Jahn-Teller Distortion in Bimetallic Oxalates

Randy S. Fishman, Satoshi Okamoto, and Fernando A. Reboredo

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6065

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A C₃-symmetric crystal-field potential in the Fe(II)Fe(III) bimetallic oxalates splits the L = 2 Fe(II) multiplet into two doublets and a singlet. In compounds that exhibit magnetic compensation, one of the doublets is predicted to lie lowest in energy and carry a non-quenched orbital angular momentum ±Lₜ, where Lₜ exceeds a threshold value. In a range of Lₜ, a Jahn-Teller (JT) distortion increases the energy splitting of the low-lying doublet and breaks the C₃ symmetry of the bimetallic planes around the ferrimagnetic transition temperature. At low temperatures, the JT distortion disappears in compounds that display magnetic compensation due to the competition with the spin-orbit coupling. A comparison with recent measurements provides strong evidence for this re-entrant, low-temperature JT transition and a prediction for the normal, high-temperature JT transition. The size of the JT distortion is estimated using first-principles calculations, which suggest that the long-range ordering of smaller, non-C₃-symmetric organic cations can eliminate magnetic compensation.

I. INTRODUCTION

Jahn-Teller (JT) transitions [1] in which electronic degeneracies are removed by crystal field potentials have been observed quite frequently in recent studies of molecule-based magnets [2]. It is well-known that the JT transition will be quenched if the degenerate levels carry orbital angular momentum and the spin-orbit coupling is sufficiently strong. When the spin-orbit coupling and JT energies are comparable, however, a pseudo-JT transition with rather interesting behavior is possible. In this paper, we study the JT transition in a class of molecule-based magnets where the spin-orbit coupling can be modified by choosing different organic cations to lie between bimetallic layers. Due to the competition between the spin-orbit and JT energies, the JT distortion may vanish at low temperatures in a re-entrant, first-order transition.

One of the most fascinating classes of molecule-based magnets, bimetallic oxalates [M(II)M'(III)(ox)₃] were first synthesized [3] in 1992. In the open honeycomb structure of each bimetallic layer, sketched in Fig.1(a), the transition-metal ions M(II) and M'(III) are coupled by the oxalate bridges ox=C≡O [4]. Depending on the metal atoms, a single bimetallic layer can be either ferromagnetic or ferrimagnetic (M(II) and M'(III) moments parallel or anti-parallel) with magnetic moments pointing out of the plane. While the organic cation A separating the layers cannot alter the sign of the exchange coupling, the organic cation A determines the average orbital angular momentum ±Lₜ carried by the low-energy doublet. Compounds exhibit MC when the low-energy doublet lies below the singlet and Lₜ exceeds the threshold Lₜ. For compounds that do not exhibit MC ("normal" compounds), either Lₜ < Lₜ or the singlet state lies lowest in energy.

In the absence of spin-orbit coupling or when Lₜ = 0, a JT distortion that breaks C₃ symmetry will always split the low-energy doublet. For large enough Lₜ, the spin-orbit coupling will quench the JT distortion. However, in a range of Lₜ that includes Lₜ, we obtain a JT-distorted phase between temperatures T_{JT}^{(l)} and T_{JT}^{(u)} that bracket T_{c}. Both the re-entrant, low-temperature transition T_{JT}^{(l)} and the normal, high-temperature transition T_{JT}^{(u)} are first order. Comparison with recent experiments [7] allows us to estimate the normal JT transition temperature T_{JT}^{(u)} in MC compounds.

This paper is divided into 5 sections. Section II develops the phenomenological model for the JT transition, with results described in Section III. First-principles calculations are described in Section IV and a discussion is contained in Section V.

II. MODEL FOR THE JAHN-TELLER TRANSITION

Our model assumes a hierarchy of three energy scales. The dominant energy is the Hund’s coupling that determines the spins S = 2 and S’ = 5/2 on the Fe(II) (3d⁶) and Fe(III) (3d⁵) sites. Next in importance is the C₃-symmetric crystal field V generated by the 6 oxygen atoms around each of the Fe sites. These 6 oxygen atoms form two triangles of slightly different sizes rotated by about 48 degrees with respect to each other, one above and the other below the plane of Fe atoms. The smallest energies are the antiferromagnetic exchange coupling J·S·S’ between the Fe(II) and Fe(III) moments within each bimetallic layer, the spin-orbit coupling λL·S on the Fe(II) sites (λ ≈ −12.65 meV [8]), and any non-C₃-
symmetric contributions of the crystal potential.

As shown in Fig.1(b), the C₃-symmetric potential V splits the $L = 2$ multiplet of the Fe(II) sites into two doublets $\psi_{1,2}$ and $\psi_{1,5}$, and a singlet $\psi_3$. The low-energy doublet $\psi_{1,2}$ carries an average orbital angular momentum $\pm L_z^{cf}$, where $L_z^{cf}$ ranges from 0 to 2 depending on the crystal-field parameters. Of course, the singlet state $\psi_3$ does not carry any orbital angular momentum.

Including the orbital contribution, the Fe(II) magnetic moment can be written $M(T) = M_S(T) + M_L(T) \leq 0$, where $M_S = 2\langle S_z \rangle$ and $M_L = \langle L_z \rangle$. Of course, the Fe(III) magnetic moment $M'(T) = M'_S(T) = 2\langle S'_z \rangle \geq 0$ has no orbital contribution. The mean-field (MF) approximation is used to treat the nearest-neighbor exchange

$$J \cdot S \cdot S' \approx J_c \left\{ -M_S S'_z + S_z M_S' \right\}/2 - M_S M_S'/4 \right\} \quad (1)$$

between neighboring Fe(II) and F(III) spins. The MF eigenvalues of $\psi_{1,2,3}$ and $\psi_{3,3}$ are

$$\epsilon_{1\sigma} = (-|\lambda| L_z^{cf} + 3J_c M_S'/2)\sigma$$

(2)

$$\epsilon_{2\sigma} = (|\lambda| L_z^{cf} + 3J_c M_S'/2)\sigma$$

(3)

$$\epsilon_{3\sigma} = (3J_c M_S'/2)\sigma + \Delta \quad (4)$$

so that the doublet $\psi_{1,2,3}$ is split by the spin-orbit coupling with $|\epsilon_{2\sigma} - \epsilon_{1\sigma}| = 2|\lambda| L_z^{cf}$. Because the crystal-field potential is assumed much larger than the spin-orbit and exchange energies, $|\Delta| \gg J_c$ or $|\lambda|$.

Using Eqs. (2) and (3) for the eigenvalues $\epsilon_{1,2,3}$, it is straightforward to evaluate $M(T)$, $M'(T)$, and the average magnetization $M_{av}(T) = (M(T) + M'(T))/2 = (|M'(T)| - |M(T)|)/2$. When $l_c \approx 0.238 < L_z^{cf} < 1$, $M_{av}(T)$ passes through 0 at the compensation temperature $T_{comp} < T_c$. Just below $T_c$, $M_{av}(T) < 0$ because the parallel spin-orbit coupling between $L$ and $S$ causes the Fe(II) moment $M(T)$ to increase in amplitude more rapidly than the Fe(III) moment $M'(T)$. But at zero temperature, the Fe(III) moment saturates at the larger value $|M'(0)| = 2S' > |M(0)| = 2S + L_z^{cf}$ so that $M_{av}(0) > 0$.

After comparing the observed values of $T_{comp}/T_c \approx 0.62$ and $T_c \approx 45$ K with the theoretical predictions, we estimated [6] that $J_c \approx 0.46$ meV and $L_z^{cf} \approx 0.28$ in MC compounds. Normal compounds can fall into two categories. Either the doublet remains lower in energy than the singlet $(\Delta > 0)$ but with $L_z^{cf} < l_c$ or the singlet lies lowest in energy $(\Delta < 0)$. Our model also predicted that two compensation points were possible in the narrow window $l_c < L_z^{cf} < l_c$. The recent observation by Tang et al. [7] of two compensation points in the compound N(u-C₃H₉)₂[Fe(II)Fe(III)ox] (data shown in Fig.3) would seem to confirm this prediction.

If a doubly-degenerate level is occupied by a single electron in the absence of spin-orbit coupling, then a local JT displacement the Fe(II) ions corresponding to one of three equivalent directions is always favored by the electronic energy. The eigenstates $\psi_{1\sigma}$ and $\psi_{2\sigma}$ on the Fe(II) sites are mixed by the JT distortion as described by the Hamiltonian [9]

$$H_{mix}^{\sigma} = \left( \begin{array}{cc} \epsilon_{1\sigma} & \xi \\
\xi & \epsilon_{2\sigma} \end{array} \right), \quad (5)$$

where $\xi$ is independent of $\sigma$. If $\epsilon_{1\sigma} = \epsilon_{2\sigma}$ are given by the MF result $\epsilon_{a\sigma} = 3J_c M'/2$, then the eigenstates of $H_{mix}$ are $\psi_{a\sigma} = (1/\sqrt{2})(\psi_{1\sigma} + \psi_{2\sigma})$ and $\psi_{b\sigma} = (1/\sqrt{2})(\psi_{1\sigma} - \psi_{2\sigma})$, with $L_{a,b,\sigma} = \langle \psi_{a,b,\sigma} | L_z | \psi_{a,b,\sigma} \rangle = 0$ and eigenvalues $\epsilon_{a,b,\sigma} = \epsilon_{1\sigma} \pm \xi$. So in the absence of spin-orbit coupling, the orbital angular momentum is enhanced by the JT effect (strictly speaking, the pseudo-JT effect when $\epsilon_{1\sigma} \neq \epsilon_{2\sigma}$). Since the second term is an elastic restoring potential and $N$ is the number of Fe(II) or Fe(III) sites per bimetallic layer. Since $\alpha > 0$, the $T = 0$ equilibrium value for $\xi$ is $|\lambda|/2\alpha > 0$.

Including the spin-orbit interaction $\lambda \cdot L \cdot S$, the eigenvalues of $H_{mix}$ are $\epsilon_{a\sigma} = \epsilon_{a,0} + t_\sigma$ and $\epsilon_{b\sigma} = \epsilon_{b,0} - t_\sigma$, where $t_\sigma = -\text{s}{\text{s}}(\sqrt{\langle \lambda L_z^{cf} \rangle}^2 - \xi)^2$. Hence, the doublet splitting $\delta = 2|t_\sigma|$ is enhanced by the JT effect (strictly speaking, the pseudo-JT effect when $\epsilon_{1\sigma} \neq \epsilon_{2\sigma}$). Since there is no spin-orbit coupling when $\sigma = 0$, $t_0 = \xi$ and $L_{a,0} = L_{b,0} = 0$. For $\sigma \neq 0$, the spin-orbit coupling maintains a nonzero orbital angular momentum $L_{a\sigma} = -L_{b\sigma}$ even in the presence of a JT distortion:

$$L_{a\sigma} = (L_z^{cf})^2 \lambda \sigma \frac{\lambda L_z^{cf} \sigma + t_\sigma}{\lambda L_z^{cf} \sigma^2 + \lambda L_z^{cf} a \sigma + \xi^2} \quad (6)$$

so that $L_{a\sigma} = L_{a,-\sigma}$. When $\xi \neq 0$, the JT distortion
free energy can be written

$$F = -T \log \left\{ Z_{II} Z_{III} e^{3J_L M_S M_{S'}} / 4T \right\} + \alpha |\lambda| \left\{ \left( \frac{\xi}{|\lambda|} \right)^2 + \gamma_3 \left( \frac{\xi}{|\lambda|} \right)^3 + \gamma_4 \left( \frac{\xi}{|\lambda|} \right)^4 \right\},$$

(7)

where

$$Z_{II} = 2 \sum_{\sigma} e^{-3J_L M_{S\sigma}/2T} \cosh(t_\sigma/T),$$

(8)

$$Z_{III} = 2 \sum_{\sigma'} e^{-3J_L M_S \sigma'/2T}.$$

(9)

The sums in the partition functions $Z_{II}$ and $Z_{III}$ are over $\sigma = 0, \pm 1, \pm 2$ and $\sigma' = \pm 1/2, \pm 3/2, \pm 5/2$. The second line in Eq.(7) corresponds to the elastic energy.

Breaking $C_3$ symmetry, a local JT distortion with $\pm \xi$ involves the displacement of an Fe(II) atom either into one of the three open hexagons or towards one of the three neighboring Fe(III) atoms. The former distortions are sketched in Fig.1(a). The anharmonic $\gamma_3 (\xi/|\lambda|)^3$ term in Eq.(7) reflects the different energy costs for those two types of distortions. So the anharmonicity and source of the first-order JT transition arise quite naturally on the open honeycomb lattice. The sign of $\gamma_3$ does not affect any physical results and is chosen to be negative only so that $\xi \geq 0$. Any fluctuations between the distorted atomic configurations are assumed slow compared to the electronic time scales.

It is simple to obtain the equilibrium values for $M_S$ and $M_{S'}$ from the extremal conditions $\partial F / \partial M_S = \partial F / \partial M_{S'} = 0$. Because the spin-orbit energy $\lambda L \cdot S$ is treated exactly, $M_L$ is not a variational parameter in the MF free energy and must be determined separately from the condition

$$M_L = -\frac{2}{Z_{II}} \sum_{\sigma} L_{a\sigma} e^{-3J_L M_{S\sigma}/2T} \sinh(t_\sigma/T).$$

(10)

Of course, the equilibrium value for the JT parameter $\xi$ is obtained by minimizing $F$ with respect to $\xi$.

III. MODEL RESULTS

The average magnetization and JT energy $\xi$ are plotted versus temperature in Figs.2(a) and (b) for $\alpha = 3.7$, $\gamma_3 = -1.9$, and $\gamma_4 = 1.1$. As expected, the MC threshold $T_c \approx 0.282$ is enhanced by the JT distortion. When $L_{zf} < 0.260$, the JT distortion $\xi(T)$ persists down to $T = 0$. For $L_{zf} = 0$ (but still taking $\Delta > 0$), $\xi(0) \approx 0.842 |\lambda| \approx 10.5$ meV and $T_{JT}^{(a)} \approx 0.578 |\lambda|$. For $L_{zf} = 0.2$, the JT distortion would increase the splitting of the $\sigma = 2$ doublet from $4|\lambda| L_{zf} = 10$ meV to $2 \sqrt{(2\lambda L_{zf})^2 + \xi^2} \approx 23$ meV.

When $L_{zf} \geq 0.260$, the JT distortion is quenched at $T = 0$ due to the strong orbital ordering. Hence, we obtain both lower and upper JT transitions, $T_{JT}^{(l)}$ and $T_{JT}^{(u)}$. At the re-entrant JT transition, the distortion $\xi$ vanishes below $T_{JT}^{(l)}$ and appears above $T_{JT}^{(l)}$. The temperature range $T_{JT}^{(a)} - T_{JT}^{(l)}$ decreases as $L_{zf}$ increases and vanishes when $L_{zf} > 0.324$. Notice that the JT transitions at $T_{JT}^{(a)}$ and $T_{JT}^{(l)}$ always bracket $T_c$.

Because the orbital contribution $M_L(T)$ to the Fe(II)
moment drops as $\xi$ jumps at the re-entrant JT transition, $T_{JT}^{(l)}$ is marked by a discontinuous change in $M_{\text{avg}}(T)$. With decreasing $L_z^f$, both the orbital contribution $M_L(T)$ and the magnitude of the change in $M_{\text{avg}}(T)$ become smaller. For $L_z < L_z^f < 0.324$, the re-entrant JT transition causes the average magnetization to change sign, as shown in Fig.2(a) for $L_z^f = 0.30$.

The quantitative agreement in Fig.3 between the theoretical prediction for $L_z^f = 0.30$ and the measurements of Ref.[7] for A=N(n-C$_4$H$_9$)$_4$ is striking. Rather than providing evidence for two compensation points, Ref.[7] indicates that a re-entrant JT transition occurs at $T_{JT}^{(l)} \approx 42$ K. According to Fig.2(b), a normal JT transition will be found at $T_{JT}^{(u)} \approx 70$ K. Indeed, recent x-ray measurements [10] on the same compound confirm that the hexagonal symmetry present at room temperature is absent in the monoclinic lattice below 60 K.

Measurements on several Fe(II)Fe(III) compounds [10, 11] suggest that all MC compounds exhibit a small jump in the magnetization between $T_c$ and $T_{\text{comp}}$. The predicted jumps in Fig.2(a) are much too large to explain those measurements. X-ray diffraction studies [12] reveal that stacking faults in several compounds promote the coexistence of two phases: one with a six-layer repeat and the other with a two-layer repeat. The small magnetization jumps observed [10, 11] in MC compounds are likely caused by a mixture of those two stacking types. As shown in the inset to Fig.3, a mixture of two phases, type 1 with $L_z^f = 0.30$ (5% of the sample) and type 2 with $L_z^f = 0.33$ (95% of the sample) [13], produces a small jump which is quite similar to the observations. The much larger jump observed by Tang et al. [7] may be caused by the greater fraction of type 1 ($L_z^f \approx 0.30$) stacking in their sample.

While there is no JT distortion ($\xi = 0$) when $\Delta < 0$, $\xi(T)$ remains nonzero down to $T = 0$ when $\Delta > 0$ and $L_z^f < 0.260$. So our model predicts that normal bimetallic oxalates with $L_z^f < 0.260$ will not exhibit a discontinuity in the magnetization, which may explain why such a jump has never been observed in a normal compound [11]. Nevertheless, normal Fe(II)Fe(III) compounds with $\Delta > 0$ (so that the doublet remains lowest in energy) should manifest a normal JT transition at $T_{JT}^{(n)} \approx 0.58|\lambda|$ or about 85 K.

But any non-C$_3$-symmetric cation like N(n-C$_4$H$_9$)$_4$ will also induce a permanent distortion of the hexagonal lattice. Depending on the size and shape of the cation, this distortion can be local, weakly-correlated, or long-ranged. A non-C$_3$-symmetric potential can be included within our model by changing the off-diagonal terms in $H_{\text{mix}}^\text{cf}$ from $\xi$ to $\xi + \xi_0$. In the absence of spin-orbit coupling and a spontaneous JT distortion $\xi$, the doublet splitting $\delta$ is then $2\xi_0$. Since the anharmonic elastic potential proportional to $\xi^3$ favors $\xi > 0$, it acts to enhance the total distortion $|\xi + \xi_0|$ when $\xi_0 > 0$ and to suppress the total distortion when $\xi_0 < 0$. For any nonzero $\xi_0$, there is a spontaneous JT distortion $\xi(T) \neq 0$ at all temperatures due to the linear term of order $-\xi \xi_0/|\lambda|$ in the free energy.

As shown in Fig.4 for $L_z^f = 0.3$ and the elastic parameters given earlier, increasing $\xi_0$ for a fixed $L_z^f$ decreases $T_{JT}^{(l)}$ while keeping $T_{\text{comp}}$ almost unchanged until $T_{JT}^{(l)} < T_{\text{comp}}$. When $\xi_0 > 0.047|\lambda| \approx 0.6$ meV, the spontaneous JT distortion $\xi$ at $T = 0$ jumps to a value near $0.81|\lambda| \approx 10$ meV and the lower JT transition disappears. When $\xi_0 < -0.019|\lambda| \approx -0.2$ meV, the spontaneous JT transition is eliminated but magnetic compensation survives until $\xi_0 < -0.43|\lambda| \approx -5.4$ meV, as seen in the inset to Fig.4(a). Except in the narrow window $0 > \xi_0 > -0.019|\lambda|$, the permanent distortion $\xi_0$ and the electronic distortion $\xi$ have the same sign.

Clearly, the electronic JT distortion $\xi$ will vanish if the Fe(II) singlet lies below the doublet with $\Delta < 0$. So two conditions are required for C$_3$ symmetry to remain unbroken at $T = 0$. First, the cation must preserve C$_3$ symmetry so that there is no permanent distortion $\xi_0$. Second, either $\Delta < 0$ or if $\Delta > 0$, the average orbital angular momentum $L_z^f$ of the doublet must be sufficiently large to quench the spontaneous JT distortion $\xi$ ($L_z^f \geq 0.260$ in Fig.2). Specific examples of symmetry breaking will be discussed in the next section.
are very localized in this ionic solid, we used a single k-point. Spin orbit coupling was not included. In order to stabilize the electronic density, the calculations were performed with an electronic temperature of 0.02 Ry or 270 meV.

Predictions of the experimental electronic and magnetic structure in highly localized systems are known to be significant challenges for most approximations of DFT. Indeed, we find that the energy difference between ferromagnetic and antiferromagnetic configurations is below the resolution of our theory. Moreover, the charge-density wave observed experimentally (which results in inter-penetrated Fe(II) and Fe(III) networks) is not found to be the ground state. This possibly signals the presence of strong self-interaction errors for the localized d orbitals [18]. The antiferromagnetic Fe(II) and Fe(III) ordering is stabilized only after enforcing the net spin within each unit cell to be equal to 1/2.

Calculations were performed for several possible stackings (ab, aab, abc) of the bimetallic Fe(II)-Fe(III) layers with A=N(n-C\textsubscript{3}H\textsubscript{7})\textsubscript{4} cations. The total energy differences between these stackings were below the accuracy of the theory, consistent with the high degree of polymorphism and the low energy cost for stacking faults suggested by the x-ray scattering experiments [12]. Since the relative energy difference \(\Delta\) between the doublet and singlet is quite sensitive to the stacking of the bimetallic planes, the angular momentum \(L^{\perp}\) of the ground state may also depend on the stacking of the bimetallic planes.

The doublet splittings and the order of magnitude of the JT distortions were estimated by focusing on a single bimetallic layer with different cations A. Within hexagonal supercells, we studied the cations A=NH\textsubscript{4} (1) and N(n-C\textsubscript{3}H\textsubscript{7})\textsubscript{4} (2). We also considered A=N(n-C\textsubscript{3}H\textsubscript{7})\textsubscript{4} (3) in a non-hexagonal supercell.

(1) Although no oxalates contain the cation NH\textsubscript{4} because it is too small to stabilize the open honeycomb lattice, calculations on this system allow us to estimate the JT distortion in a C\textsubscript{3}-symmetric environment. First, we relaxed the forces on all atoms constraining the symmetry to remain C\textsubscript{3}. We found that the Fermi level for the majority band lies at a doublet localized at the Fe(II) sites and occupied by a single electron. This configuration is consistent with our model, which requires the partial occupation of a doublet to explain the MC and the JT distortion. Second, we displaced the Fe(II) ion from the symmetric position on a grid of points \(r\). From the \textit{ab-initio} calculations, we extracted the total energy \(E(r)\) of the configuration and the energy splitting \(\delta(r)\) induced in the partially-occupied doublet. Because the calculations where performed at an electronic temperature \((\sim 270 \text{ meV})\) much larger than the splittings, both electronic levels of the doublet have an equal occupation of 1/2. At this large electronic temperature, no JT electronic energy was gained and the symmetric point \(r = 0\) remained the position with minimum energy, as expected.

We can, however, estimate the energy gain at \(T = 0\) as \(E(r) - \delta(r)/2\). This approximation assumes that the

FIG. 4: (Color online) The (a) average magnetization and (b) the JT mixing energy \(\xi\) normalized by \(|\lambda|\) versus temperature \(T/|\lambda|\) for several values of the permanent distortion \(\xi_0/|\lambda|\) from -0.02 to 0.05 in increments of 0.01. Inset in (a) is the magnetization versus \(T/|\lambda|\) for \(\xi_0/|\lambda|\) between -0.5 and 0 in increments of 0.1. These plots use \(L_z^{\perp} = 0.3\), \(J_z/|\lambda| = 0.037\) and the elastic constants given in the text.

IV. FIRST-PRINCIPLES CALCULATIONS

In order to estimate the orders of magnitude of the spontaneous JT distortion \(\xi\) and the permanent distortion \(\xi_0\), we performed a series of first-principles calculations within the framework of density-functional theory (DFT). We employed the local spin density approximation (SDA) in the plane-wave-pseudopotential approach with the PBE [14] exchange correlation functional as implemented in the Quantum-ESPRESSO package [15]. We used Vanderbilt ultrasoft pseudopotentials [15–17] including, in the case of Fe [15, 17], d electrons in the valence and non-linear core corrections. An energy cut-off of 45 Ry was used. Since the orbitals at the Fermi level
total energy difference is given by the sum of the occupied eigenvalues at zero temperature and neglects a small change in the electronic density [19]. With this expression, we obtain the approximate Fe(II) position and doublet splitting at zero temperature. In absence of the spin-orbit coupling, we estimate that the Fe(II) moves 0.03 Å (the nearest-neighbor Fe(II)-Fe(III) distance is about 5.4 Å) with an energy gain of 2 meV and a doublet splitting of 8 meV. This JT splitting is quite close to the spin-orbit coupling $|\lambda| L_z^J S \approx 7.5$ meV with $L_z^J = 0.3$.

(2) Moderately-sized cations such as N(n-C$_3$H$_7$)$_4$ are themselves non-C$_3$-symmetric and break the C$_3$ symmetry of the crystal-field potential at the Fe(II) sites. While it is possible to construct a N(n-C$_3$H$_7$)$_4$-isomer with three C$_3$H$_7$ radicals below the oxalate plane, thereby preserving C$_3$ symmetry, the remaining propyl chain (oriented towards the hexagonal hole in the oxalates plane) must break C$_3$ symmetry. This symmetry violation produces a crystal-field splitting $2\delta_0$ of the doublet and a permanent distortion of the open honeycomb lattice.

Calculations were performed in a hexagonal unit-cell containing a single A=N(n-C$_3$H$_7$)$_4$ cation with periodic boundary conditions, corresponding to an ordered configuration where every N(n-C$_3$H$_7$)$_4$ cation is oriented in the same way. After relaxing the positions of the atoms, we obtained an intrinsic doublet splitting $2\delta_0$ of about 10 meV at an electronic temperature of 270 meV.

These calculations also indicate that the intrinsic distortion introduced by the cation will be increased at low temperature by the electronic energy gain of the Fe(II) JT distortion. So in the absence of spin-orbit coupling, the parameters $\xi$ and $\xi_0$ of our model have the same sign for this cation.

(3) The molecule N(n-C$_3$H$_7$)$_4$ is just small enough to allow individual cations to rotate independently of each other. Hence, a uniform distortion of the crystal is possible. Such a uniform distortion of the open honeycomb structure has been observed in bimetallic oxalates with radical cations [20]. For an ordered arrangement of A=N(n-C$_3$H$_7$)$_4$ cations and allowing the supercell to break hexagonal symmetry, we obtain a doublet splitting $\delta \approx 20$ meV, which should increase to about 30 meV when the electronic temperature approaches zero.

By contrast, larger cations such as A=N(n-C$_4$H$_9$)$_4$ studied in Ref.[7] are unable to independently rotate within each unit cell. Because they are locked into a highly-disordered configuration during synthesis, such cations will only break the local C$_3$ symmetry around each Fe(II) ion. Since the spin-orbit coupling competes with the small, local lattice distortions, magnetic compensation is still possible when the cations are large and disordered. This leads to an interesting conjecture: due to their ability to spatially order, smaller cations like N(n-C$_3$H$_7$)$_4$ may be more effective at enhancing the departure from C$_3$ symmetry and suppressing magnetic compensation than larger cations like N(n-C$_4$H$_9$)$_4$.

V. DISCUSSION

Our first-principles calculations imply that large cations like N(n-C$_4$H$_9$)$_4$ will induce a substantial, local distortion $\xi_0$ of the hexagonal lattice. For smaller cations like N(n-C$_3$H$_7$)$_4$, this distortion may propagate throughout the bimetallic layer because the cations are able to reach a global minimum of the free energy, which is an ordered state at low temperatures. For an ordered configuration of N(n-C$_3$H$_7$)$_4$ cations with $|\xi_0| \approx 5$ meV, the value suggested by our first-principles results, Fig.4 implies that the re-entrant JT transition will be absent and any magnetic compensation will be very weak. Indeed, N(n-C$_3$H$_7$)$_4$(Fe(II)Fe(III)O$_3$)$_3$ bimetallic oxalates [5] show no signs of a JT transition or magnetic compensation below $T_c$.

With the spin-orbit coupling set to zero ($L_z^J = 0$), the doublet splitting $\delta = 2\xi(\xi_0) \approx 21$ meV obtained using the parameters of Fig.3 is more than twice as large as that obtained from first-principles calculations in a C$_3$-symmetric environment (see I above). So it is likely that the organic cation N(n-C$_4$H$_9$)$_4$ plays a significant role in breaking the local C$_3$ symmetry and enhancing the doublet splitting. A more sophisticated description of the experimental measurements may be possible once additional information about the atomic structure becomes available.

To summarize, we have provided strong evidence for the existence of a re-entrant JT transition in the Fe(II)Fe(III) bimetallic oxalates. Observation of the JT distortion between $T^{(l)}_J \approx 42$ K and $T^{(u)}_J \approx 70$ K would provide unambiguous support for the predicted multiplet splitting in MC compounds. We hope that this work will inspire systematic x-ray scattering measurements that will verify the predictions made in this paper, including the long-range ordering of small, non-C$_3$-symmetric cations in this important class of layered, molecule-based magnets.

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[1] See for example, Bersuker, I. B. The Jahn-Teller Effect; Cambridge University Press: Cambridge, 2006 and references therein.

[2] (a) Sorai, M.; Nakano, M.; Miyazaki, Y. Chem. Rev. 2006, 106, 976; (b) Beghidi, C.; Rogez, G.; Kortus, J.; Wesolek, M.; Welter, R. J. Am. Chem. Soc. 2006, 128, 3140; (c) Hatnean, J. A.; Raturi, R.; Lefebvre, J.; Leznoff, D. B.; Lawes, G.; Johnson, S. A. J. Am. Chem. Soc.
Diagonal terms in $\hat{H}_{\text{mix}}$ involving $\xi$ can be neglected because the doublet states are related by the time-reversal operations $\psi_{1\sigma} = -K\psi_{2,-\sigma}$ and $\psi_{2\sigma} = -K\psi_{1,-\sigma}$, where $K$ is the time-reversal operator. So for any spin-independent electrostatic potential $V = K^{-1}VK$, $\langle \psi_{1\sigma} | V | \psi_{1\sigma} \rangle = \langle \psi_{2,-\sigma} | K^{-1}VK | \psi_{2,-\sigma} \rangle = \langle \psi_{2\sigma} | V | \psi_{2\sigma} \rangle$, leading only to a shift of the doublet with respect to the singlet.