by five parameters due to the crystal symmetry. Our results are also characterized by the same parameters. Note that the $z$-component of the DM vector, $D_z$, for the $M$–O–$M$ triad along the $c$-axis is always zero for both the d$^3$ (figure 2(b)) and d$^5$ (figure 2(d)) cases.

Points in figure 2 refer to our calculated DM vector ($\mathbf{D}$), while lines denote the DM vector ($\mathbf{D}'$) whose direction is determined by the symmetry analysis ($\mathbf{D}' \propto \hat{x}_1 \times \hat{x}_2$), but the strength is taken to be the same as the calculated one. It is shown that $\mathbf{D}$ and $\mathbf{D}'$ are consistent with $\phi_{ab} = \cos^{-1} \left[ \frac{2 - 5 \cos^2 \omega}{2 + 4 \cos^2 \omega} \right]$ and $\phi_{c} = \cos^{-1} \left[ \frac{1 - 4 \cos^2 \omega}{3} \right]$, respectively.

\textsuperscript{4} $J_p$ is one of the parameters that determine the anisotropic superexchange interaction. Its effect, however, is negligible in the present case because two or more p-hole states are prohibited due to large $\Delta$.

\textsuperscript{5} Structural details of ideal orthorhombic perovskites have been presented by O’Keeffe and Hyde [37]. For ideal orthorhombic perovskites, the bond angles are determined by $\phi_{ab} = \cos^{-1} \left[ \frac{2 - 5 \cos^2 \omega}{2 + 4 \cos^2 \omega} \right]$ and $\phi_{c} = \cos^{-1} \left[ \frac{1 - 4 \cos^2 \omega}{3} \right]$.
Table 1. Physical parameters (in units of eV) employed in this study. Most of the parameters are taken from the literature [24, 25] together with some conventional parameter values for LaMO$_3$ systems. $10Dq$ is the crystal field splitting of d-orbitals and $\Delta$ is the charge transfer energy of oxygen p- to TM d-orbitals. For simplicity, we have set $J_p = 0.0$ eV.

| $M^{3+}$ | $10Dq$ | $\Delta$ | $U_d$ | $J_d$ | $U_p$ | $J_p$ | $t_{pd\sigma}$ | $t_{pd\pi}$ | $\lambda$ |
|----------|--------|----------|------|------|------|------|----------------|--------------|--------|
| Cr$^{3+}$ (d$^3$) | 1.6 | 5.5 | 5.2 | 0.60 | 3.0 | 0.0 | -2.25 | 1.19 | 0.034 |
| Mn$^{3+}$ (d$^4$) | 1.6 | 4.5 | 7.5 | 0.75 | 3.0 | 0.0 | -1.99 | 1.10 | 0.044 |
| Fe$^{3+}$ (d$^5$) | 1.8 | 2.5 | 7.5 | 0.80 | 3.0 | 0.0 | -1.66 | 0.88 | 0.057 |

Figure 2. The DM interaction for the ideal perovskite system with $A_{1g}$ symmetry (d$^3$ and d$^5$ cases) as a function of the bond angle $\phi$. For d$^3$ and d$^5$, we have adopted physical parameters for LaCrO$_3$ and LaFeO$_3$, respectively, as shown in table 1. Points represent the $x$-, $y$- and $z$-components of the DM vector ($D$) obtained by using our model. Lines represent components of the virtual DM vector ($D'$) whose direction is parallel to $\hat{n} = \hat{x}_1 \times \hat{x}_2$ and strength is assumed to be the same as $D$. The labels $ab$-plane and $c$-axis stand for the $M$–O–$M$ triad in the $ab$-plane and along the $c$-axis, respectively. The almost identical behavior of $D$ and $D'$ reflects that the DM vector for $A_{1g}$ symmetry is given by the simple symmetry analysis ($D \propto \hat{x}_1 \times \hat{x}_2$).
Table 2. Calculated DM vectors (in units of meV) of the LaMO\(_3\) systems. We assumed that local magnetic moments for \(M = \text{Cr, Fe and Mn}\) are 3/2, 5/2 and 2, respectively, and adopted bond angles, \(\phi_{\text{Cr}} = 161.4^\circ\), \(\phi_{\text{Fe}} = 159.1^\circ\), \(\phi_{\text{Mn}} = 155.5^\circ\) and \(\phi_{\text{Mn}} = 155.1^\circ\) from the literature [27, 28, 31]. The other parameters are presented in table 1. The isotropic superexchange parameters estimated in the present scheme are \(J_{\text{ab}} = 6.95\), \(J_{\text{ab}}^\text{Fe} = 6.61\), \(J_{\text{ab}}^\text{Fe} = 9.91\), \(J_{\text{ab}}^\text{Fe} = 9.95\), \(J_{\text{ab}}^\text{Fe} = -1.59\) and \(J_{\text{ab}}^\text{Fe} = 1.39\) (in units of meV). These \(J\)'s describe well the \(G\)-type AF state for LaCrO\(_3\) and LaFeO\(_3\) and the \(A\)-type AF state for LaMnO\(_3\).

| \(M\)     | \(D_x\)  | \(D_y\)  | \(D_z\)  | \(D/J\) | \(D_x\)  | \(D_y\)  | \(D/J\) |
|-----------|----------|----------|----------|---------|----------|----------|---------|
| Cr (d\(^3\)) | -0.028   | 0.028    | -0.039   | 0.006   | 0.008    | 0.062    | 0.009   |
| Fe (d\(^5\)) | -0.109   | 0.099    | -0.127   | 0.020   | 0.030    | 0.212    | 0.021   |
| Mn (d\(^4\)) | 0.237    | -0.215   | 0.177    | 0.245   | -0.060   | -0.034   | 0.049   |

are 0.095 meV for d\(^3\) (\(S = 3/2\)) and 0.290 meV for d\(^5\) (\(S = 5/2\)), respectively. We have also checked the relation between \(D\) and \(\lambda\). We have found that, regardless of the d-electron configuration and bond angle \(\phi\), components of \(D\) increase almost linearly from zero with \(\lambda\), as is consistent with Moriya’s perturbative derivation [6].

Based on these analyses, we have estimated the DM parameters of LaCrO\(_3\) and LaFeO\(_3\), which are 3d\(^3\) and 3d\(^5\) systems, respectively. We adopted experimental bond angles \(\phi_{\text{Cr}} = 161.4^\circ\) and \(\phi_{\text{Fe}} = 159.1^\circ\) for LaCrO\(_3\) [27] and \(\phi_{\text{Fe}} = 157.2^\circ\) and \(\phi_{\text{Mn}} = 156.4^\circ\) for LaFeO\(_3\) [28]. The evaluated DM parameters are presented in table 2. The canting angle between adjacent two spins is given by \(\tan^{-1}(D/J)\). Then the canting angles for LaCrO\(_3\) and LaFeO\(_3\) are estimated to be 0.52° and 1.20°, respectively. The latter for LaFeO\(_3\) is in agreement with the experimental value [29] of 1.03°. Also, for LaCrO\(_3\), the very small value of \(D/J\) is consistent with the experimental observation that only the strong \(G\)-type antiferromagnetic (AF) order is detected in neutron powder diffraction without noticeable intensity for the \(F\)-type order [30].

3.2. \(E_g\) symmetry

In the case of d\(^4\) and d\(^5\) configurations such as Mn\(^{3+}\) and Cu\(^{2+}\), the perovskite oxides suffer another lattice deformation due to the JT distortion. Strong coupling between doubly degenerate \(e_g\) levels and the JT modes, orthorhombic \(q_2\) and tetragonal \(q_3\) modes, produces the \(C\)-type orbital ordering. Two \(e_g\) levels, \(|\theta\rangle\) and \(|\theta + \pi\rangle\), are split by \(\Delta_{JT}\), and occupied \(e_g\) orbitals are alternatively ordered by \(|\theta\rangle/|2\pi - \theta\rangle\) in the \(ab\)-plane and \(|\theta\rangle/|\theta\rangle\) along the \(c\)-axis, where \(\theta = \tan^{-1} \left( \frac{q_3}{q_1} \right) \) and \(|\theta\rangle = \cos \frac{\theta}{2} |x^2 - y^2\rangle + \sin \frac{\theta}{2} |x^2 + y^2\rangle\). Thus d-orbitals at each site have an anisotropic orbital shape, as shown in figure 3(a). In these cases, the finite \(\delta_i\)’s break the mirror symmetry via the \(M-O-M\) plane, and thereby the DM vector should be influenced by this broken symmetry.

Considering the level splitting of \(e_g\) levels due to the \(C\)-type orbital ordering, we have investigated the magnetic interactions of the LaMnO\(_3\) system. Figures 3(b) and (c) show the DM vector behavior for \(M-O-M\) with d\(^4\) configuration as a function of bond angle \(\phi\). Here the JT parameter \(\theta\) is set to 108° that corresponds to \(\theta\) of LaMnO\(_3\) [31], and \(\Delta_{JT}\) is set to
0.9 eV. Other physical parameters are presented in table 1. Noteworthy is the clear deviation between $\mathbf{D}$ and $-\mathbf{D}'$, which is in contrast to the cases of $d^3$ and $d^5$. For $M$–O–$M$ in the $ab$-plane (figure 3(b)), strengths of calculated $D_x$ and $D_z$ are reversed in comparison to $D'_x$ and $D'_z$, even though the deviation is not so large. The disparity becomes evident for $M$–O–$M$ along the $c$-axis (figure 3(c)). Whereas both $D_x$ and $D_y$ are of similar size ($D_x \sim 1/2 D_z$), $D'_y$ predominates over $D'_x$; that is, $\mathbf{D}'$ is really close to the $b$-axis. This finding reflects that the orbital symmetry, induced by ordering of anisotropic $e_g$ orbitals, yields a DM vector that does not follow the conventional form of $\mathbf{D} \propto \hat{x}_1 \times \hat{x}_2$.

For LaMnO$_3$, the DM vector for Mn–O–Mn along the $c$-axis was found to be inconsistent with that from the symmetry analysis; that is, it is not perpendicular to the plane consisting of the corresponding Mn–O–Mn ions. Mochizuki and Furukawa [32] speculated that this disparity may arise from the additional contribution of indirect paths containing more than one oxygen. But our results in figure 3(c) verify that the anisotropic orbital symmetry of Mn-3d orbitals in LaMnO$_3$ is the origin of the disparity.
Let us examine more carefully the DM interaction for LaMnO$_3$. We adopted the bond angles $155.5^\circ$ in the $ab$-plane and $155.1^\circ$ along the $c$-axis [31] and assumed that $S = 2$. Estimated DM parameters are presented in table 2. The absolute value of the DM vector for Mn–O–Mn along the $c$-axis is about 0.069 meV, which is in good agreement with experimental value of 0.086 meV from the ESR measurement [33]. The ratio of $D/J = 0.049$ along the $c$-axis is also reasonable in view of the experimental value of $D/J \sim 0.045$, which is estimated from the weak ferromagnetic moment of 0.18μ$_{B}$/Mn in the $A$-type LaMnO$_3$ [34]. For Mn–O–Mn in the $ab$-plane, however, our estimated DM parameters seem to be inconsistent with the existing ESR experiment [35]. It was reported that the DM vector for Mn–O–Mn in the $ab$-plane is about four times smaller than that along the $c$-axis. In our calculation, its value in the $ab$-plane is about four times larger than the other. At the moment, we do not know the source of this discrepancy, which remains to be resolved.

We have checked the behavior of $\mathbf{D}$ with respect to $\lambda$ for the $d^4$ system. As in $d^3$ and $d^5$ systems, components of $\mathbf{D}$ increase almost linearly, and a very small variation of $J_{ab}$ and $J_c$ takes place in the limit of $\lambda < 0.1$ eV. There is no change of the magnetic state with respect to $\lambda$. According to Horsch et al [36], spin and orbital states of $d^2$ systems exhibit complex phase diagrams depending on the SO and Hund-coupling strengths. Fortunately, the $d^4$ system of present interest suffers the strong JT distortion ($\sim 0.9$ eV). The orbital fluctuation is totally suppressed, and the orbital moment is almost quenched. For this reason, its magnetic behavior with respect to $\lambda$ is similar to that of orbital inert systems.

To explore the relation between the DM interaction and orbital symmetry more precisely, we have investigated the DM vector behavior with respect to the JT parameter $\theta$ and the rotation angle $\delta$. The $\theta$ dependence of the DM vectors in the $ab$-plane and along the $c$-axis is presented in figures 4(a) and (b). In all cases, the DM vector varies depending on the occupied orbital details, even though there is no change of structural details, i.e. the bond geometry. As for the $\delta$ dependence in figures 4(c) and (d), we have considered an artificial $M$–O–$M$ triad, where all cluster geometry, except for $\delta$ ($\delta_1 = \delta_2 = \delta$), is the same as that of the triad along the $c$-axis in the ideal perovskite structure. At $\delta = 0^\circ$ and $90^\circ$, the direction of the DM vector is parallel to $\hat{x}_1 \times \hat{x}_2$ because the mirror symmetry via the $M$–O–$M$ plane is preserved. However, in other cases, not only its direction but also strength vary depending on $\delta$. In contrast, the DM vector for the $d^5$ system is almost independent of the variation of $\delta$, as shown in figure 4(d). This finding reveals that the DM interaction in the case of $E_g$ symmetry is strongly coupled with the orbital degree of freedom as well as the bond geometry. When discussing the properties of multiferroic perovskite manganites, Sergienko and Dagotto [12] stated in the conclusion that the DM interaction is independent of the orbital structure, and it involves only the interaction between spins induced by the symmetry-breaking ionic displacements. It is apparent that their statement is not consistent with our findings. Since the induced electric polarization in their study is mostly due to the DM vectors for Mn–O–Mn in the $ab$-plane, their conclusion may still be valid in many cases (see figure 3(b)). Nevertheless, it should be pointed out that their statement could not be always right for multiferroic perovskites including Mn ion.

4. Conclusion

Employing the microscopic superexchange model incorporating the effect of the SO interaction, we have studied the DM interaction in the perovskite oxides with $A_{1g}$ ($d^3$ and $d^5$) and $E_g$ ($d^4$) orbital symmetry. In orthorhombic perovskite oxides, $M$–O–$M$ mirror symmetry is broken due
Figure 4. The JT parameter $\theta$-dependent behavior of the DM vector (a) in the $ab$-plane for $\phi = 155.5^\circ$ and (b) along the $c$-axis for $\phi = 155.1^\circ$. The $\delta$-dependent behavior of the DM vector (c) along the $c$-axis for $d^4$ configuration with $\phi = 155.5^\circ$ and (d) for $d^5$ configuration with $\phi = 156.4^\circ$. For (c) and (d), we considered the $M–O–M$ triad along the $c$-axis in the ideal perovskite structure and assumed that $\delta_1 = \delta_2 = \delta$. 

to finite $\delta_1$ ($\delta_2$) (see figure 1). This kind of broken symmetry is not crucial for $A_{1g}$ cases. The hopping property between two adjacent magnetic ions does not depend on $\delta$'s due to isotropic orbital shape. Hence, the DM interaction is given by the conventional form ($D \propto \hat{x}_1 \times \hat{x}_2$).

In contrast, for the $E_g$ ($d^4$) system that has stabilized orbital ordering, an occupied $e_g$ orbital shape strongly depends on $\delta$ and $\theta$. This kind of orbital shape change affects the hopping property. It implies that the broken mirror symmetry gives rise to unconventional DM vector behavior; that is, the DM vector is not proportional to $\hat{x}_1 \times \hat{x}_2$. That is why the DM interaction in the perovskite manganite shows symmetric behavior quite different from that in the perovskite chromate or ferrite.

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