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Spin-Frustrated Trinuclear Cu(II) Clusters with Mixing of 2(S = 1/2) and S = 3/2 States by Antisymmetric Exchange. 2. Orbital Origin of In-Plane Dzialoshinsky–Moriya Exchange Parameters

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The microscopic origin of the in-plane (G_x, G_y) and out-of-plane (G_z) Dzialoshinsky–Moriya (DM) exchange parameters is considered for the Cu_3(II) clusters. For the systems with the $d_{x^2-y^2}$ ground state of the Cu ions, only *Z* components of the pair DM exchange parameters are active ($G_z \neq 0$, $G_{x,y} = 0$) in the cases of the orientations of the local anisotropy axes z_i parallel ($z_i \| Z$) and perpendicular ($z_i \perp Z$, $x_i \| (-Z)$) to the molecular trigonal *Z* axis. The dependences of the G_x, G_y, and G_z DM exchange parameters on the tilt of the local magnetic orbitals were obtained for the antiferromagnetic (AFM) clusters with the $d_{x^2-y^2}$ and d_{z^2} ground state of the Cu ions. The tilt of the local $d_{x^2-y^2}$ orbitals results in the change of the G_z parameter and appearance of the in-plane DM exchange interactions (G_x or/and G_y parameters). The dependence of the G_z and G_x, G_y DM exchange parameters on the tilt angle is essentially different. The in-plane DM exchange coupling (G_x, G_y parameters) can significantly exceed the out-of-plane DM coupling (G_z parameter). The nonzero G_z and G_x, G_y parameters can be positive or negative. For the {Cu_3} nanomagnet with the $d_{x^2-y^2}$ ground state and relatively strong DM coupling, the model explains the three DM exchange parameters of the same value ($|G_z| = |G_x| = |G_y|$) by the small tilt of the local anisotropy axes z_i of the CuO_4 local groups of the trimer from the positions $z_i \perp Z$. The dependence of the DM exchange parameters (G_z, G_x, G_y) on the tilt for the AFM Cu_3 clusters with the d_{z^2} ground states of the Cu ions differs significantly from that for the AFM systems with the ground state $d_{x^2-y^2}$ of the individual ions. Large in-plane DM exchange parameters G_x or/and G_y result in the mixing of the 2(S = 1/2) and S = 3/2 states and zero-field splitting (ZFS) $2D_{DM}$ of the excited S = 3/2 state. The DM exchange contribution $2D_{DM}$ to ZFS of the excited S = 3/2 state possesses the significant dependence on the tilt of the local magnetic orbitals.

1. Introduction

The spin frustration in the ground 2(S = 1/2) state of the AFM Cu_3 clusters makes them the best candidates for the experimental observation of the Dzialoshinsky–Moriya[1,2] (DM) exchange interaction

$$H_{DM} = \sum \mathbf{G}_{ij}[\mathbf{S}_i \times \mathbf{S}_j] \tag{1}$$

as well as the effects of distortions.[3] The DM exchange and the cluster distortions were found in the Cu_3(II) clusters[3–11] (see Table 1 of ref 12). The DM exchange is also active in the 2(S = 1/2) ground state (GS) of the V_3(IV),[13,14] Cr_3(III),[3,15,16] Fe_3(III),[3,15,17–19] [Cr_2Fe], [Fe_2Cr],[3,20] and Co_3(II)[21] clusters. The DM exchange determines the spin canting of the 2*D kagome* lattice formed of the [Fe_3]

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triangles.[22,23] The G_z DM parameter determines ZFS $\Delta_z^0 = |G_z|\sqrt{3}$, magnetic anisotropy and EPR characteristics of GS 2(S = 1/2) of the trigonal Cu_3 cluster,[3–11] $G_z = (G_{12,Z} + G_{23,Z} + G_{31,Z})/3$, $Z||C_3$. The Cu_3 clusters[7–10] are characterized by the large DM(z) exchange parameters G_z = 28–47 cm^{-1},[7–10] G_z/J_{av} = 0.155–0.225, $G_{x,y} = 0$. The microscopic origin of the large G_z parameter was explained by Solomon et al. for the AFM[9a] and FM[10a] Cu_3 clusters by the large overlap of the d-functions of the neighboring Cu ions in the ground and excited states. There is no mixing of the 2(S = 1/2) and S = 3/2 states[9a] for the Cu_3 clusters with $G_z \neq 0$, $G_{x,y} = 0$.

The effect of quantum magnetization, owing to the spin-frustrated 2(S = 1/2) doublets of the AFM {Cu_3} nanomagnet[11a] and V_3 cluster[14] (as well as V_3 clusters of the V_{15} molecular magnet[24–29]), was described[11a,14] by the mixing of GS 2(S = 1/2) and excited S = 3/2 state in the point of their crossing at high magnetic fields ($g\mu_B H = 3J/2$) due to the relatively strong in-plane DM exchange coupling, $G_{x,y}/J_{av} = 0.12$[11a] (G_x, G_y are the components of the pair DM exchange vectors lying in the plain of the trimeric cluster[11a,14,24–29]).

The in-plane components G_x, G_y of the DM vector contribute significantly to the zero-field splitting (ZFS) of the S = 3/2 state of the Cu_3 clusters[12] and V_{15} molecular magnet.[28a] However, the microscopic conditions of the existence of the in-plane components of the DM exchange for the {Cu_3} clusters were not considered in the previous publications concerning the spin-frustrated Cu_3 and V_3 clusters, where G_x, G_y DM exchange parameters play the principal role.[11a,14,24–29]

The correlation between the geometrical arrangement of the local coordinate systems of the Cu ions and molecular g-factors of the S = 3/2 state of the {Cu_3} nanomagnet was discussed in ref 11b. The observation[11b] of the $g_{||} = 2.060$ ($||C_3$) and $g_\perp = 2.243$ components of the molecular g-factor of the S = 3/2 state was explained by the local parallel direction z_i^{loc} (which corresponds to $g_{||}^{loc}$) perpendicular to Z and the local perpendicular directions (which correspond to $g_\perp^{loc}$) agree with the cluster Z (C_3) axis.[11b] The magnetic and EPR data of this {Cu_3} nanomagnet was described[11a] by the three components $G_x = G_y = G_z$ (= 0.37 cm^{-1}) of the pair $\mathbf{G}_{ij}$ vectors. The correlations between the geometrical arrangement of the local coordinate systems of the Cu ions and the G_x, G_y, G_z parameters, as well as the origin of the three DM parameters of the same relatively large value, were not considered in ref 11a.

Chirality of the S = 1/2 GS is important for explanation of the magnetism at high magnetic fields of the {Cu_3}[11a] and [V_3][14] nanomagnets. The sign of G_z determines chirality of GS. The microscopic conditions for the $G_z > 0$ or $G_z < 0$ parameters of the {Cu_3} nanomagnet were not considered.

In this paper, we investigate the microscopic origin of the in-plane G_x, G_y and out-of-plane G_z components of the vector

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coefficient $\mathbf{G}_{ij}$ of the DM exchange coupling in the Cu_3 clusters, the dependences of the sign and value of the G_x, G_y, G_z DM parameters on the tilt of the local magnetic orbitals for the AFM clusters with GS $d_{x^2-y^2}$ and d_{z^2} of the Cu ions, the correlations between the local magnetic anisotropy of the Cu ions and the DM exchange parameters, and the influence of the tilt of the local d-orbitals on ZFS of the S = 3/2 state.

2. Microscopic Origin of the DM Exchange Parameters of the Cu_3 Clusters with the Local z_i Axes Parallel to the Cluster Z Axis ($z_i \| Z$)

The orientation and the value of the pair DM vectors $\mathbf{G}_{ij}$ play an important role in the mixing of the 2(S = 1/2) and S = 3/2 states of the Cu_3 clusters. We consider the antisymmetric exchange in the Moriya[2] model of the DM coupling of the superexchange origin (eq 2) that allows obtaining the dependence of the DM exchange parameters on the tilt of the magnetic orbitals, finding the conditions of the existence of the in-plane DM exchange and correlation between the G_z and G_x, G_y DM coefficients. In the case of the superexchange coupling, the DM exchange coefficients for the [ab] pair was derived by Moriya[2] in the form

$$\mathbf{G}_{ab} = 8it\mathbf{C}_{ab}/U = 2i\mathbf{C}_{ab}J/t$$

$$\mathbf{C}_{ab} = -(\lambda/2)[(\langle e_a|\mathbf{L}_a|g_a\rangle^*/\Delta(g_a, e_a))t(e_a, g_b) + (\langle e_b|\mathbf{L}_b|g_b\rangle/\Delta(g_b, e_b))t(g_a, e_b)] \quad (2)$$

where λ is the spin–orbital coupling (SOC) parameter, $\Delta(g_a, e_a) = \Delta_g^e$ is the energy interval between GS $|g_a\rangle$ and excited $|e_a\rangle$ states of the a center, $\langle e_a|\mathbf{L}_a|g_a\rangle^*$ is the complex conjugate of the matrix element[30,31] of the orbital angular momentum operator $\mathbf{L}_a$ that couples $|g_a\rangle$ and $|e_a\rangle$, ab = 12, 23, 31; $t(e_a, g_b) = \langle e_a||g_b\rangle$ denotes the transfer of a hole between the excited (e_a) and ground (g_b) orbitals on the a and b sites, $J = 4t^2/U$ is the Anderson parameter of superexchange,[2] U is the constant of the Coulomb interaction between holes on the Cu site, $t = t(g_a, g_b)$ denotes the transfer of a hole between the ground orbitals.[2] The DM exchange parameters depend on the ground and excited states, orientation of the local coordinate systems and the overlap of the neighboring d-functions in the Cu_3 cluster.

We shall consider first the conditions of the existents of the pair in-plane DM(x, y) exchange parameters G_x, G_y of the Cu_3 clusters with GS $d_{x^2-y^2}$ of the Cu ions. In the case of the Cu_3 cluster with the lobes of the $d_{x^2-y^2}$ and d_{xy} magnetic orbitals lying in the plane of the triangle, the local parallel directions (z_i axes) are parallel to molecular Z (C_3) axis, the local x_i axes (local perpendicular directions) of the ith ion are oriented from the ith metal ion through the center O of the triangle, y_i and x_i lie in the plane of the triangle (the local coordinate systems of the center 1 are shown in Figure 1 with $\alpha = 0$, $x_3 \| X$, $y_3 \| Y$, $z_3 \| Z$). In this case, the components of the molecular g-factor $g_{\|}^{mol}$ and $g_{\perp}^{mol}$ of the S = 3/2 state

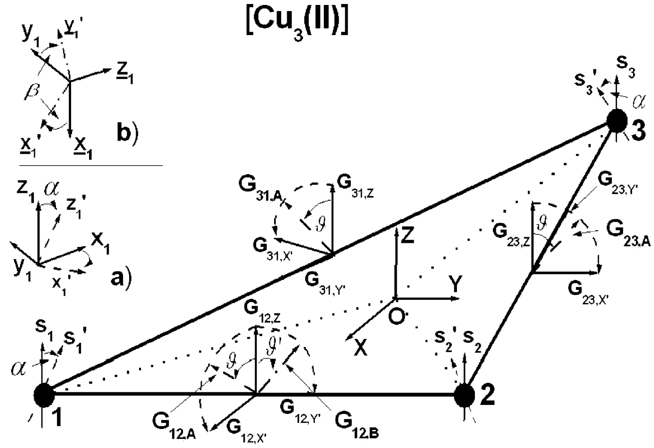

Figure 1. Local x_i, y_i, z_i, pair X_{ij}', Y_{ij}', Z_{ij}' and cluster XYZ coordinate systems of the Cu_3 cluster. (a) $z_i \| C_3$. (b) $z_i \perp C_3$.

coincide with the components of the local axial g-factors $g_{\|}^{mol} = g_{\|}^{loc}$, $g_{\perp}^{mol} = g_{\perp}^{loc}$. The angle between the neighboring local x_i [y_i] and x_j [y_j] axes is 120°. The correlations between the pair coordinate systems X_{ij}', Y_{ij}', Z_{ij}' in Figure 1 and the cluster coordinate system (XYZ) have the form $X_{12}' = X$, $Y_{12}' = Y$; $X_{23}' = -1/2X + \sqrt{3}/2Y$, $Y_{23}' = -\sqrt{3}/2X - 1/2Y$; $X_{31}' = -1/2X - \sqrt{3}/2Y$, $Y_{31}' = \sqrt{3}/2X - 1/2Y$; $Z_{ij}' = Z$ ($Z_{ij}' \| Z$). Following the consideration of the DM exchange in the slightly tilted Cu(II) dimers[2,32,33] and antisymmetric double exchange in the mixed-valence trimers,[34,35] the local 3d-orbitals ($d_{(x^2-y^2)i} = d^i_{(x^2-y^2)}$, $d_{(z^2)i}$, $d_{(xy)i}$, $d_{(yz)i}$, $d_{(xz)i}$) of the centers $i = 1$, $j = 2$ were written in the local coordinate system (x_3, y_3, z_3) of the third ion, which coincides with the cluster coordinate system XYZ (eq S1 in the Supporting Information). In the case of the angle α = 0 in Figure 1, the nonzero electron-transfer (ET) integrals between the ground $d_{(x^2-y^2)i}$ and excited $d_{(xy)j}$ states (t') of the neighboring (ij) ions of the trimer, relevant for the DM coefficients $\mathbf{G}_{ij}$ in eq 2, have the form $t' = t[d_{(x^2-y^2)i}, d_{(xy)j}] = -t[d_{(xy)i}, d_{(x^2-y^2)j}] = \sqrt{3}/2t_{X^2-Y^2}$ where ij = 12, 23, 31; $t_{X^2-Y^2} = \langle d_{(x^2-y^2)i}||d_{(x^2-y^2)j}\rangle$ is the ET integral in the cluster coordinate system. The ET integrals t between the ground $d_{(x^2-y^2)i}$ and $d_{(x^2-y^2)j}$ states, which determine the Anderson superexchange parameter J, have the form $t = t[d_{(x^2-y^2)i}, d_{(x^2-y^2)j}] = -1/2t_{X^2-Y^2}$. In the trigonal cluster, the ground-to-ground (t) and ground-to-excited (t') states ET parameters are both effective and differ in sign, the relations $t_{X^2-Y^2} = t_{XY}$ and $t_{XZ} = t_{YZ}$ take place.[34,35] In the Cu_3 cluster, the local $d_{(x^2-y^2)i}$ ground state is SO coupled with the $d_{(xy)i}$ excited-state via L_z^i operator ($\langle d_{xy}|L_z|d_{x^2-y^2}\rangle = 2i$[31]), the projections of the L_i operator on the Z axis are $L_z^i = L_z^i$. By substituting t' in eq 2, one obtains the pair DM exchange parameters $G_{ij,K'} = G_k$ (ij = 12, 23, 31) in the case $z_i \| Z$

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$$G_z = -4\sqrt{3}\lambda(t_{X^2-Y^2})^2/U\Delta^{xy}_{x^2-y^2} = -4\sqrt{3}\lambda J_0/\Delta^{xy}_{x^2-y^2},\quad G_x = G_y = 0 \quad (3)$$

where $\Delta^{xy}_{x^2-y^2} = \Delta(x^2 - y^2, xy)$ is the energy interval between the ground $d_{(x^2-y^2)i}$ and excited $d_{(xy)i}$ states and $J_0 = (t_{X^2-Y^2})^2/U$ is the Anderson parameter of the superexchange[2] between the ground states. Only G_z components (3) of the pair DM exchange parameters are nonzero, $G_{12,Z} = G_{23,Z} = G_{31,Z} = G_z$, $G_{ij,Z'} = G_{ij,Z}$ in Figure 1. The pair "in-plane" DM exchange parameters are equal to zero: $G_{ij,X'} = G_x = 0$, $G_{ij,Y'} = G_y = 0$ in Figure 1. The rotation of the lobes of the $d_{(x^2-y^2)i}$ and $d_{(xy)i}$ magnetic orbitals (or the tilt of the local coordinate (x_iy_i) axes) in the plane of the triangle around the local z_i ($\|Z$) axes does not change the result (3): $G_x = G_y = 0$ in the cluster with $g_{\|}^{mol} = g_{\|}^{loc}$, $g_{\perp}^{mol} = g_{\perp}^{loc}$. There is no DM($x$, y) exchange mixing between the 2(S = 1/2) and S = 3/2 states in the case of $z_i\|Z$.

The parameter $-\lambda/\Delta^{xy}_{x^2-y^2}$ ($=\Delta g_{\|}(Cu^{2+})/8$[30]) in eq 3 has the value 0.02–0.03,[30] that results in the large positive DM(z) parameter $G_z \approx (0.14–0.21)J_0$ for the Cu_3 clusters with $z_i\|Z$. This estimate is close to the values of the relations G_z/J_{av} in the range 0.12–0.21 observed experimentally for the Cu_3 clusters[7–10] (see Table 1 in ref 12). For the Cu_3 clusters with the interion superexchange coupling, Eq 3 explains the possibility of the large DM(z) exchange parameters G_z, which exceed by the order magnitude the Moriya estimate[2] $G_z \approx (\Delta g/g)J \approx (0.01–0.02)J$ in the dimers with the small angle between the z_i and z_j axes of the neighboring ions.

The microscopic origin of the large DM exchange parameter G_z in the AFM and FM Cu_3 clusters was explained by Solomon et al.[9a,10a] in the Moriya[2] model of the DM parameters $\mathbf{G}_{ab}$ in the case of the direct exchange interaction. For the AFM Cu_3 cluster with $z_a\|Z$, only the Z component of the DM exchange is active[9a]

$$G_z = -8(\lambda/\Delta_{xy})J^{(xy)_a(x^2-y^2)_b}_{(x^2-y^2)_a(x^2-y^2)_b}$$

where

$$J^{e_ag_b}_{g_ag_b} = \langle g_ag_b\|g_be_a\rangle$$

is the exchange integral[9a] between the ground and excited states (see ref 9a). The large magnitude of G_z was explained[9a] by the presence of the effective exchange pathways in the ground-to-excited states exchange mechanism. There is no mixing of the S = 3/2 and 2(S = 1/2) states since $G_x = G_y = 0$.

The result (3): the trigonal AFM Cu_3 clusters with $z_i\|Z$ are characterized by the large G_z parameter ($G_x = G_y = 0$), which was obtained in the Moriya superexchange model[2] (eq 2), confirms the conclusion[9a] about the large DM exchange parameter G_z in the trigonal AFM Cu_3 clusters with $z_i\|Z$, which was obtained[9a] in the model of the direct exchange.

The Moriya[2] coefficient Γ^{zz}_{ab} of the anisotropic exchange coupling $H_{AN} = \sum \mathbf{S}_a\mathbf{\Gamma}_{ab}\mathbf{S}_b$ is proportional to $(\lambda/\Delta_{xy})^2$ or $(\Delta g_{\|}/g)^2$ $\{\Gamma^{zz}_{ab} = (J_0/t^2)C^{Z}_{ab}C^{Z}_{ba} = 12J_0(\lambda/\Delta_{xy})^2\}$, that results in the estimate $\Gamma^{zz}_{ab} \approx (0.005–0.011)J_0$ with the parameter $-\lambda/\Delta_{xy} = 0.02–0.03$.[30] For comparison, the anisotropic exchange contribution $2D_0 = I^{zz} = 0.0195$ cm^{-1}[12] to ZFS of the S = 3/2 state of the {Cu_3} nanomagnet has the value of 0.7% of the Heisenberg parameter[11a] $J_{av} = 2.92$ cm^{-1}.

3. DM Exchange Parameters for the Clusters with $z_i\perp Z$

The other geometrical arrangement of the local coordinate systems of the Cu ions with GS $d_{(x^2-y^2)i}$ was discussed by Kortz et al.[11b] for the {Cu_3} nanomagnet. The observed $g_{\|} = 2.060$ ($\|C_3$) and $g_{\perp} = 2.243$ components of the molecular g-factor for S = 3/2 state was explained[11b] by the geometrical arrangement of the CuO_4 local groups of the trimer with their local parallel directions $\underline{z}_i$ perpendicular to the C_3 axis and the perpendicular local directions agree with the cluster C_3 axis. In this case, the cluster (molecular) g-factors were presented in the form $g_{\|}^{mol} = g_{\|}^{loc}$, $g_{\perp}^{mol} = (g_{\|}^{loc} + g_{\perp}^{loc})/2$, $g_{\|}^{loc} = 2.426$, $g_{\perp}^{loc} = 2.060$.[11b] For this arrangement with the local $\underline{z}_i$ axes oriented along the iO lines from the ith metal ion through the center O of the triangle, Figure 1, $\alpha = 90°$, the local $\underline{x}_i$ axes are antiparallel to Z, $\underline{y}_i$ ($=y_i$) and $\underline{z}_i$ lie in the plane of the triangle (the local $\underline{x}_1$ $\underline{y}_1$ $\underline{z}_1$ axes are shown in Figure 1b for the center 1). The lobes of the $d_{(\underline{x}^2-\underline{y}^2)}i$ and $d_{(\underline{xy})i}$ magnetic orbitals lie in the plane perpendicular to the plane of the triangle. In this case, the local d-functions in the cluster coordinate system are described by eq S2 of the Supporting Information. The nonzero ET integrals (1) $\underline{t}_{ij}' = \underline{t}'$—between the ground $d_{(\underline{x}^2-\underline{y}^2)}i$ and excited $d_{(\underline{xy})j}$ states, ij = 12, 23, 31 (relevant for $\mathbf{G}_{ab}$ in eq 2) and (2) $\underline{t}_{ij} = \underline{t}$—between the $d_{(\underline{x}^2-\underline{y}^2)}i$ and $d_{(\underline{x}^2-\underline{y}^2)}j$ ground states have the form $\underline{t}' = \sqrt{3}t_{X^2-Y^2}/4$, $\underline{t} = 1/8(6t_{Z^2} - t_{X^2-Y^2})$, respectively. In this cluster, the local $d_{(\underline{x}^2-\underline{y}^2)}i$ GS is SO coupled with the $d_{(\underline{xy})i}$ excited-state via the L^i_x operator;[31] the projections of the L_i operator on the Z axis are $L^i_Z = -L^i_x$. In the considered arrangement of the local parallel directions $\underline{z}_i\perp Z$, the pair DM exchange parameters $G_{ij,N'} = G_n'$ of the Cu_3 cluster have the form:

$$G_z = \sqrt{3}\lambda[t_{X^2-Y^2}(6t_{z^2} - t_{X^2-Y^2})]/4U\Delta^{yz}_{x^2-y^2} = 4\sqrt{3}\lambda J_0{}'\, t_{X^2-Y^2}/\Delta^{yz}_{x^2-y^2}(6t_{z^2} - t_{X^2-Y^2}),\quad G_x{}' = G_y{}' = 0 \quad (4)$$

$Z_{ij}'\|Z$, $\Delta^{yz}_{x^2-y^2} = \Delta(x^2 - y^2, yz)$ is the interval between the ground ($d_{(\underline{x}^2-\underline{y}^2)}i$) and excited ($d_{(\underline{xy})i}$) states, $J_0' = 4\underline{t}^2/U$. The pair DM parameter $G_{ij,Z'} = G_z'$ for $\underline{z}_i\perp Z$ (eq 4) differs from G_z for $z_i\|Z$ (eq 3) by the $\Delta^{yz}_{x^2-y^2}$ interval in the denominator ($\Delta^{xy}_{x^2-y^2}$ in (3), $\Delta^{xy}_{x^2-y^2} > \Delta^{yz}_{x^2-y^2}$) and by the multiplier in eq 4 which depends on the ET parameters $t_{X^2-Y^2}$ and t_{Z^2}. In the case that $t_{X^2-Y^2} = t_{Z^2}$, the cluster DM parameter G_z for the case $\underline{z}_i\perp Z$ (eq 4) is negative and smaller in magnitude than that in the case $z_i\|Z$ (eq 3). In this case of $\underline{z}_i\perp Z$, $\underline{x}_i\|(-Z)$ Figure 1b (as well as for $z_i\|Z$), both in-plane DM parameters are equal to zero: $G_{x,y}' = 0$. There is no [S = 3/2–2(S = 1/2)] mixing.

4. Dependence of the DM Exchange Parameters on the α-Tilt of the Local Magnetic Orbitals for the Cluster with $z_i\|Z$

The in-plane $G_{ij,X'}$ or/and $G_{ij,Y'}$ components of the pair DM exchange vectors will be nonzero in the case when the local Cu centers are tilted from the positions where $G_{ij,Z'} \neq 0$ and $G_{ij,X'} = G_{ij,Y'} = 0$. The tilt of the local z_i and x_i axes by an angle $\alpha \neq 0$ around the local y_i axes is shown in Figure 1a for the center 1, α is the angle between the local z_i axes and molecular Z axis. In Figure 1, this α-tilt of the local spins is shown schematically. In this case, the local d-functions depend on the tilt angle α (see eq S3 in the Supporting Information) that, in turn, results in the angle dependence of the ground-excited ($t_{1\rho}'$) and ground-ground (t_1) ET integrals (eq S4), which determine the DM parameters $\mathbf{G}_{ij}$ (2) and the Anderson superexchange parameter J, respectively. The dependence of the pair DM exchange parameters $G_{ij,N'} = G_{1n}$ (eq 2), ij = 12, 23, 31, on the α-tilt has the form

$$G_{1z} = G_0 F_{1Z} F_{1t}, \quad G_{1x} = -G_0 F_{1X} F_{1t}, \quad G_{1y} = 0$$

$$F_{1Z} = [4t_{X^2-Y^2}(1 - 0.5\sin^2\alpha)(2k\cos^2\alpha + \sin^2\alpha) + t_{XZ}\sin^2 2\alpha(1-2k)]/t_{X^2-Y^2}$$

$$F_{1X} = \sin 2\alpha\{2t_{X^2-Y^2}(1 - 0.5\sin^2\alpha)(1-k) + [t_{XZ}(1+2k) + 3t_{Z^2}]\sin^2\alpha\}/t_{X^2-Y^2}$$

$$F_{1t} = -0.125[4t_{X^2-Y^2}(1 - 0.5\sin^2\alpha)^2 + t_{XZ}\sin^2 2\alpha - 6t_{Z^2}\sin^4\alpha]/t_{X^2-Y^2}$$

$$G_0 = \sqrt{3}\lambda(t_{X^2-Y^2})^2/U\Delta^{yz}_{x^2-y^2}, \quad k = \Delta^{yz}_{x^2-y^2}/\Delta^{xy}_{x^2-y^2} \qquad (5)$$

The DM exchange coefficients (5) depend on the ET parameters $t_{X^2-Y^2}$, t_{Z^2}, and t_{XZ} and the relation k between the ground-excited states ligand field intervals. The G_0 parameter may be represented in the form $G_0 = -G_z/4k$ where G_z (eq 3) is the DM(z) exchange parameter for the case $z_i \| Z$. Figure 2 shows the dependence of the pair G_{1z} and G_{1x} DM exchange parameters (eq 5) on the tilt angle α for the cluster with $G_z(\alpha = 0) = 32$ cm^{-1} in the case of the parameters $t_{X^2-Y^2} = t_{Z^2} = t_{XZ}$, $k = 2$. In the cases of $\alpha = 0$ ($z_i \| Z$) and $\alpha = 90°$ ($z_i \perp Z$) in Figure 2, eq 5 is reduced to eqs 3 and 4, respectively, for the cases of the lobes of the $d_{(x^2-y^2)i}$ magnetic orbitals lying in the plane of the triangle and perpendicular to the plane, that corresponds to the positive and negative out-of-plane G_{1z} DM parameter in Figure 2. In the considered case $\alpha \neq 0$ in Figure 1, $y_i \perp Z$, the pair $G_{ij,Y'}$ DM parameters are equal to zero, $G_{1y} = 0$ (dash-dotted line in Figure 2). The in-plane G_{1x} DM parameter vanishes for $\alpha = 0$ ($z_i \| Z$) and $\alpha = 90°$ ($z_i \perp Z$). The nonzero G_{1x} and G_{1z} component of the DM exchange may be positive or negative, Figure 2. Small deviation α from the orientations $z_i \| Z$ results in small G_{1x} parameters. The in-plane G_{1x} parameter may be larger than (or of the same value as) the out-of-plane G_{1z} parameter (Figure 2). For the considered set of the t_n and k parameters, the G_{1x} and G_{1z} parameters are equal in value $|G_{1x}| = |G_{1x}|$ for the tilt $\approx \pm 8°$ of the local z_i axes from the $z_i \perp Z$ (α = 90°) orientations ($tg\theta = G_{1x}/G_{1z} = F_{1X}/F_{1Z} = \pm 1$, indicated by the vertical dash-dotted lines in Figure 2). The nonzero G_{1x} parameter results in the mixing of the 2(S = 1/2) and S = 3/2 states of the Cu_3 clusters.[12]

The nonzero G_{1z} and G_{1x} components of the pair DM vectors and $G_{1y} = 0$ (Figure 2) result in the deviation of the pair vectors $\mathbf{G}_{1,ij} = \mathbf{G}_{ij,A}$, $|G_{ij,A}| = \sqrt{(G_{1x}^2 + G_{1z}^2)}$ (dashed vectors $\mathbf{G}_{ij,A}$ in Figure 1) by the angle θ from the orientation $Z_{ij}' \| Z$ in the planes ($X_{ij}'Z_{ij}'O$) perpendicular to the plane of the triangle and the ij bond in Figure 1. The existence of the nonzero G_{1z} and G_{1x} components of the pair DM vectors corresponds to the α-tilt of the local spins S_i.

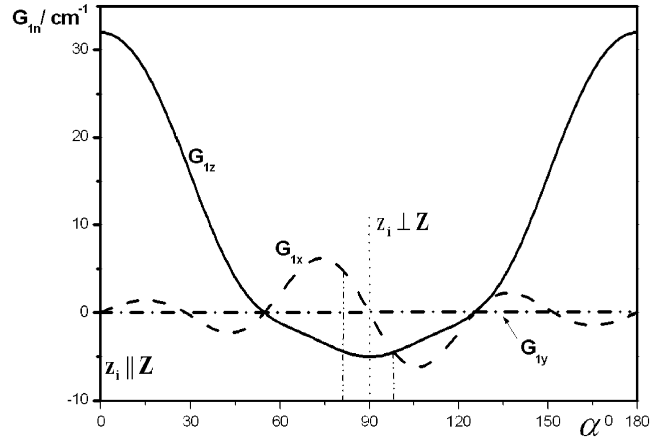

Figure 2. Dependence of the in-plane G_{1x} and out-of-plane G_{1z} DM exchange parameters on the α-tilt for the Cu_3 cluster with the $d_{x^2-y^2}$ ground state of the Cu ions; $G_{1y} = 0$.

5. Dependence of the DM Exchange Parameters G_{ij} on the β-Rotation of the Local Magnetic Orbitals around the Local z_i Axes in the Case $z_i \perp Z$

In the case of $z_i \perp C_3$ and $x_i \| (-Z)$ (section 3), only Z components $G_{ij,Z'} = G_z$ of the pair DM coefficients are nonzero (eq 4). The dependence of the ground-to-excited ET integrals ($t_{2\rho}'$) and ground-to-ground (t_2) ET integrals on the tilt (rotation) of the lobes of the local magnetic orbitals $d_{(x^2-y^2)i}$ (or local x_iy_i axes) by an angle β around z_i in the planes perpendicular to the z_i axes is shown in eq S5 of the Supporting Information. The dependence of the pair DM exchange parameters $G_{ij,N'} = G_{2n}$ on the β-tilt is described by eq 6

$$G_{2z} = G_0 F_{2Z} F_{2t}, \quad G_{2y} = G_0 F_{2Y} F_{2t}, \quad G_{2x} = 0$$

$$F_{2Z} = 2[t_{X^2-Y^2}\cos^2 2\beta - 2t_{XZ}\sin^2 2\beta]/t_{X^2-Y^2},$$

$$F_{2Y} = 0.5\sin 4\beta[t_{X^2-Y^2}(1-k) + 2t_{XZ}(1+2k) + 6t_{Z^2}]/t_{X^2-Y^2}$$

$$F_{2t} = 0.125[(6t_{Z^2} - t_{X^2-Y^2})\cos^2 2\beta - t_{XZ}\sin^2 2\beta]/t_{X^2-Y^2} \qquad (6)$$

The β-tilt results in the nonzero G_{2z} and G_{2y} parameters and zero G_{2x} parameter. Figure 3 plots the dependence of the out-of-plane G_{2z} (solid curves) and in-plane G_{2y} (dashed curves) DM parameters on the β-tilt (eq 6) for the system with $t_{X^2-Y^2} = t_{Z^2} = t_{XZ}$, $k = 2$ ($G_{2x} = 0$, dash-dotted line). The DM(z) parameter for $\beta = 0$ is $G_{2z}(\beta = 0) = -32$ cm^{-1} in Figure 3, $J_0(\beta = 0) = 160$ cm^{-1}.

The case of the angle $\beta = 45°$ between the local x_i axes and the cluster Z axis in eq 6 and Figure 1b corresponds to the directions of the local x_iy_i axes of the local CuO_4 fragments of the {Cu_3} nanomagnet (see Figure 1b in ref 11a). In this case of $\beta = 45°$, only G_{2z}' component of the DM exchange is active (eq 7, Figure 3)

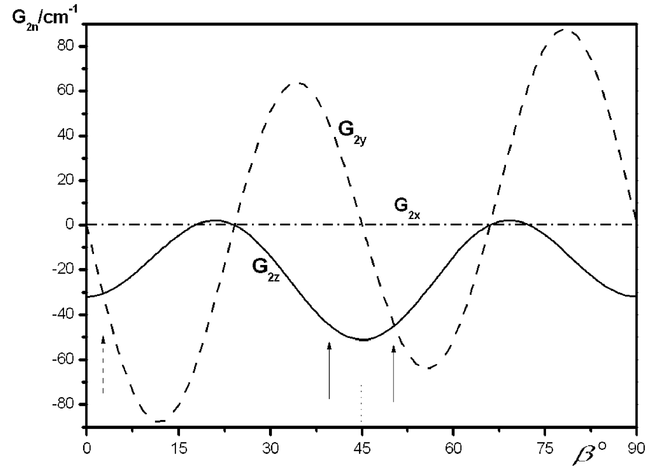

Figure 3. Dependence of the in-plane G_{2y} and out-of-plane G_{2z} DM exchange parameters on the β-rotation for the cluster with the $d_{x^2-y^2}$ ground state of the Cu ions, $G_{2x} = 0$, $z_i \perp C_3$.

$$G_{2z}{}' = \lambda\sqrt{3}(t_{XZ})^2/2U\Delta^{yz}_{x^2-y^2}, \quad G_{2x}{}' = 0, \quad G_{2y}{}' = 0 \quad (7)$$

there is no mixing of the 2(S = 1/2) and S = 3/2 states by the DM(x, y) exchange.

Small rotation (by ±5.5°) of the $d_{(x^2-y^2)i}$ magnetic orbitals around the local z_i axes ($z_i \perp Z$) from the orientation $\beta = 45°$ leads to the in-plane G_{2y} and out-of-plane G_{2z} DM parameters equal in magnitude $|G_{2y}| = |G_{2z}|$ (shown by the vertical arrows in Figure 3). Relatively small tilt from the positions where $G_{2z} \neq 0$ and $G_{2y} = 0$ ($\alpha = 0$, $\pi/4$, $\pi/2$) also results in the large in-plane G_{2y} DM(y) parameter which can significantly exceed the corresponding G_{2z} component, $|G_{2y}| >> |G_{2z}|$, Figure 3. The nonzero DM(y) parameter G_{2y} results in the mixing of the spin-frustrated 2(S = 1/2) GS and excited S = 3/2 state of the Cu_3 clusters.

The nonzero G_{2z} and G_{2y} components of the pair DM exchange parameters (Figure 3, $G_{2x} = 0$) result in the pair $\mathbf{G}_{2,ij}$ (=$\mathbf{G}_{ij,B}$) vectors, $|\mathbf{G}_{ij,B}| = \sqrt{(G_{2y}{}^2 + G_{2z}{}^2)}$. Each pair DM vector $\mathbf{G}_{ij,B}$ lies in the plane, which includes the ij bond and the pair Z_{ij}' axis, perpendicular to the plane of the triangle, with the deviation θ' from the Z_{ij}' direction, $tg\theta' = G_{2y}/G_{2z} = F_{2Y}/F_{2Z}$. The dash-dotted vector $\mathbf{G}_{12,B}$ of the 12 pair is shown in Figure 1. Three $\mathbf{G}_{ij,B}$ vectors form the spiral structure, ij = 12, 23, 31. Figure 3 shows the possibility of the clusters with large G_{2y} parameters and zero G_{2z} component. In the case $G_{2y} \neq 0$ and $G_{2x,2z} = 0$, the $\mathbf{G}_{12,B}$, $\mathbf{G}_{23,B}$, and $\mathbf{G}_{31,B}$ DM vectors lie in the plane of the triangle in the cyclic structure along the ij bonds.

6. DM Exchange Parameters of the {Cu_3} Nanomagnet

The magnetic and EPR data[11a] of the {Cu_3}nanomagnet with the local $\bar{z}_i$ directions $\perp C_3$[11b] were described by Choi et al.[11a] in the DM exchange model with three components of the pair $\mathbf{G}_{ij}$ vectors of the same value of magnitude, $G_x = G_y = G_z = 0.37$ cm^{-1}, $G = \sqrt{(G_x{}^2 + G_y{}^2 + G_z{}^2)}$, $G/J_{av} = 0.22$. In ref 11b, the local parallel direction $\bar{z}_i$ perpendicular to the C_3 axis and the perpendicular local direction along the cluster Z (C_3) axis (section 3) was proposed for the local geometry of the Cu ions of this {Cu_3} nanomagnet.[11a]

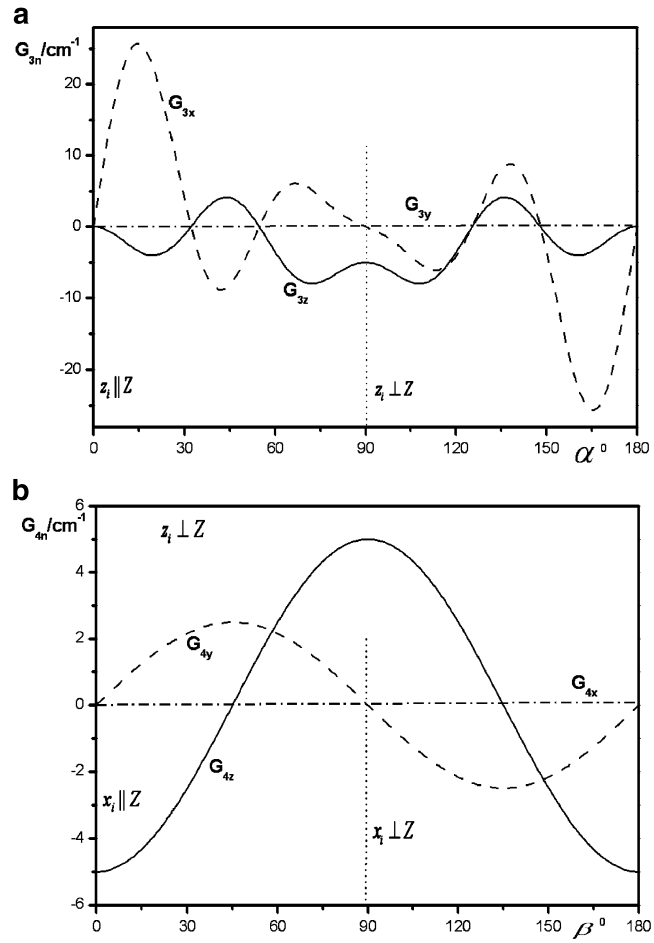

Figure 4. Cu_3 cluster with the ground d_{z^2} state of the Cu ions. (a) Dependence of the G_{3x} and G_{3z} DM exchange parameters on the α-tilt, $G_{3y} = 0$. (b) Dependence of the G_{4y} and G_{4z} DM exchange parameters on the β-tilt, $z_i \perp C_3$, $G_{4x} = 0$.

Figure 3 and eqs 4 and 9 show that only Z components $G_{ij,Z'} = G_z(Z'||Z)$ of the pair vector coefficients are nonzero in the cases of $\bar{z}_i \perp C_3$, $\bar{x}_i||(-Z)$ and $\bar{z}_i \perp C_3$, $\beta = 45°$. The in-plane components vanish, $G_x = G_y = 0$; there is no DM(x, y) mixing of the 2(S = 1/2) and S = 3/2 states in this exact arrangement proposed in ref 11b.

At the same time, our consideration of the angle dependence of the G_z, G_x, and G_y parameters for the system with $t_{X^2-Y^2} = t_{Z^2} = t_{XZ}$, $k = 2$ (Figures 2 and 3) shows that even small tilt of the local magnetic orbitals by an angle α (±8°) (from the position α = 90°, Figure 2) and the rotation by an angle β (±5.5°) around the local $\bar{z}_i$ axes ($\bar{z}_i \perp C_3$) from the position $\beta = 45°$ in Figure 3 can result in the out-of-plane $|G_z|$ and in-plane $|G_x|$, $|G_y|$ DM parameters of the same order of magnitude. These small tilts do not change the correlation between the observed molecular g-factors and the local g-factors, which was proposed in ref 11b.

As follows from Figures 2 and 3, the DM parameter G_z is negative for the set of the ET parameters $6t_{Z^2} > t_{X^2-Y^2}$ (see eq 4) and for the orientation of the local axes $\bar{z}_i \perp C_3$, $\beta \sim 45°$ proposed in ref 11b for the {Cu_3} nanomagnet. The negative sign of G_z is not consistent with the positive sign of the G_z parameter used in ref 11a for the {Cu_3} nanomagnet. Additional evidence of negative G_z is the result of the

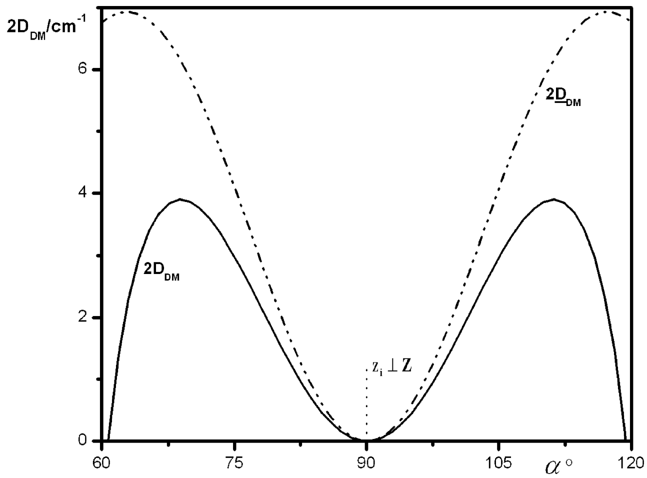

Figure 5. α-Tilt dependence of the ZFS $2D_{DM}'$ of the excited S = 3/2 state induced by the in-plane (G_{1x}) DM exchange mixing.

previous paper,[12] that the relation $\Delta_{12}' > \Delta_{23}'$ for the tunneling gaps Δ_{12}' between the first and second levels and Δ_{23}' between the second and third levels at high magnetic fields as well as the tunneling gaps $\Delta_{45}' > \Delta_{56}'$ presented in Figure 4 ($H \| Z$) of ref 11a correspond to negative G_z parameter. The sign of G_z determines the chirality of the ground state. The sign of G_z can be found experimentally from the relations between the tunneling gaps Δ_{12}' and Δ_{23}' (see eq 9 in ref 12).

7. DM Exchange Parameters for the Clusters with the d_{z^2} Ground State of the Cu Ions

The DM parameters depend on the ground state of the Cu ions. The DM exchange parameters for the FM Cu_3 clusters with the d_{z^2} ground state of the Cu ions and $z_i \perp C_3$ were obtained first in ref 10a in the model of the direct exchange interion coupling: only the Z component of the DM exchange is active[10a]

$$G_z = 4\sqrt{3}\left(\lambda/\Delta_{d_{z^2}}^{d_{xz}}\right) J_{d_{z^2}^{\bar{\alpha}} d_{z^2}^{\beta}}^{d_{z^2}^{\alpha} d_{xz}^{\beta}}, \quad G_x = G_y = 0$$

For the AFM Cu_3 clusters with the superexchange interion coupling between the Cu ions with the d_{z^2} ground state, the dependence of the DM parameters $G_{ij,N'} = G_{3n}$ on the α-tilt between the z_i and Z axes (Figure 1a) has the form

$$G_{3z} = G_u F_{3Z} F_{3t}, \quad G_{3x} = G_u F_{3X} F_{3t}, \quad G_{3y} = 0$$

$$F_{3Z} = \sin^2\alpha\left[t_{X^2-Y^2}\sin^2\alpha - 2t_{XZ}\cos^2\alpha\right]/t_{Z^2}$$

$$F_{3X} = 0.5\sin 2\alpha\left[2t_{Z^2}(1 - 1.5\sin^2\alpha) + t_{XZ}(3\cos^2\alpha - 1)\right]/t_{Z^2}$$

$$F_{3t} = \left[t_{Z^2}(1 - 1.5\sin^2\alpha)^2 - 0.375(t_{X^2-Y^2}\sin^4\alpha + t_{XZ}\sin^2 2\alpha\right]/t_{Z^2}$$

$$G_u = 6\sqrt{3}\lambda(t_{Z^2})^2/U\Delta_{z^2}^{yz} \quad (8a)$$

$\Delta_{z^2}^{yz}$ is the interval between the ground d_{z^2} and excited d_{yz} states mixed by SOC. Figure 4a plots the dependence of the DM exchange parameters on the α-tilt for the Cu trimer with the ground d_{z^2} state and the parameters $t_{X^2-Y^2} = t_{Z^2} = t_{XZ}$, $G_u = 40$ cm^{-1}. In the case $z_i \| C_3$ (α = 0 in Figure 4a), all DM parameters are equal to zero. In the configuration $z_i \perp C_3$ (α = 90° in Figure 4), only the out-of-plane component of the DM exchange is active,

$$G_{3Z}' = 3\sqrt{3}\lambda[t_{X^2-Y^2}(2t_{z^2} - 3t_{X^2-Y^2})]/4U\Delta_{z^2}^{yz},$$
$$G_{3x}' = 0, \quad G_{3y}' = 0 \quad (8b)$$

The comparison of Figure 4a and Figure 2 demonstrates the difference of the DM parameters of the clusters with the ground d_{z^2} and $d_{x^2-y^2}$ magnetic orbitals, respectively. The cluster with the Cu ground $d_{x^2-y^2}$ state is characterized by the strong out-of-plane DM coupling (G_{1z}) in the case $z_i \| Z$ (Figure 2, α = 0), the small α-tilt leads to small in-plane DM(x) parameter G_{1x} and reduction of the out-of-plane G_{1z} parameter. In contrast with that, all DM parameters G_{3n} of the cluster with the d_{z^2} ground state are equal to zero in the case $z_i \| Z$ (Figure 4a, α = 0). Relatively small α-tilt of the d_{z^2} magnetic orbitals from the orientation $z_i \| Z$ (α = 0) results in the large in-plane DM(x) exchange parameter G_{3x} and small out-of-plane G_{3z} (Figure 4a), that leads to the mixing of the 2(S = 1/2) and S = 3/2 states.

In the case $\underline{z}_i \perp Z$ for the AFM cluster with the d_{z^2} ground state of the Cu ions, the dependence of the DM parameters $G_{ij,N'} = G_{4n}$ on the β-rotation of the local $\underline{x}_i\underline{y}_i$ axes around the local axes $\underline{z}_i(\perp Z)$ has the form

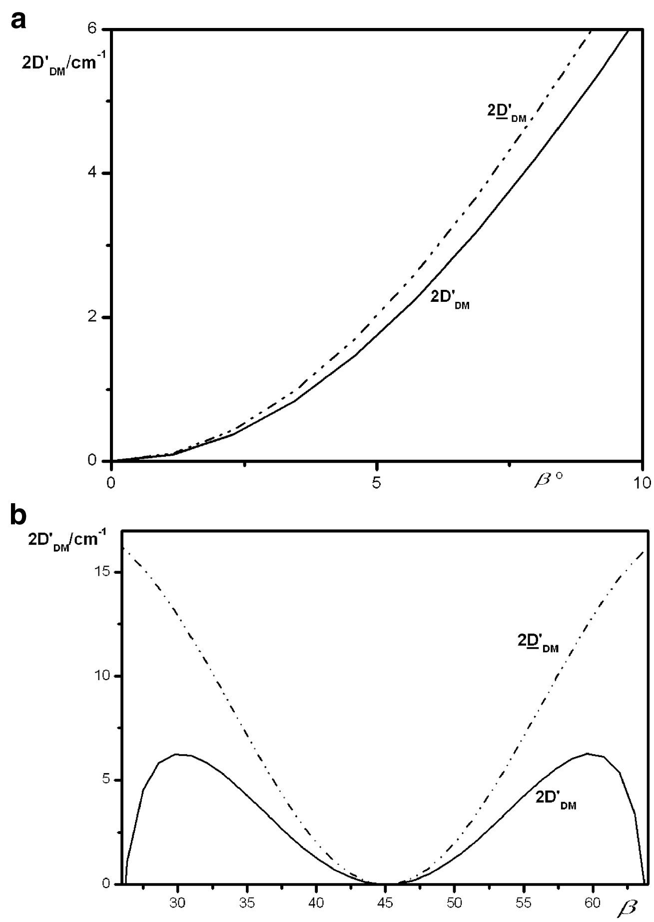

Figure 6. β-Tilt dependence of the ZFS $2D_{DM}'$ of the excited S = 3/2 state induced by the in-plane (G_{2y}) DM exchange mixing, $z_i \perp C_3$. (a) 0 < β < 10°. (b) 25 < β < 65°.

$$G_{4z} = G_u F_{4Z} F_{4t}, \quad G_{4y} = G_u F_{4Y} F_{4t}, \quad G_{4x} = 0$$
$$F_{4Z} = \cos 2\beta (t_{X^2-Y^2}/t_{Z^2}), \quad F_{4Y} = -0.5 \sin 2\beta (t_{X^2-Y^2}/t_{Z^2}),$$
$$F_{4t} = (2t_{Z^2} - 3t_{X^2-Y^2})/t_{Z^2} \quad (9)$$

The ground-to-ground states ET parameter does not depend on the β-tilt: $t_4 = (2t_{z^2} - 3t_{X^2-Y^2})/8$ in this case. Figure 4b shows the dependence of the G_{4z} and G_{4y} DM parameters (eq 9) on the β-rotation around the $\underline{z}_i$ axes for the parameters $t_{X^2-Y^2} = t_{XZ}, G_u = 40\ \mathrm{cm}^{-1}$. Both components G_{4z} and G_{4y} change the value and sign. In the cases when $G_{4y} \neq 0$ and $G_{4z,4x} = 0$, the pair DM vectors $G_{ij,Y'}$ are oriented in the spiral structure along the ij bonds in the triangle plane.

8. Dependence of ZFS of the S = 3/2 State Induced by the DM Exchange on the Tilt of the Local Magnetic Orbitals

As shown in ref 12, the DM exchange contribution $2D_{DM}$ to ZFS $2D_{eff} = 2(D_0 + D_{DM})$ of the S = 3/2 state of the trigonal AFM cluster has the form

$$2D_{DM} = (G_x^{\,2}/4J_0)[1 + 2G_z/J_0\sqrt{3}] \quad (10)$$

where $J_0 = 4t^2/U$ is the parameter of the Anderson superexchange. G_x^2 in $2D_{DM}$ should be changed on $(G_x^2 + G_y^2)$ in the case $G_y \neq 0$. Using the α-tilt dependence of the G_{1x}, G_{1z} ($G_{1y} = 0$) DM exchange parameters (eq 4) and J_0 with $t = t_1$ in eq 10, one obtains the dependence of the DM exchange contribution $2D_{DM}$ on the α-tilt from the orientation $z_i \perp Z$ for the cluster with the Cu ground $d_{x^2-y^2}$ states (Figure 5, solid curves). The dash-dotted curves in Figure 5 describe the ZFS $2\underline{D}_{DM}$ induced by the in-plane DM(x) exchange without an account of the G_{1z} parameter in eq 10. The account of G_{1z} reduces the ZFS $2D_{DM}$ for the tilt from the orientation $z_i \perp Z$ (Figure 5) and enlarges the ZFS $2D_{DM}$ for the tilt α from the orientation $z_i \| Z$. The DM exchange mixing results in the large contribution $2D_{DM}$ to the cluster ZFS $2D_{eff}$ of the S = 3/2 state (Figure 5).

In the case of the rotation of the lobes of the magnetic orbitals $d_{x^2-y^2}$ of individual ions (local $\underline{x}_i\underline{y}_i$ axes) on the angle β around local $\underline{z}_i$ axes in the planes perpendicular to $\underline{z}_i$ (section 5), the pair DM exchange is characterized by the G_{2z} and G_{2y} components ($G_{2x} = 0$), eq 6, Figure 3. The DM exchange contribution to the cluster ZFS has the form $2D_{DM}' = (G_{2y}^2/4J_0')[1 + 2G_{2z}/J_0'\sqrt{3}]$ in this case, where $J_0' = 4t_2^2/U$, t_2 is determined in eq S6 of the Supporting Information. Even a small β-tilt results in the large DM(y) parameter $G_{2y} > G_{2z}$ (Figure 3) that, in turn, leads to the large DM exchange contribution $2D_{DM}'$ to ZFS of the S = 3/2 state, Figure 6. The dash-dotted lines in Figure 6 describe the ZFS $2\underline{D}_{DM}'$ induced only by the in-plane DM exchange G_{2y} without an account of the G_{2z} parameter. The contribution $2D_{DM}'$ to ZFS of the S = 3/2 state induced by the in-plane DM exchange coupling may be of the same order of magnitude as the experimentally observed values $2D$.

9. Conclusion

The origin of the in-plane DM exchange parameters and correlations between the DM exchange parameters of the Cu_3 clusters and the local anisotropy of the Cu ions were considered. For the Cu_3 clusters with the local axes z_i of anisotropy parallel to the molecular trigonal axis $z_i \| Z$ (Figure 1, α = 0) as well as for $z_i \perp Z$ (β = 0, 45, 90°), only z components of the DM exchange are active, $G_z \neq 0$ (eqs 3, 4, and 7, respectively). The G_z ($z_i \| Z$) (eq 3) and G_z ($z_i \perp Z$) (eqs 4 and 7) parameters differ in value and sign. The in-plane DM exchange parameters are equal to zero in these cases, $G_{x,y} = 0$. The α-tilt of the individual spins results in the change of the out-of-plane G_{1z} parameter and an appearance of the in-plane G_{1x} DM parameter (Figure 2). The β-rotation of the $d_{x^2-y^2}$ orbitals around the z_i axes ($z_i \perp Z$) leads to appearance of the in-plane G_{2y} DM parameter (Figure 3).

The dependence of the out-of-plane G_z and in-plane G_x and G_y DM exchange parameters on the tilt angle is significantly different. The in-plane DM G_x, G_y parameters can significantly exceed the out-of-plane G_z parameter. The nonzero G_z and G_x, G_y DM parameters may be positive or negative. For the {Cu_3} nanomagnet,[11a] the model (i) explains the three relatively large DM exchange parameters of the same value ($G_x = G_y = G_z$) by the small tilt of the local anisotropy axes z_i of the CuO_4 local groups of the trimer from the positions $z_i \perp Z$ and (ii) predicts negative sign of G_z. The dependence of the DM exchange parameters on the tilt is different for the AFM Cu clusters with the ground state $d_{x^2-y^2}$ and d_{z^2} of the Cu ions. Large G_x, G_y DM parameters result in the mixing of the 2(S = 1/2) and S = 3/2 states and large positive DM exchange contribution $2D_{DM}$ to the ZFS of the S = 3/2 state, which depends on the tilt of the local magnetic orbitals.

Supporting Information Available: Equations S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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