PHYSICAL REVIEW B VOLUME 61, NUMBER 6 1 FEBRUARY 2000-II

Charge and orbital ordering in underdoped $La_{1-x}Sr_xMnO_3$

T. Mizokawa
Solid State Physics Laboratory, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands and Department of Complexity Science and Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

D. I. Khomskii and G. A. Sawatzky
Solid State Physics Laboratory, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

(Received 25 October 1999)

We have explored spin, charge, and orbitally ordered states in $La_{1-x}Sr_xMnO_3$ ($0<x<1/2$) using model Hartree-Fock calculations on d-p-type lattice models. At $x=1/8$, several charge and orbitally modulated states are found to be stable and almost degenerate in energy with a homogeneous ferromagnetic state. The present calculation indicates that a ferromagnetic state with a charge modulation along the c axis which is consistent with the experiment by Yamada *et al.* might be responsible for the anomalous behavior around $x=1/8$.

$La_{1-x}Sr_xMnO_3$ has been extensively studied because of its interesting magnetic and electric properties.[1,2] An antiferromagnetic insulator $LaMnO_3$ evolves into a ferromagnetic metal with substitution of Sr for La or with hole doping.[2] Underdoped $La_{1-x}Sr_xMnO_3$ with $x\sim1/8$, which is located between the antiferromagnetic insulating region and the ferromagnetic metallic region, shows many anomalous behaviors.[2–6] $La_{0.875}Sr_{0.125}MnO_3$ is a paramagnetic insulator above T_{CA} (180 K) and has a canted antiferromagnetic state below it.[3] Recently, it has been found that $La_{0.875}Sr_{0.125}MnO_3$ becomes a ferromagnetic insulator below 140 K.[5,6] One important question is why the hole-doped system can exist as an insulator. The superstructure observed by Yamada *et al.*[4] indicates that charge ordering is responsible for the insulating behavior. However, it is still controversial whether charge ordering is realized in $La_{0.875}Sr_{0.125}MnO_3$ or not. Ahn and Millis studied the charge and orbital ordering in $La_{0.875}Sr_{0.125}MnO_3$ using a model of strong electron-lattice coupling limit and found that the charge ordering proposed by Yamada *et al.* can be reproduced using their model.[7] On the other hand, using the resonant x-ray scattering, Endoh *et al.* confirmed that the superlattice peak found by Yamada *et al.* does not show resonance at the Mn K edge and concluded that there is no Mn^{3+}/Mn^{4+} charge ordering in $La_{0.875}Sr_{0.125}MnO_3$.[6] Another interesting question is what is the origin of the ferromagnetism. Since the system is insulating, the simple double exchange mechanism cannot be applied. A model Hartree-Fock (HF) calculation for $LaMnO_3$ has predicted that, if the Jahn-Teller distortion is suppressed, a ferromagnetic insulating state with orbital ordering would be realized.[8] This means that the superexchange interaction between the Mn^{3+} ions can be ferromagnetic because of orbital ordering.[9] Endoh *et al.* observed orbital ordering below 145 K using x-ray scattering technique and argued that the orbital ordering is essential for the ferromagnetic and insulating state.[6] However, the orbital ordered state without charge ordering is expected to be metallic and may not be consistent with the fact that $La_{0.875}Sr_{0.125}MnO_3$ is insulating. In the doped manganites, the orbital modulation should couple with the charge modulation in a similar way that the spin modulation couples with the charge modulation in the doped cuprates.[10] In order to understand the electronic structure of the ferromagnetic and insulating state in the doped manganites, it is necessary to consider the complicated interplay between the charge and orbital orderings. In this paper, we study the possibility of charge and orbitally ordered states in underdoped $La_{1-x}Sr_xMnO_3$ using the model HF calculation and explore the origin of the ferromagnetic insulating state in underdoped $La_{1-x}Sr_xMnO_3$.

We use the multiband d-p model with 16 Mn and 48 oxygen sites in which full degeneracy of Mn $3d$ orbitals and the oxygen $2p$ orbitals are taken into account.[8] The Hamiltonian is given by

$$H=H_p+H_d+H_{pd}, \tag{1}$$

$$H_p=\sum_{k,l,\sigma}\epsilon_k^p p_{k,l\sigma}^+ p_{k,l\sigma}+\sum_{k,l>l',\sigma}V_{k,ll'}^{pp}p_{k,l\sigma}^+ p_{k,l'\sigma}+\text{H.c.}, \tag{2}$$

$$\begin{aligned}H_d=&\epsilon_d\sum_{i,m\sigma}d_{i,m\sigma}^+ d_{i,m\sigma}+u\sum_{i,m}d_{i,m\uparrow}^+ d_{i,m\uparrow}d_{i,m\downarrow}^+ d_{i,m\downarrow}\\&+u'\sum_{i,m\neq m'}d_{i,m\uparrow}^+ d_{i,m\uparrow}d_{i,m'\downarrow}^+ d_{i,m'\downarrow}\\&+(u'-j')\sum_{i,m>m',\sigma}d_{i,m\sigma}^+ d_{i,m\sigma}d_{i,m'\sigma}^+ d_{i,m'\sigma}\\&+j'\sum_{i,m\neq m'}d_{i,m\uparrow}^+ d_{i,m'\uparrow}d_{i,m\downarrow}^+ d_{i,m'\downarrow}\\&+j\sum_{i,m\neq m'}d_{i,m\uparrow}^+ d_{i,m'\uparrow}d_{i,m'\downarrow}^+ d_{i,m\downarrow},\end{aligned} \tag{3}$$

$$H_{pd}=\sum_{k,m,l,\sigma}V_{k,lm}^{pd}d_{k,m\sigma}^+ p_{k,l\sigma}+\text{H.c.} \tag{4}$$

$d_{i,m\sigma}^+$ are creation operators for the $3d$ electrons at site i. $d_{k,m\sigma}^+$ and $p_{k,l\sigma}^+$ are creation operators for Bloch electrons with wave vector k which are constructed from the mth com-

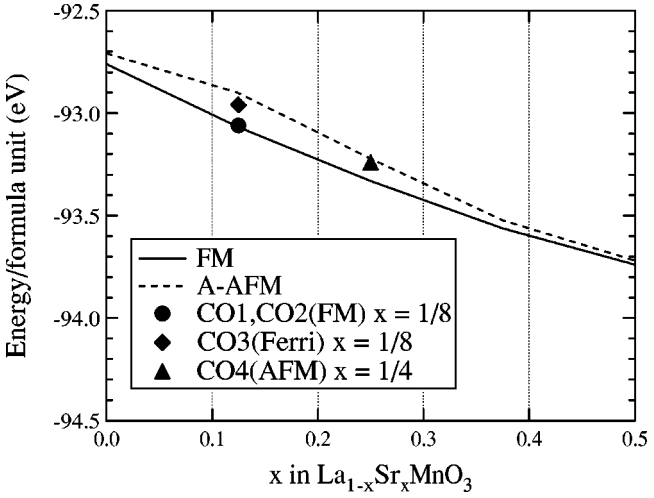

FIG. 1. Energies per formula unit cell of the various charge ordered states, the ferromagnetic state (solid curve), and the *A*-type antiferromagnetic state (dashed curve) as functions of hole concentration *x*.

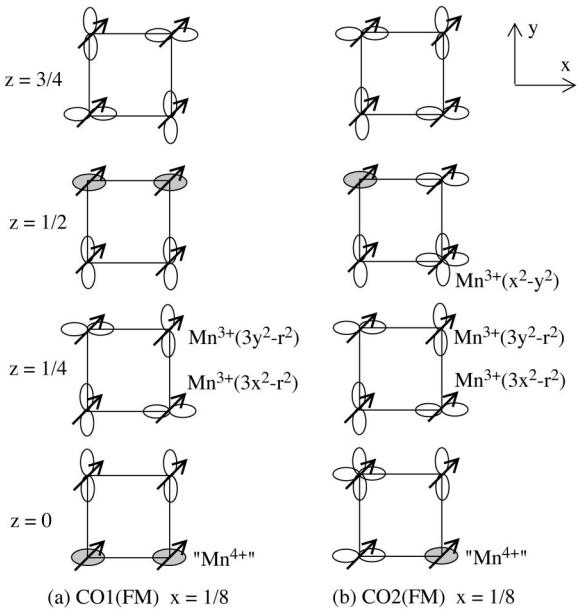

FIG. 2. Schematic drawings of the charge and orbital orderings for the ferromagnetic state at $x=1/8$. The unit cell consists of four layers of $z=0$, 1/4, 1/2, and 3/4, each of which has four Mn sites. The arrows indicate spin directions at each site and the shaded orbitals are for Mn^{4+}-like hole-rich sites.

ponent of the $3d$ orbitals and from the lth component of the $2p$ orbitals, respectively. The intra-atomic Coulomb interaction between the $3d$ electrons is expressed using Kanamori parameters, u, u', j, and j'.[11] The transfer integrals between Mn $3d$ and oxygen $2p$ orbitals $V^{pd}_{k,lm}$ are given in terms of Slater-Koster parameters $(pd\sigma)$ and $(pd\pi)$. The transfer integrals between the oxygen $2p$ orbitals $V^{pp}_{k,ll'}$ are expressed by $(pp\sigma)$ and $(pp\pi)$. Here, the ratio $(pd\sigma)/(pd\pi)$ is -2.16. $(pp\sigma)$ and $(pp\pi)$ are fixed at -0.60 and 0.15, respectively, for the undistorted lattice. When the lattice is distorted, the transfer integrals are scaled using Harrison's law.[12] The charge-transfer energy Δ is defined by $\epsilon^0_d-\epsilon_p+nU$, where ϵ^0_d and ϵ_p are the energies of the bare $3d$ and $2p$ orbitals and U $(=u-20/9j)$ is the multiplet-averaged d-d Coulomb interaction. Δ, U, and $(pd\sigma)$ for $LaMnO_3$ are 4.0, 5.5, and -1.8 eV, respectively, which are taken from the photoemission study.[13]

In Fig. 1, the energies of the spin, charge, and orbitally ordered states are compared with those of the ferromagnetic and *A*-type antiferromagnetic states, which are plotted as functions of the hole concentration *x*. At *x* of 1/8, several charge ordered states exist as stable solutions. Schematic drawings of the ferromagnetic charge ordered states are shown in Fig. 2. The unit cell consists of the four layers of $z=0$, 1/4, 1/2, and 3/4 along the *c* axis. Each layer has four different Mn sites. In the charge-ordered states, the hole-rich planes ($z=0$ and 1/2) and the hole-poor planes ($z=1/4$ and 3/4) are alternatingly stacked along the *c* axis. In the hole-poor plane, either $d_{3x^2-r^2}$-like or $d_{3y^2-r^2}$-like orbital is mainly occupied at each site and the $3x^2-r^2/3y^2-r^2$-type orbital ordering. This orbital ordering in the hole-poor plane is essentially the same as that in $LaMnO_3$ although it is weak compared to that in $LaMnO_3$. While the orbital orderings at $z=0$ and at $z=3/4$ are out of phase for CO1 [see Fig. 2(a)], those are in phase for CO2 as shown in Fig. 2(b). Probably, the orbital ordering in the hole-poor plane is related to the observation by Endoh *et al.*[6] In the hole-rich plane, for CO1, the Mn^{4+}-like sites form a kind of stripe as shown in Fig. 2(a) and the extra holes are sitting at the oxygen sites between the Mn^{4+}-like sites. For the CO2 state, the Mn^{4+}-like sites form a square lattice and the extra holes are distributed at the oxygen sites surrounding the Mn^{4+}-like site. The orbital ordering at the Mn^{3+}-like sites in the hole-rich plane is very weak and depends on the orbital ordering in the hole-poor plane. These two ferromagnetic states with the charge and orbital modulations are degenerate in energy within the accuracy of the present calculation and are the lowest in energy among the charge-ordered states obtained in the present model calculations. Since $LaMnO_3$ is a charge-transfer-type Mott insulator, the Mn^{4+}-like site has approximately four electrons. For example, in the CO1 state, the number of $3d$ electrons at the Mn^{3+}-like sites in the hole-poor plane is ~ 4.08 and that of the Mn^{3+}-like and the Mn^{4+}-like sites in the hole-rich plane are ~ 4.03 and ~ 4.01, respectively. This calculated result can explain why the resonant x-ray scattering cannot distinguish between the Mn^{3+}-like and Mn^{4+}-like sites.[6]

These ferromagnetic states with the charge modulations are still metallic without lattice distortion. We have studied the effect of the lattice distortion which is shown in the right column of Fig. 3. The hole-poor plane ($z=1/4$) can couple with the Jahn-Teller distortion of $LaMnO_3$. On the other hand, in the hole-rich plane ($z=0$) for CO1, the shift of oxygen ion sitting between the Mn^{4+}-like sites causes a doubling along the stripe of the Mn^{4+}-like sites and is expected to open a band gap. Actually, we found that the small shift of these oxygens less than 0.1 Å (Fig. 3), which gives the superstructure along the *c* axis and is consistent with the experiment by Yamada *et al.*,[4] can open a band gap for the two charge-modulated ferromagnetic states. The lattice distortion shown in Fig. 3 is enough to open a band gap for the CO2 state although the breathing-type distortion at the Mn^{4+}-like sites is expected to be more effective. These fer-

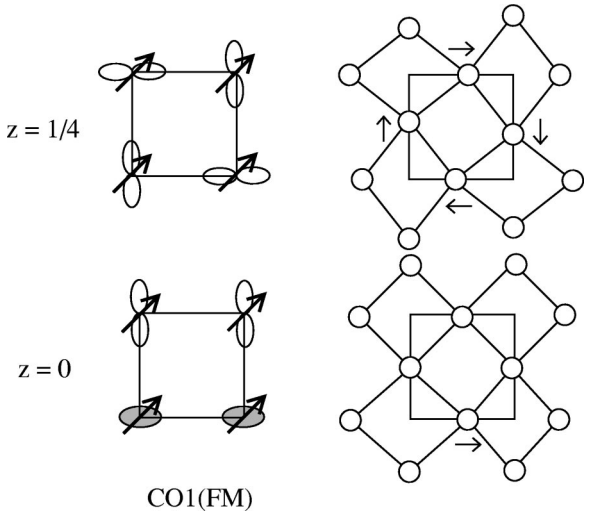

FIG. 3. Schematic drawings of the charge and orbital orderings (left column) and the lattice distortions (right column) for the hole-rich ($z=0$) and hole-poor ($z=1/4$) planes in the ferromagnetic state. The open circles and the arrows indicate the oxygen ions and the shifts of the oxygen ions, respectively.

romagnetic states with the lattice distortions are strong candidates for the ferromagnetic and insulating state found in $La_{0.875}Sr_{0.125}MnO_3$.

A sketch of the ferrimagnetic state accompanied by the charge and orbital ordering is shown in Fig. 4(a). In this arrangement, each hole-rich Mn^{4+}-like site is surrounded by six hole-poor Mn^{3+} sites. This can be viewed as a lattice of orbital polaron[14] which is displayed in Fig. 5(a). The superexchange interaction between the Mn^{3+}-like and Mn^{4+}-like sites is ferromagnetic and that between the Mn^{3+}-like sites is

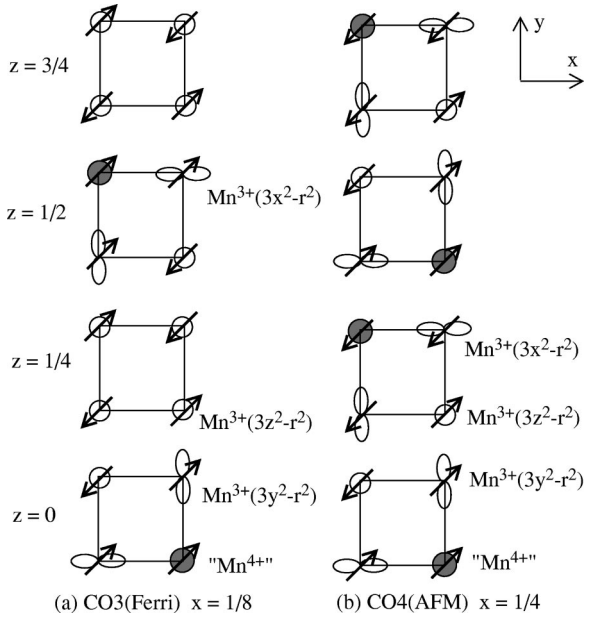

FIG. 4. Schematic drawings of the charge and orbital orderings (a) for the ferrimagnetic states at $x=1/8$ and (b) for the antiferromagnetic state at $x=1/4$. The unit cell consists of four layers of $z=0$, 1/4, 1/2, and 3/4, each of which has four Mn sites. The arrows indicate spin directions at each site and the shaded orbitals are for Mn^{4+}-like hole-rich sites.

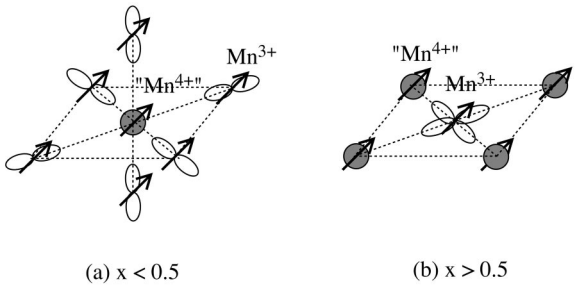

FIG. 5. Schematic drawings of the orbital polarons (a) for $x<0.5$ and (b) for $x>0.5$. The arrows indicate spin directions at each site and the shaded orbitals are for Mn^{4+}-like hole-rich sites.

antiferromagnetic in this ferrimagnetic state. The orbital polaron might be related to the ~ 12 Å magnetic clusters observed in $La_{0.67}Ca_{0.33}MnO_3$.[15] It is expected that the existence of this orbital polaron makes the magnetic interaction along the c axis ferromagnetic and gives three-dimensional ferromagnetic coupling. Since the Mn^{3+}-like sites should be accompanied by the Jahn-Teller distortion, the orbital polaron might also be related to the Jahn-Teller polaron observed in $La_{1-x}Ca_xMnO_3$ with $x<0.5$.[16] On the other hand, in $La_{1-x}Ca_xMnO_3$ with $x>0.5$, the number of Mn^{4+}-like sites is larger than that of Mn^{3+}-like sites. In such a case, the orbital polaron, in which a Mn^{4+}-like site is surrounded by four Mn^{3+}-like sites [see Fig. 5(b)], is expected to be relevant. This orbital polaron gives two-dimensional ferromagnetic coupling. Actually, it has been reported that $Nd_{1-x}Sr_xMnO_3$ with $x>0.5$ has the A-type antiferromagnetic state, in which the ferromagnetic ab planes are antiferromagnetically coupled along the c axis.[17] This orbital polaron might be relevant in the A-type antiferromagnetic state of $Nd_{1-x}Sr_xMnO_3$.

At $x=1/4$, the homogeneous ferromagnetic state is very stable and no ferromagnetic charge-modulated state was obtained. However, it is found that an antiferromagnetic state with charge and orbital ordering exists as a stable solution which is schematically shown in Fig. 4(b). This charge-ordered state can be viewed as a lattice of the orbital polaron coupled antiferromagnetically. Although this state is higher in energy than the homogeneous ferromagnetic state as shown in Fig. 1, a lattice distortion of breathing type may stabilize the charge-ordered state relative to the ferromagnetic state.

There are two possible ways to describe the charge-ordered states: a polaron lattice language and a charge-density wave language. When the electron-lattice coupling term dominates the other terms, the polaron lattice picture is appropriate. The ferrimagentic charge-ordered state obtained above can be viewed as an orbital polaron lattice and is expected to strongly couple with lattice distortions or the Jahn-Teller distortions. On the other hand, the charge-density-wave language becomes more appropriate when the kinetic-energy term is relevant. It is natural to speculate that the electron-lattice coupling is weak in the ferromagnetic charge-modulated state compared to the orbital polaron lattice. The present calculation neglecting lattice distortions indicates that a kind of Umklapp process can give the modulation along the c axis and that the charge-density-wave picture might be relevant in $La_{0.875}Sr_{0.125}MnO_3$. Since the

number of $3d$ electrons at the Mn^{4+}-like site is almost the same as that of the Mn^{3+}-like site, the electron-lattice coupling is expected to be small. Actually the observed lattice modulation along the c axis is very small.[4] This is also consistent with the experimental observation that resonant x-ray scattering fails to distinguish between Mn^{3+}-like and Mn^{4+}-like sites.[6] The present calculation fails to give a finite band gap without extra lattice distortion, suggesting that the weak electron-lattice coupling is still important to give the band gap. Here, it should be noted that a perfect nesting is not required in the present system because the Coulomb interaction term between the $3d$ electrons is very large and is comparable to the kinetic-energy term and that, in this sense, the magnetic coupling between two Mn sites can be viewed as a kind of superexchange coupling.

In conclusion, we have studied possible charge and orbitally ordered states in underdoped $La_{1-x}Sr_xMnO_3$ using the model HF calculation. It has been found that the ferromagnetic state with the charge ordering along the c axis, which is consistent with the experiment by Yamada *et al.*,[4] is stable at $x=1/8$. It has been argued that the charge and orbital ordering in the ferrimagnetic state can be interpreted as orbital polaron lattice. In order to clarify the interplay between the charge/orbital ordering and the lattice distortion, the underdoped manganites should be studied in the future using a more realistic model which includes the electron-lattice interaction.

The authors would like to thank J. L. Garcia-Muños for useful discussions. This work was supported by the Nederlands Organization for Fundamental Research of Matter (FOM) and by the European Commission TRM network on oxide spin electronics (OXSEN).

[1] J. B. Goodenough, Phys. Rev. **100**, 564 (1955); J. B. Goodenough and J. S. Zou, Nature (London) **386**, 229 (1997).

[2] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, Phys. Rev. B **51**, 14 103 (1995).

[3] H. Kawano, R. Kajimoto, M. Kubota, and H. Yoshizawa, Phys. Rev. B **53**, R14 709 (1996).

[4] Y. Yamada, O. Hino, S. Nohdo, R. Kanao, T. Inami, and S. Katano, Phys. Rev. Lett. **77**, 904 (1996).

[5] R. Senis, V. Laukhin, B. Martínez, J. Fontcuberta, X. Obradors, A. A. Arsenov, and Y. M. Mukovskii, Phys. Rev. B **57**, 14 680 (1998); S. Uhlenbruck, R. Teipen, R. Klingeler, B. Büchner, O. Friedt, M. Hücker, H. Kierspel, T. Niemöller, L. Pinsard, A. Revcolevschi, and R. Gross, Phys. Rev. Lett. **82**, 185 (1999); M. Paraskevopoulos, J. Hemberger, A. Loidl, A. A. Mukhin, V. Yu Ivanov, and A. M. Balbashov, cond-mat/9812276 (unpublished).

[6] Y. Endoh, K. Hirota, S. Ishihara, S. Okamoto, Y. Muwakami, A. Nishizawa, T. Fukuda, H. Kimura, H. Nojiri, K. Kaneko, and S. Maekawa, Phys. Rev. Lett. **82**, 4328 (1999).

[7] K. H. Ahn and A. J. Millis, Phys. Rev. B **58**, 3697 (1998).

[8] T. Mizokawa and A. Fujimori, Phys. Rev. B **51**, 12 880 (1995); **54**, 5368 (1996).

[9] K. I. Kugel and D. I. Khomskii, Zh. Éksp. Teor. Fiz., Pis'ma Red. **15**, 629 (1972) [JETP Lett. **15**, 446 (1972)]; Usp. Fiz. Nauk. **136**, 621 (1981) [Sov. Phys. Usp. **25**, 231 (1982).]

[10] W. Koshibae, Y. Kawamura, S. Ishihara, S. Okamoto, J. Inoue, and S. Maekawa, J. Phys. Soc. Jpn. **66**, 957 (1997); V. I. Anisimov, I. S. Elfimov, M. A. Korotin, and K. Terakura, Phys. Rev. B **55**, 15 494 (1997); T. Mizokawa and A. Fujimori, *ibid.* **56**, R493 (1997).

[11] J. Kanamori, Prog. Theor. Phys. **30**, 275 (1963).

[12] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Dover, New York, 1989).

[13] T. Saitoh, A. E. Bocquet, T. Mizokawa, H. Namatame, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano, Phys. Rev. B **51**, 13 942 (1995).

[14] M. Paraskevopoulos, J. Hemberger, A. Loidl, A. A. Mukhin, V. Yu. Ivanov, and A. M. Balbashov, cond-mat/9812305 (unpublished); R. Kilian and G. Khaliullin, Phys. Rev. B **60**, 13 458 (1999).

[15] J. M. De Teresa, M. R. Ibarra, P. A. Algarabel, C. Ritter, C. Marquina, J. Blasco, J. Garcia, A. del Moral, and Z. Arnold, Nature (London) **386**, 256 (1997).

[16] A. Lanzara, N. L. Saini, M. Brunelli, F. Natali, A. Bianconi, P. G. Radaelli, and S.-W. Cheong, Phys. Rev. Lett. **81**, 878 (1998).

[17] H. Kawano, R. Kajimoto, H. Yoshizawa, Y. Tomioka, H. Kuwahara, and Y. Tokura, Phys. Rev. Lett. **78**, 4253 (1997).