

Inverse Jahn-Teller Transition 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, USA

(Received 31 March 2008; published 12 September 2008)

Because of the competition between the spin-orbit coupling and the Jahn-Teller (JT) energies in Fe(II) Fe(III) bimetallic oxalates, we theoretically predict that an undistorted phase with C_3 symmetry about each Fe site may be recovered at low temperatures. Both lower and upper JT transitions bracketing the ferrimagnetic transition temperature T_c are predicted for compounds that exhibit magnetic compensation. Comparisons with recent measurements and first-principles calculations provide strong evidence for the inverse JT transition below T_c .

DOI: [10.1103/PhysRevLett.101.116402](https://doi.org/10.1103/PhysRevLett.101.116402)

PACS numbers: 71.70.Ej, 75.10.Dg, 75.30.Gw, 75.50.Xx

Jahn-Teller (JT) transitions [1] in which an electronic degeneracy is removed by a crystal distortion have been observed quite frequently in recent studies of molecule-based magnets [2]. Because the mixing and splitting of degenerate levels reduces their orbital angular momenta, a JT distortion is prevented if the spin-orbit coupling $\lambda \mathbf{L} \cdot \mathbf{S}$ is sufficiently strong [3]. In this Letter, we study the JT transition in the bimetallic oxalates, a class of molecule-based magnets where the average orbital angular momentum of the degenerate electronic levels is nearly but not completely quenched by the crystal-field potential and can be controlled by choosing different organic cations to lie between the bimetallic layers. Due to the competition between the spin-orbit and JT energies, the JT distortion may only appear at intermediate temperatures around the ferrimagnetic transition temperature T_c . An inverse JT transition then marks the reentrance of the undistorted phase at low temperatures.

Bimetallic oxalates $A[M(\text{II})M'(\text{III})(\text{ox})_3]$ were first synthesized [4] in 1992. On the open honeycomb structure sketched in the inset to Fig. 1(a), transition-metal ions $M(\text{II})$ and $M'(\text{III})$ are coupled by the oxalate bridge $\text{ox} = \text{C}_2\text{O}_4$ [5]. Bimetallic layers are separated by the organic cation A . Depending on the metal atoms, the interactions within each bimetallic layer can be either ferromagnetic (FM) or antiferromagnetic (AFM) ($M(\text{II})$ and $M'(\text{III})$ moments parallel or antiparallel) with moments pointing out of the plane.

Several Fe(II)Fe(III) bimetallic oxalates exhibit magnetic compensation (MC) due to the cancellation of moments on the Fe(II) and Fe(III) sublattices at the compensation temperature T_{comp} below T_c [6]. Assuming a hierarchy of three energies, we recently explained why MC occurs for some organic cations A but not for others [7]. The dominant energy is the Hund's coupling that yields the high-spin states $S = 2$ and $S' = 5/2$ on the Fe(II) and Fe(III) sites. Next in importance is the C_3 symmetric crystal-field V_c generated by the 6 oxygen atoms around each of the Fe sites. The weakest energies are the AFM exchange coupling $J_c \mathbf{S} \cdot \mathbf{S}'$ between the Fe(II) and Fe(III) moments within each bimetallic layer, the spin-orbit cou-

pling $\lambda \mathbf{L} \cdot \mathbf{S}$ on the Fe(II) sites ($\lambda \approx -12.65$ meV), and any non- C_3 symmetric contributions of the crystal potential such as produced by a JT distortion. Because they can be tuned by the choice of $M(\text{II})$, $M'(\text{III})$ and A , the competition between these three smaller energies leads to a wide range of behavior in the bimetallic oxalates.

As shown in Ref. [7], V_c splits the Fe(II) multiplet into two doublets, $\psi_{1,2;\sigma}$ and $\psi_{4,5;\sigma}$, and a singlet $\psi_{3\sigma}$, where the spin σ takes integer values between -2 and $+2$. The low-energy doublet $\psi_{1,2;\sigma}$ carries an average orbital angular momentum L_z^{cf} that depends on the organic cation A . Lying an energy Δ above the doublet $\psi_{1,2;\sigma}$, the singlet $\psi_{3\sigma}$ carries no orbital angular momentum. MC with a single compensation temperature occurs when $1 > L_z^{\text{cf}} > l_c \approx 0.237$. After comparing the observed values of $T_{\text{comp}}/T_c \approx 0.62$ and $T_c \approx 45$ K with the theoretical predictions, we estimated [7] that in MC compounds, $J_c \approx 0.5$ meV and $L_z^{\text{cf}} \approx 0.28$. "Normal" compounds that do not exhibit MC can fall into two categories. Either the doublet remains lower than the singlet ($\Delta > 0$) but with $L_z^{\text{cf}} < l_c \approx 0.234$ or the singlet lies below the doublet ($\Delta < 0$). Our model also predicted that two compensation temperatures were possible in the very narrow window $l_c < L_z^{\text{cf}} < l_c$. Recent measurements [8] on the compound $\text{N}(n\text{-C}_4\text{H}_9)_4 \times [\text{Fe}(\text{II})\text{Fe}(\text{III})\text{ox}_3]$ (data plotted in Fig. 2) would seem to confirm that prediction.

Assuming that a doubly degenerate level is occupied by a single electron in the absence of spin-orbit coupling, then the local displacement Q of each Fe(II) ion along one of three equivalent directions [see the inset to Fig. 1(a)] is always favored by the electronic energy. The mixing of the Fe(II) eigenstates $\psi_{1\sigma}$ and $\psi_{2\sigma}$ by the JT distortion is described by the Hamiltonian [9]

$$\underline{H}_{\sigma}^{\text{mix}} = \begin{pmatrix} \epsilon_{1\sigma} & \xi \\ \xi & \epsilon_{2\sigma} \end{pmatrix}, \quad (1)$$

where the JT distortion energy ξ is independent of σ . Using first-principles calculations, we shall later estimate the electron-strain coupling constant $V_{\text{el-str}} = \xi/Q$.

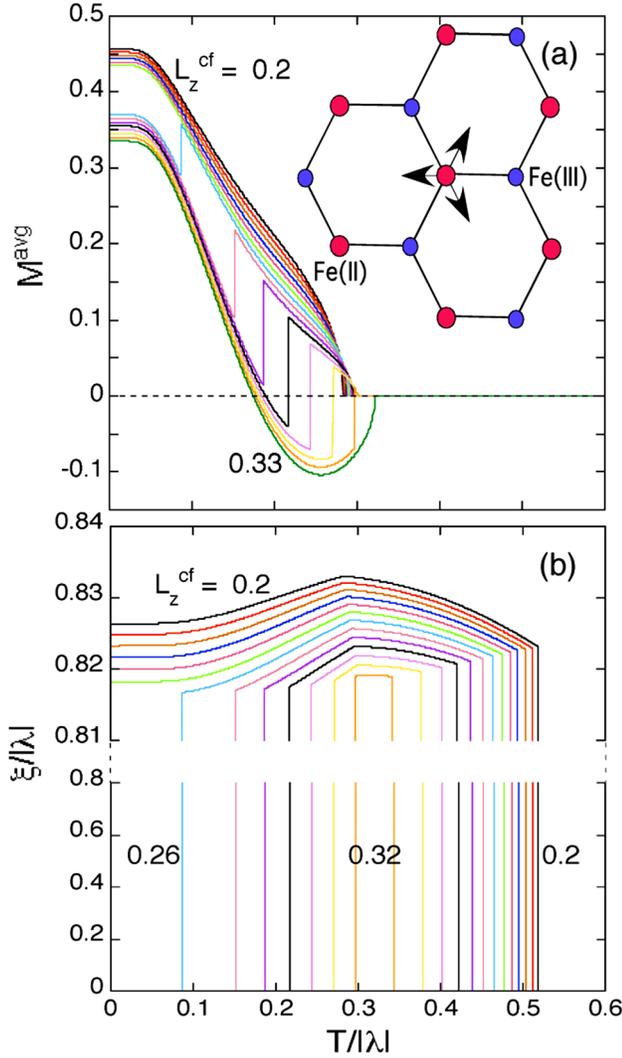


FIG. 1 (color online). The (a) average magnetization and (b) JT distortion energy ξ normalized by $|\lambda|$ versus temperature $T/|\lambda|$ for a range of L_z^{cf} in increments of 0.01 using $J_c/|\lambda| = 0.037$ and the elastic constants given in the text. Inset in (a) is a portion of the open honeycomb lattice, displaying three equivalent displacements \mathbf{Q} of the Fe(II) ion into the adjacent hexagons.

If $\epsilon_{1\sigma} = \epsilon_{2\sigma}$ are given by the mean-field (MF) result $\epsilon_{0\sigma} = 3J_c M_{S'} \sigma / 2$ with the Fe(III) moment $M_{S'}(T) = 2\langle S'_z \rangle$, then the eigenstates of $\underline{H}_\sigma^{\text{mix}}$ are $\psi_{a\sigma} = (\psi_{1\sigma} + \psi_{2\sigma})/\sqrt{2}$ and $\psi_{b\sigma} = (\psi_{1\sigma} - \psi_{2\sigma})/\sqrt{2}$ with $L_{a,b;\sigma} = \langle \psi_{a,b;\sigma} | L_z | \psi_{a,b;\sigma} \rangle = 0$ and eigenvalues $\epsilon_{a,b;\sigma} = \epsilon_{0\sigma} \pm \xi$. So without spin-orbit coupling, the orbital angular momentum is quenched by the JT distortion and the doublet splitting is $\delta = 2|\xi|$.

With the spin-orbit interaction $\lambda \mathbf{L} \cdot \mathbf{S}$ treated exactly, the eigenvalues of $\underline{H}_\sigma^{\text{mix}}$ are $\epsilon_{a\sigma} = \epsilon_{0\sigma} + t_\sigma$ and $\epsilon_{b\sigma} = \epsilon_{0\sigma} - t_\sigma$, where $t_\sigma = -\text{sgn}(\sigma) \{ (\lambda L_z^{\text{cf}} \sigma)^2 + \xi^2 \}^{1/2}$. Hence, the doublet splitting $2|t_\sigma|$ 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 $L_{a0} = L_{b0} = 0$. For $\sigma \neq 0$, the spin-orbit cou-

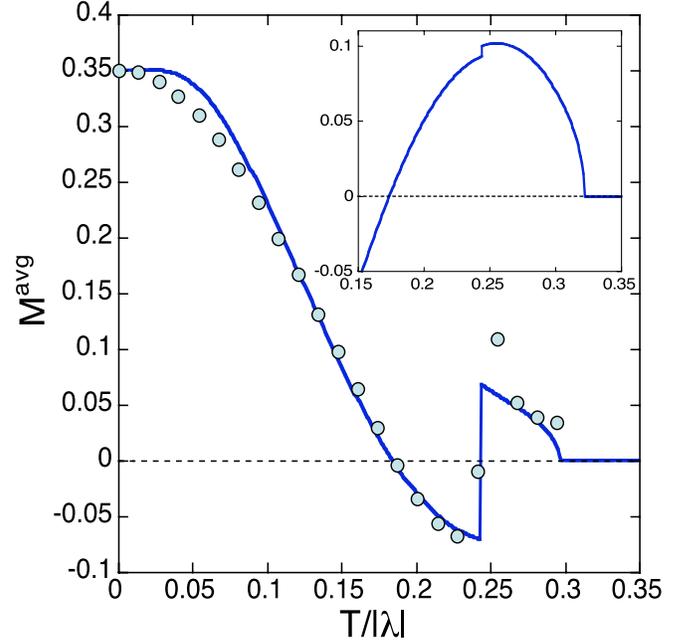


FIG. 2 (color online). The average magnetization versus $T/|\lambda|$ for $L_z^{\text{cf}} = 0.30$ and the experimental data of Ref. [8] [rescaled so that $M^{\text{avg}}(0) = 0.35$] using $J_c/|\lambda| = 0.037$ and the elastic constants given in the text. Inset is the predicted average magnetization versus $T/|\lambda|$ for a mixture of $L_z^{\text{cf}} = 0.30$ (5%) and $L_z^{\text{cf}} = 0.33$ (95%) components, with both magnetizations chosen to be positive just below T_c .

pling maintains a nonzero average orbital angular momentum $L_{a\sigma} = -L_{b\sigma}$ even in the presence of a distortion that breaks C_3 symmetry [7].

Including the orbital contribution, the Fe(II) magnetic moment is $M(T) = M_S(T) + M_L(T)$, where $M_S = 2\langle S_z \rangle$ and $M_L = \langle L_z \rangle$. The MF free energy can then be written

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

with $Z_{\text{II}} = 2 \sum_{\sigma} \exp(-3J_c M_{S'} \sigma / 2T) \cosh(t_\sigma / T)$ and $Z_{\text{III}} = 2 \sum_{\sigma'} \exp(-3J_c M_S \sigma' / 2T)$. Sums are over $\sigma = 0, \pm 1, \pm 2$ and $\sigma' = \pm 1/2, \pm 3/2, \pm 5/2$. The second line in Eq. (2) is an elastic restoring potential with $\alpha > 0$. The anharmonic term of order $\xi^3 \propto Q^3$ reflects the different energy costs for displacing Fe(II) either into one of the three open hexagons or towards one of the three neighboring Fe(III) ions. So the anharmonicity and source of the first-order JT transition arise quite naturally on an open honeycomb lattice. The sign of γ_3 is chosen to be negative so that $\xi \geq 0$.

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 coupling $\lambda \mathbf{L} \cdot \mathbf{S}$ is treated exactly, M_L is not a variational parameter and must be determined separately from the condition

$M_L = -(2/Z_{II})\sum_{\sigma} L_{a\sigma} \exp(-3J_c M_S \sigma / 2T) \sinh(t_{\sigma}/T)$. Of course, the equilibrium value for the JT distortion energy $\xi(T)$ is obtained by minimizing F with respect to ξ . With $M(T) < 0$ and $M'(T) > 0$, the average magnetization is given by $M^{\text{avg}}(T) = (M(T) + M'(T))/2$.

Both $M^{\text{avg}}(T)$ and $\xi(T)$ are plotted versus temperature in Figs. 1(a) and 1(b) for $\alpha = 3.7$, $\gamma_3 = -1.9$, and $\gamma_4 = 1.1$. As expected, the MC threshold $l_c \approx 0.282$ is enhanced by the JT distortion. When $L_z^{\text{cf}} \geq 0.260$, the JT distortion is quenched at $T = 0$ due to the strong orbital order $M_L(0) = -L_z^{\text{cf}}$. The distortion energy $\xi(T)$ vanishes both below the inverse, JT transition temperature $T_{\text{JT}}^{(l)}$ and above the normal, JT transition temperature $T_{\text{JT}}^{(u)}$. The temperature range $T_{\text{JT}}^{(u)} - T_{\text{JT}}^{(l)}$ decreases as L_z^{cf} increases and vanishes when $L_z^{\text{cf}} > 0.324$. Notice that the first-order JT transitions at $T_{\text{JT}}^{(u)}$ and $T_{\text{JT}}^{(l)}$ always lie on either side of T_c .

Because the orbital contribution $|M_L(T)|$ to the Fe(II) moment drops as $\xi(T)$ rises at the inverse JT transition, $T_{\text{JT}}^{(l)}$ is marked by a discontinuous jump in $M^{\text{avg}}(T)$. With decreasing L_z^{cf} , both the orbital contribution $|M_L(T)|$ and the size of the jump in $M^{\text{avg}}(T)$ become smaller. For $l_c < L_z^{\text{cf}} \leq 0.324$, $M^{\text{avg}}(T)$ changes sign at $T_{\text{JT}}^{(l)}$, as shown in Fig. 2 for $L_z^{\text{cf}} = 0.30$.

At high temperatures, fluctuations of the neighboring magnetic moments that are neglected within MF theory will also break the local C_3 symmetry and compete with the spin-orbit interaction. At low temperatures, however, magnetic fluctuations are suppressed and the spin-orbit interaction acts to restore C_3 symmetry. Therefore, the predicted inverse JT transition cannot be eliminated by magnetic fluctuations. A nonmonotonic magnetization has also been predicted in amorphous metals [10] and magnetic semiconductors [11].

The quantitative agreement shown in Fig. 2 between the theoretical predictions for $L_z^{\text{cf}} = 0.30$ and the measurements of Ref. [8] is striking. Rather than providing evidence for two compensation temperatures, Ref. [8] indicates that an inverse JT transition occurs at $T_{\text{JT}}^{(l)} \approx 42$ K. According to Fig. 1(b), a normal JT transition will be found at $T_{\text{JT}}^{(u)} \approx 70$ K. Indeed, recent x-ray measurements [12] 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 [12,13] suggest that most MC compounds exhibit a much smaller jump in the magnetization between T_{comp} and T_c than predicted by Fig. 1(a). X-ray studies [14] reveal that due to stacking faults, two phases coexist: one with a six-layer repeat and the other with a two-layer repeat. As shown in the inset to Fig. 2, a mixture of two phases, type 1 with $L_z^{\text{cf}} = 0.30$ (5% of the sample) and type 2 with $L_z^{\text{cf}} = 0.33$ (95% of the sample), produces a small jump that is consistent with the measurements. The much larger jump in Ref. [8] may be caused by the greater fraction of type 1 ($L_z^{\text{cf}} \approx 0.30$) stacking in their sample.

While there is no JT distortion when $\Delta < 0$ (with the singlet lowest in energy), $\xi(T)$ remains nonzero down to $T = 0$ when $\Delta > 0$ and $L_z^{\text{cf}} < 0.260$. For small L_z^{cf} , $\xi(0) \approx 0.842|\lambda| \approx 10.5$ meV and $\delta(0) \approx 21$ meV is the doublet splitting. So bimetallic oxalates with $L_z^{\text{cf}} < 0.260$ will not exhibit a discontinuity in the magnetization, which may explain why such a jump has never been observed in a normal compound [13]. Nevertheless, normal Fe(II)Fe(III) compounds with $\Delta > 0$ should manifest a normal JT transition at $T_{\text{JT}}^{(u)} \approx 0.58|\lambda| \approx 85$ K.

But any non- C_3 -symmetric cation like $\text{N}(n\text{-C}_4\text{H}_9)_4$ 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 $\underline{H}_{\sigma}^{\text{mix}}$ from ξ to $\xi + \xi_0$. In the absence of spin-orbit coupling and a spontaneous JT distortion ξ , the doublet splitting is given by $\delta = 2|\xi_0|$.

In order to estimate the orders of magnitude of the spontaneous and permanent distortions, ξ and ξ_0 , a series of first-principles calculations within the framework of density-functional theory (DFT) were performed. We employed the local spin density approximation in the plane-wave-pseudopotential approach with the PBE [15] exchange correlation functional as implemented in the Quantum-ESPRESSO package [16]. We used Vanderbilt ultrasoft pseudopotentials [16–18] including, in the case of Fe [16,18], d electrons in the valence and nonlinear core corrections. An energy cut-off of 45 Ry was applied. Since the orbitals at the Fermi level are very localized in this ionic solid, we used a single \mathbf{k} point. Spin-orbit coupling was not included. In order to stabilize the electronic density, the calculations were performed at an electronic temperature of 0.02 Ry or 270 meV.

It is well known that predictions of the experimental electronic and magnetic structure in highly-localized systems pose significant challenges for most approximations of DFT. Indeed, the energy difference between the FM and AFM configurations lies below the resolution of our theory. Moreover, possibly due to the presence of strong self-interaction errors for the localized d orbitals [19] charge order was stabilized only by forcing the net spin within each unit cell to equal 1/2.

Calculations were performed for three possible stackings (ab , aab , abc) of the bimetallic layers with $A = \text{N}(n\text{-C}_3\text{H}_7)_4$. The total energy differences between these stackings were below the accuracy of the theory, consistent with the high density of stacking faults suggested by experiments [14]. Since the relative energy difference Δ between the doublet and singlet is quite sensitive to the stacking of the bimetallic planes, L_z^{cf} will also depend on the stacking pattern.

The orders of magnitude of the JT distortion and doublet splitting were estimated by focusing on a single bimetallic layer with different cations A . Within hexagonal super-

cells, we studied the cations (i) $A = \text{NH}_4$ and (ii) $A = \text{N}(n\text{-C}_3\text{H}_7)_4$. We also considered (iii) $A = \text{N}(n\text{-C}_3\text{H}_7)_4$ in a nonhexagonal supercell.

(i) Although NH_4 is too small to stabilize an open honeycomb lattice, calculations with this cation allow the JT distortion and doublet splitting to be estimated in a C_3 symmetric environment. After relaxing the forces on all atoms while constraining the C_3 symmetry, the Fermi level for the majority band lies at a partially-occupied doublet localized on the Fe(II) sites. Displacing the Fe(II) ions on a grid \mathbf{r} provides the total energy $E(\mathbf{r})$ and doublet splitting $\delta(\mathbf{r})$. Because the electronic temperature (~ 270 meV) is much larger than the splittings, both doublet levels are equally occupied. So the energy is still minimized at the symmetric point $\mathbf{r} = 0$.

Nevertheless, assuming that the total energy difference is given by the sum of the occupied eigenvalues and neglecting a small change in the electronic density [20], we estimate the energy gain at $T = 0$ as $E(\mathbf{r}) - \delta(\mathbf{r})/2$. In the absence of spin-orbit coupling, each Fe(II) ion moves about $Q \approx 0.03$ Å [the nearest-neighbor Fe(II)-Fe(III) distance is 5.4 Å] with an energy gain of 2 meV and a doublet splitting of $2|\xi| \approx 8$ meV, corresponding to an electron-strain coupling constant $V_{\text{el-str}} \approx 130$ meV Å⁻¹.

(ii) Moderately-sized cations such as $A = \text{N}(n\text{-C}_3\text{H}_7)_4$, which are themselves non- C_3 symmetric, produce a permanent splitting $2\xi_0$ of the doublet. We considered a hexagonal unit-cell containing a single cation A with periodic boundary conditions where every cation is oriented in the same way. After relaxing the atomic positions, we obtained an intrinsic doublet splitting $2\xi_0$ of about 10 meV.

(iii) Since $\text{N}(n\text{-C}_3\text{H}_7)_4$ is just small enough to allow individual cations to rotate independently, a uniform distortion of the crystal is possible. By contrast, larger cations such as $A = \text{N}(n\text{-C}_4\text{H}_9)_4$ are unable to independently rotate within each unit cell. Locked into a highly-disordered configuration during synthesis, such cations can only break the local C_3 symmetry around each Fe(II) ion. This leads to an interesting conjecture: due to their ability to spatially order, smaller cations like $\text{N}(n\text{-C}_3\text{H}_7)_4$ may be more effective at breaking C_3 symmetry and suppressing MC than larger cations like $\text{N}(n\text{-C}_4\text{H}_9)_4$ studied in Ref. [8].

With the spin-orbit coupling set to zero ($L_z^{\text{cf}} = 0$), the doublet splitting $\delta(0) \approx 21$ meV obtained using the parameters of Fig. 1(b) is about twice as large as obtained from first-principles calculations in a C_3 symmetric environment [see cation (i) above]. Therefore, the cation $\text{N}(n\text{-C}_4\text{H}_9)_4$ may play a significant role in breaking the local C_3 symmetry and enhancing the doublet splitting.

To summarize, we have presented strong evidence for the existence of a JT distortion in Fe(II)Fe(III) bimetallic oxalates, providing the first example of an inverse JT

transition from an undistorted phase at low temperatures to a distorted phase at intermediate temperatures [21].

We would like to acknowledge conversations with Dr. Murilo Tiago. This research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC for the U. S. Department of Energy under Contract No. DE-AC05-00OR22725 and by the Division of Materials Science and Engineering of the U. S. DOE.

-
- [1] See, for example, I. B. Bersuker, *The Jahn-Teller Effect* (Cambridge University Press, Cambridge, England, 2006), and references therein.
 - [2] M. Sorai, M. Nakano, and Y. Miyazaki, *Chem. Rev.* **106**, 976 (2006); C. Beghidja, G. Rogez, J. Kortus, M. Wesolek, and R. Welter, *J. Am. Chem. Soc.* **128**, 3140 (2006); J. A. Hatnean *et al.*, *J. Am. Chem. Soc.* **128**, 14992 (2006); C. J. Milios *et al.*, *J. Am. Chem. Soc.* **129**, 6547 (2007).
 - [3] J. B. Goodenough, *Magnetism and the Chemical Bond* (Interscience, New York, 1963).
 - [4] H. Tamaki *et al.*, *J. Am. Chem. Soc.* **114**, 6974 (1992).
 - [5] See the review R. Clément *et al.*, *Mon. für Chem.* **134**, 117 (2003).
 - [6] C. Mathonière, S. G. Carling, and P. Day, *J. Chem. Soc., Chem. Commun.* 1551 (1994); C. Mathonière *et al.*, *Inorg. Chem.* **35**, 1201 (1996); M. Clemente-León, E. Coronado, C. J. Gómez-García, and A. Soriano-Portillo, *Inorg. Chem.* **45**, 5653 (2006).
 - [7] R. S. Fishman and F. A. Reboredo, *Phys. Rev. Lett.* **99**, 217203 (2007); *Phys. Rev. B* **77**, 144421 (2008).
 - [8] G. Tang *et al.*, *Physica (Amsterdam)* **392B**, 337 (2007).
 - [9] Because of time-reversal invariance, diagonal terms in H_{σ}^{mix} involving the crystal-field potential must satisfy $\langle \psi_{1\sigma} | V_c | \psi_{1\sigma} \rangle = \langle \psi_{2\sigma} | V_c | \psi_{2\sigma} \rangle$, leading only to a shift of the doublet with respect to the singlet.
 - [10] Y. Kakehashi, *Phys. Rev. B* **43**, 10820 (1991).
 - [11] A. G. Petukhov, I. Žutić, and S. C. Erwin, *Phys. Rev. Lett.* **99**, 257202 (2007).
 - [12] I. D. Watts *et al.*, *J. Phys. Chem. Solids* **66**, 932 (2005).
 - [13] C. J. Nuttall and P. Day, *Chem. Mater.* **10**, 3050 (1998).
 - [14] C. J. Nuttall and P. Day, *J. Solid State Chem.* **147**, 3 (1999); N. S. Ovanesyan *et al.*, *Dalton Trans.* **18**, 3101 (2005).
 - [15] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
 - [16] S. Baroni *et al.*, <http://www.pwscf.org>.
 - [17] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
 - [18] A. M. Rappe *et al.*, *Phys. Rev. B* **41**, 1227 (1990).
 - [19] J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
 - [20] See Eq. (17) in J. Ihm, A. Zunger, and M. Cohen, *J. Phys. C* **12**, 4409 (1979).
 - [21] See EPAPS Document No. E-PRLTAO-101-001838 for a more extended description of the formalism developed in this Letter and for more results on the permanent distortion ξ_0 . For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.