Double Exchange Alone Does Not Explain the Resistivity of $La_{1-x}Sr_xMnO_3$

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The $La_{1-x}Sr_xMnO_3$ system with $0.2 \lesssim x \lesssim 0.4$ has traditionally been modeled with a "double-exchange" Hamiltonian in which it is assumed that the only relevant physics is the tendency of carrier hopping to line up neighboring spins. We present a solution of the double-exchange model, show it is incompatible with many aspects of the data, and propose that in addition to double-exchange physics a strong electron-phonon interaction arising from the Jahn-Teller splitting of the outer Mn d level plays a crucial role.

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The $La_{1-x}A_xMnO_3$ system (A represents a divalent alkali element such as Sr or Ca) has attracted much recent attention because of the very large magnetoresistance exhibited for $0.2 \lesssim x \lesssim 0.4$ [1]. Treatments [2–4] of the physics of this system have focused primarily on the phenomenon of "double exchange" [5]. In this Letter we solve the double-exchange model and deduce several experimental consequences which, we show, disagree with data by an order of magnitude or more. The discrepancy must be resolved by including additional physics, which we suggest involves polaron effects due to a very strong electron-phonon coupling coming from a Jahn-Teller splitting of the Mn^{3+} ion. We mention several experiments which would verify or falsify our suggestion.

In $La_{1-x}A_xMnO_3$ the electronically active orbitals are the Mn $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals [6]. The mean number of d electrons per Mn is $4 - x$. The Hund's rule coupling is believed to be very strong relative to the d-d hopping and the spin-orbit coupling [7] so the spins of all of the d electrons on a given site must be parallel. Three of the d electrons go into tightly bound corelike d_{xy}, d_{xz}, d_{yz} orbitals forming a core spin S_i^c of magnitude $\frac{3}{2}$, to which the outer shell electron (which may hop from site to site) is aligned by the Hund's rule coupling. The Hamiltonian containing this physics is

$$H_{d\text{-ex}} = -\sum_{\langle ij\rangle a,b,\alpha} t_{ij}^{ab} d_{ia\alpha}^\dagger d_{jb\alpha} - J_H \sum_{i\alpha\beta} \vec{S}_i^c \cdot d_{ia\alpha}^\dagger \vec{\sigma}_{\alpha\beta} d_{ia\beta} . \quad (1)$$

Here $d_{ia\alpha}^\dagger$ creates an electron in an outer-shell orbital state $a, b = x^2 - y^2$ or $3z^2 - r^2$ and spin α, J_H is the Hund's rule coupling connecting the core spin to the outer-shell electrons, and the appropriate limit, which we shall take, is $J_H \to \infty$. To study Eq. (1) we parametrize S_i^c by polar angles θ_i, ϕ_i, rotate the electrons so that the spin quantization axis at site i is parallel to S_i^c, and project onto the spin component parallel to $\vec{S}_i^c$. The matrix $\mathbf{R}_i$ which accomplishes this is $\mathbf{R}_i = (\cos\theta_i/2)\,\mathbf{1} + i\sin(\theta_i/2)\sin\phi_i\,\boldsymbol{\sigma}^x + i\sin(\theta_i/2)\cos\phi_i\,\boldsymbol{\sigma}^y$. The electrons may be integrated out, and the partition function Z written as

$$Z = \int \mathcal{D}\cos\theta\,\mathcal{D}\phi_i \exp\mathcal{A} , \quad (2)$$

with action $\mathcal{A}$ given by

$$\mathcal{A} = \mathrm{Tr}\ln[\partial_\tau - \mu + \mathbf{R}_i^+\partial_\tau\mathbf{R}_i - t_{ij}^{ab}(\mathbf{R}_i^\dagger\mathbf{R}_j + \mathbf{R}_j^\dagger\mathbf{R}_i)]_{11} + iS_c\int_0^B d\tau\sum_i \dot{\phi}_i(1 - \cos\theta_i) . \quad (3)$$

Here the first term comes from integrating out the electrons and the second is the Berry phase term for the core spins. The subscript 11 expresses the requirement that as $J_H \to \infty$ the outer shell electron must be parallel to $\vec{S}_c$. At low T we may expand about the ordered ferromagnetic state $\theta_i = 0$. The effective action becomes $\mathcal{A} = \mathcal{A}_F + \mathcal{A}_{\mathrm{sw}}$. $\mathcal{A}_F$ is the free energy for free fermions moving in the band structure defined by t_{ij}^{ab}. $\mathcal{A}_{\mathrm{sw}}$ may be written in terms of the magnetization variables M_x and M_y describing deviations from the ordered state (with magnetization taken parallel to z) as

$$\mathcal{A}_{\mathrm{sw}} = \tfrac{1}{2}\int_0^B d\tau\int\frac{d^3k}{(2\pi)^3} i\Big(S_c + \frac{1-x}{2}\Big)\vec{M}_k \times \partial_\tau\vec{M}_{-k} - 2Ka_0^2k^2\vec{M}_k\cdot\vec{M}_{-k} + \mathcal{O}(M^4) . \quad (4)$$

Here $K = \sum_{ab} t_{i,i+\hat{x}}^{ab}\langle c_{ia}^\dagger c_{i+\hat{x}b}\rangle$ is the electron stress-energy tensor and is related to the integral of the optical conductivity as described below, a_0 is the lattice constant, and $c_i^\dagger$ creates a spin polarized electron on site i. Equation (4) is the action for a quantum ferromagnet with spin $S^* = S_c + (1 - x)/2$ and stiffness K. This action implies that the magnon dispersion is

$$\omega_{\mathrm{mag}} = (K/S^*)(ka)^2 . \quad (5)$$

A similar result for the magnon dispersion was obtained by Kubo and Ohata [3] using different methods.

The quantity K is important because it is the only energy scale in the theory. A theoretical estimate of K is $K \sim 2tn$, where n is the electron density per unit cell per orbital and t the average hopping energy. A recent band theory calculation found a bandwidth of 2.5 eV, implying $t \sim 0.2$ eV and $K \sim 0.1$ eV for $x \approx 0.2$ [8]. One experimental estimate comes from the zone boundary magnon frequency, which has been measured to be

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90 meV in $La_{1.7}Pb_{0.3}MnO_3$, implying $K \approx 0.045$ eV [9]. K may also be experimentally determined from the optical conductivity $\sigma(\omega)$. In a one-band model with only nearest neighbor hopping $\int_0^\infty d\omega\, \sigma(\omega) = \pi e^2 K/a_0$ [10]. To extract K from conductivity data on a real material one must remove the interband contributions to σ. Ambiguities arise because there is often no clear demarcation between interband and intraband contributions. The optical conductivity of $La_{1-x}Sr_xMnO_3$ has been measured for $x = 0.175$ and $x = 0.3$ [11]. At $x = 0.175$ and low T, $\sigma(\omega) \approx (500\ \mu\Omega\,\mathrm{cm})^{-1} \approx 0.3$ eV, independent of ω, and it seems reasonable to assume that for $\omega < 1$ eV the conductivity is dominated by the conduction band. Using $a_0 = 4$ Å, one finds $K \approx 0.03$ eV ≈ 400 K, rather less than the band structure estimate for $x = 0.175$. The rough correspondence between the optical and magnetic measurements of K suggests that the double-exchange model provides a good representation of the physics at low T, although to settle the issue a measurement of both quantities in the same sample is needed.

From K we may estimate the ferromagnetic transition temperature T_c as follows. The cubic lattice Heisenberg model with exchange constant J has a magnon dispersion $\omega = 2JS(ka)^2$ [12]. The known relation [13] between J and T_c then implies $T_c \approx 2.9K(S^* + 1)/S^*$. The band structure value for K then implies $T_c \approx 0.3$ eV, while the optical or magnon value implies $T_c \approx 0.1$ eV. Both values are much higher than the observed $T_c \approx 200$ K for $x = 0.175$. The great difference between the observed and estimated T_c implies that additional physics becomes important as T is raised.

We now consider the double-exchange model in the regime $T \sim T_c$. Because the low T properties are those of a quantum model with $S \approx 2$, near T_c we may consider classical spins and so neglect the imaginary time dependence of the angular variables in Eq. (3). The problem then becomes that of electrons moving on a lattice with hopping amplitude $\bar{t}_{ij}^{ab} = t_{ij}^{ab}[\cos(\theta_i/2)\cos(\theta_j/2) + \cos(\phi_i - \phi_j)\sin(\theta_i/2)\sin(\theta_j/2)]$. We further assume that contributions to the partition function in which fermions move on closed loops in real space may be neglected. We may then rotate the ϕ_i independently and therefore replace $\bar{t}$ by the familiar double-exchange form $\bar{t}_{ij}^{ab} = t_{ij}^{ab}\sqrt{(S^2 + \vec{S}_i \cdot \vec{S}_j)/2S^2}$ [5]. We may then replace Eq. (1) by

$$H_{\mathrm{eff}} = -\sum_{ijab} \frac{t_{ij}^{ab}}{\sqrt{2}} \sqrt{1 + \frac{\vec{S}_i \cdot \vec{S}_j}{S^2}}\, (c_{ia}^\dagger c_{jb} + \mathrm{H.c.}), \qquad (6)$$

where the $\vec{S}_i$ are now understood to be classical spins. The free energy function describing the spin distribution is obtained by integrating out the conduction electrons at a fixed distribution of spins. This problem is one of conduction electrons moving in a lattice with fluctuating hopping; for such problems it is known that to a good approximation the free energy of the conduction electrons depends only on the average hopping [14] so the spin energy $E(\{S_i\})$ is given by $E(\{S_i\}) = -T\sum_k \ln[1 + e^{\beta(\bar{\epsilon}_k - \mu)}]$ with $\bar{\epsilon}_k = -2\bar{t}(\cos k_x a + \cos k_y a + \cos k_z a)$ and $\bar{t} = \left\langle t_{ij}^{ab}\sqrt{1 + \vec{S}_i \cdot \vec{S}_j/S^2}\right\rangle$. In particular, if the temperature is less than the Fermi temperature of the electrons,

$$E(\{S_i\}) = -\sum_{\langle ij\rangle} \frac{t_{ij}^{ab}}{\sqrt{2}} \sqrt{1 + \frac{\vec{S}_i \cdot \vec{S}_j}{S^2}}\, \langle c_{ia}^\dagger c_{jb}\rangle. \qquad (7)$$

In other words, the spin energy involves nearest neighbor coupling with scale again set by the electron kinetic energy. In the nearest neighbor Heisenberg model at T_c, $\langle \vec{S}_i \cdot \vec{S}_j\rangle/S^2 \approx 1/3$ [13], so an expansion in $\vec{S}_i \cdot \vec{S}_j/S^2$ is reasonable, and we may conclude that the spin energy is given by the nearest neighbor Heisenberg model, with $J = K/2\sqrt{2}$. Thus thermal effects change our estimates of the energy scales by only a factor of $\sqrt{2}$, and the discrepancy between the calculated and measured T_c remains.

We now turn to the resistivity of the model near T_c. The electron-spin interaction in Eq. (6) leads to an electron self-energy with real and imaginary parts. The real part leads to a contribution to the electron velocity which increases as the temperature decreases and expresses the physics that as $\langle \vec{S}_i \cdot \vec{S}_j\rangle$ increases, so does the electron hopping. The imaginary part leads to scattering, due physically to fluctuations in $\vec{S}_i \cdot \vec{S}_j$. If the spins are treated classically, this scattering is mathematically identical to conventional impurity scattering, and leads to a resistivity proportional to $(p_F^2 \ell)^{-1}$ where p_F is the electron Fermi wave vector, and ℓ is the mean free path. The mean free path in this static spin approximation is a purely geometric property determined by the amplitude and spatial correlations of the fluctuations in $\vec{S}_i \cdot \vec{S}_j$ and, in particular, is independent of the electron velocity. Therefore to compute the resistivity it suffices to calculate the scattering of the electrons off the spin fluctuations, neglecting the possibly large velocity renormalization. Because, as we shall see, fluctuations in $\vec{S}_i \cdot \vec{S}_j$ are small, the scattering is sufficiently weak that the Born approximation suffices. Also, because the scattering is static the optical conductivity must have essentially the Drude form, in contradiction to experiment at $T \approx T_c$ [11]. Finally, Langer and Fisher [15] have shown that singularities in spin correlation functions at T_c cause two types of singularities in the resistance: One is a contribution $d\rho/dT \sim |T - T_c|^{-\alpha}$, where α is the specific heat exponent (which is believed to be slightly negative for the three-dimensional Heisenberg model); the other is that for $T < T_c$ there is an additional contribution to the resistivity proportional to M^2.

There is no rigorous expression for the dc resistivity. To obtain a reasonable approximate expression we use the "memory function" method [16]. In this method one defines the memory function $M(\omega, T)$ via $\sigma(\omega, T) = (\pi e^2 K/2a_0)[i\omega + M(\omega, T)]^{-1}$ and *approximates* M as

$$M(\omega, T) = \frac{1}{K\omega} \int_0^\infty dt\, e^{i\omega t} \langle [H, j]_t, [H, j]_0\rangle, \qquad (8)$$

where the current operator j is

$$j = i \sum_{ijab} \sqrt{2} t_{ij}^{ab} (c_{ia}^{\dagger} c_{jb} - c_{jb}^{\dagger} c_{ia}) \left(1 + \frac{\vec{S}_i \cdot \vec{S}_j}{2S^2}\right), \quad (9)$$

and H is given by Eq. (6). The Heisenberg representation is assumed, and the subscript on the commutator denotes the time argument of the operators. This approximation for M reproduces exactly the leading term in the high-frequency expansion of σ and, although not rigorous, is believed to be reasonably accurate at all ω except in special cases such as proximity to a localization transition or for one-dimensional models. By definition the temperature dependent resistivity $\rho(T) = a_0 M(\omega = 0, T)/\pi e^2 K$. In models such as the double-exchange model, K is set by the hopping parameter t, and M/K is independent of K and is determined by $p_F \ell$. We have evaluated $M(\omega = 0, T)$ from Eqs. (6) and (8) to leading order in $1/S$ and $p_F a$. We find

$$\rho(T) = e^2 \sum_{R,\delta_1,\delta_2} [\langle \vec{S}(0) \cdot \vec{S}(-\vec{\delta}_1) \vec{S}(R) \cdot \vec{S}(R + \delta_2) \rangle / S^4] B(R). \quad (10)$$

Here $\vec{R}$ labels sites on the cubic lattice, and δ_1 and δ_2 are any of the vectors $\hat{x}, \hat{y}, \hat{z}$ connecting a site to one of the nearest neighbors. B is proportional to the electron current-current correlation function weighted by a factor accounting for the ineffectiveness of small q scattering in degrading the current. In the free electron approximation in which the fermions have a k^2 dispersion and $t^a = t^b = t$,

$$B(R) = \frac{9}{32(p_F a)^4} \left[\frac{\sin^2 p_F(\vec{R} + \hat{x})}{(p_F|\vec{R} + \hat{x}|)^2} + \frac{\sin^2 p_F|\vec{R} - \hat{x}|}{(p_F|R - \hat{x}|)^2} - \frac{2 \sin^2 p_F R}{(p_F R)^2} \right]. \quad (11)$$

We have evaluated Eq. (10) using Eq. (11) for B and calculated the spin correlator in the spherical model [17]. Results are shown in Fig. 1 for $p_F a = 1$ and two magnetic fields: $H = 0$ and $H = 0.1T_c$. Results for $p_F a = 0.75$ are very similar. Note that the results are consistent with the general arguments [15]: In the spherical model $\alpha = -1$ so $d\rho/dT$ has a derivative discontinuity at T_c, and below T_c an additional term, proportional to M^2, is operative. Note, however, that in the present model the resistivity *increases* below T_c or in a field. The increase should be compared to the very sharp drop in ρ found experimentally (see, e.g., the inset to Fig. 1). It occurs because for $T < T_c$ or $H \neq 0$ there is a nonzero magnetization M which leads to two effects: the total amplitude of the spin fluctuations is decreased, *and* one must add terms in which two of the spins in Eq. (11) are replaced by factors of M, leading to additional scattering. For sufficiently large M the decrease in fluctuation amplitude is the dominant effect. Our calculation shows, however, that near T_c the additional scattering terms are dominant and lead to an increase in the resistivity. We think it unlikely that this increase is an artifact of the spherical model because the peak is so large and so far below T_c that critical fluctuations should not suppress it. The issue could be tested by calculating the four spin correlator via Monte Carlo simulation.

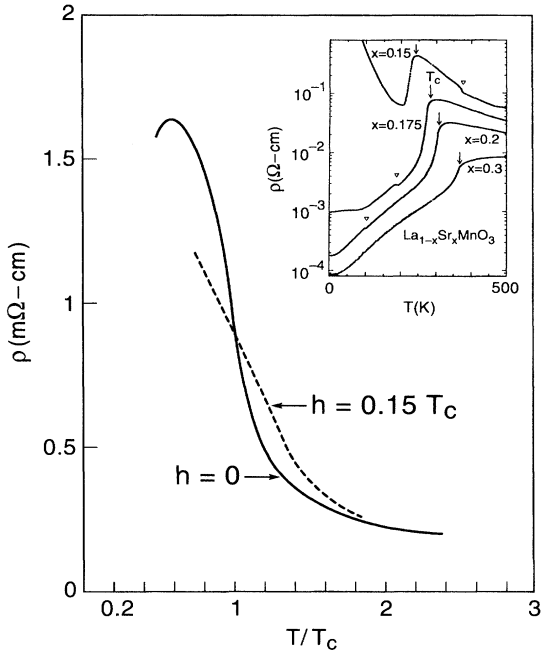

FIG. 1. Resistivity calculated from the double-exchange model as described in the text. The solid line is the resistivity in zero field; the dashed line is the resistivity in a field of $0.15T_c$. The inset displays data from Tokura *et al.*

It is interesting to compare our results to the explicit calculations of Langer and Fisher [15] who used our Eq. (1) but assumed $J_H \ll t$ and obtained a formula similar to Eqs. (10) and (11), except that instead of the four spin correlator they obtained simply $\langle \vec{S}(0) \cdot \vec{S}(R) \rangle$ because for $J_H \ll t$ local fluctuations of S_i scatter the electrons while for $J_H \gg t$ local fluctuations of $\vec{S}_i \cdot \vec{S}_j$ scatter the electrons. This difference implies that in the Langer-Fisher model the only effect of a nonzero M is to decrease the total amplitude of the spin fluctuations, leading to a decrease in ρ below T_c. Also, the peak at $T > T_c$ found for small k_F by Langer and Fisher is much weaker in the present model. The peak occurs because the function B has range p_F^{-1}, and for $p_F \xi \leq 1$ the divergence of the spin correlator in Eq. (11) leads to a peak in ρ. The two spin correlator in the Langer-Fisher expression for ρ diverges as $\xi^{2-\eta}$, while the four spin correlator relevant to the double-exchange case has the weaker divergence $\xi^{1-2\eta}$. In the calculations we have performed for $0.5 \leq k_F a \leq 1$ the divergence is not visible.

The resistivity implied by Eq. (6) has been previously calculated by Kubo and Ohata [3], Searle and Wang [2], and Furukawa [4]. Searle and Wang and Furukawa used mean-field approximations in which all spin correlations are neglected, i.e., $\langle \vec{S}_i \cdot \vec{S}_j \rangle - \langle S_i \rangle \langle S_j \rangle = 0$. It is evident from the previous discussion that these correlations are

essential. Furukawa used an "infinite dimensional" approximation in which he found that for $T > T_c$ the core spins fluctuated very rapidly (i.e., on the scale set by t) and led to an enormous imaginary part ($\approx J_H$) to the electron self-energy. It is difficult to reconcile these results with those presented here. In our work J_H drops out of the problem, and the S_i are seen to be well described near T_c by a classical Heisenberg model which entails fluctuation rates of order T or less. Kubo and Ohata obtained via a different method an expression similar to our Eq. (10), but evaluated the spin correlation function using an approximation which neglected the fluctuations in $\langle \vec{S}_i \cdot \vec{S}_j \rangle$ which are responsible for the up-turn we find in ρ near T_c.

Some representative experimental data from Ref. [18] are shown in the inset to Fig. 1. Similar experimental results have been obtained by many authors [1,2,19,20]. Although the qualitative temperature dependence calculated for $T > T_c$ is consistent with the data, several important discrepancies are evident: The calculated resistivity has the wrong magnitude (by several orders of magnitude), a too slow doping dependence, and an incorrect behavior for $T < T_c$ or in a field. The discrepancies may be traced to the fact, evident already in Eqs. (6) and (10), that in the double-exchange model the magnetic fluctuations do not significantly reduce the electron bandwidth, so a Fermi liquid picture of weakly scattered basically bandlike electrons follows.

The discrepancies we have listed suggest that some other mechanism, not present in the double-exchange model, must act to substantially reduce the electron kinetic energy K at $T \approx T_c$. We suggest that this mechanism is a polaron effect due to a very strong electron-phonon coupling stemming from a Jahn-Teller splitting of the Mn^{3+} ion. Other authors, most notably Kusters *et al.* [19] have argued in favor of a magnetic polaron picture. Our calculation shows that the standard double-exchange Hamiltonian does not contain magnetic polaron effects because the effective carrier-spin interaction is too weak. On the other hand, the Jahn-Teller coupling is very strong. It causes the cubic-tetragonal transition observed at $T^* \approx 800$ K in $LaMnO_3$ [6], and, in fact, T^* is a dramatic underestimate of the basic Jahn-Teller energy. Using the standard Jahn-Teller Hamiltonian and the measured [21] oxygen displacements one finds that this energy is ~ 0.5 eV, much greater than the measured electron kinetic energy at $x = 0.175$. It therefore seems likely that the Jahn-Teller energy remains important even in the metallic regime $0.15 < x < 0.45$ and that the physics involves a crossover between a high T, polaron dominated, magnetically disordered regime and a low T metallic magnetically ordered regime. Understanding this crossover requires a theory of the interplay of polaron and metallic physics which is beyond the scope of this paper. However, it is clear that if polaron physics reduces the mean free path to less than a lattice constant, the argument previously given that the resistivity is independent of the carrier mass (i.e., of K) does not apply. Mathematically, if the electron self-energy is very large, then the hopping part of the electron Green's function is proportional to t, not $1/t$; the memory function, Eq. (11) scales as t^4, not t; and the increase in velocity for $T < T_c$ or $H \neq 0$ will compete with the extra scattering terms and may lead to a drop in resistivity for $T < T_c$, as observed. Finally, we note that a crucial test of the importance of polaron physics is the measurement of the rms oxygen displacements. If the polaron picture is correct, then the displacements should be large (of order 0.1 Å) at $T > T_c$ and small for $T < T_c$.

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[1] S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994).
[2] C. W. Searle and S. T. Wang, Can. J. Phys. **48**, 2023 (1970).
[3] K. Kubo and N. Ohata, J. Phys. Soc. Jpn. **33**, 21 (1972).
[4] N. Furukawa, J. Phys. Soc. Jpn. **63**, 3214 (1994).
[5] C. Zener, Phys. Rev. **82**, 403 (1951); P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955); P. G. deGennes, Phys. Rev. **118**, 141 (1960).
[6] J. Goodenough, Phys. Rev. **100**, 564 (1955).
[7] C. Herring, in *Magnetism,* edited by J. Rado and H. Suhl (Academic, New York, 1965), Vol. 2.
[8] L. F. Mattheiss (private communication).
[9] T. G. Perring *et al.* (unpublished).
[10] A. J. Millis and S. N. Coppersmith, Phys. Rev. B **42**, 10 807 (1990).
[11] T. Arima (unpublished).
[12] C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963), Eq. 26, Chap. 2.
[13] G. S. Rushbrooke, G. A. Baker, Jr., and P. J. Wood, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, New York, 1974), Eq. (5.4).
[14] J. M. Ziman, *Models of Disorder* (Cambridge University Press, Cambridge, 1979).
[15] M. E. Fisher and J. S. Langer, Phys. Rev. Lett. **20**, 665 (1968).
[16] W. Gotze and P. Wolfe, Phys. Rev. B **6**, 1226 (1972).
[17] See, e.g., H. E. Stanley, *Phase Transitions and Critical Phenomena* (Oxford University Press, New York, 1971), Sect. 8.4.
[18] Y. Tokura, A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and N. Furukawa (unpublished).
[19] R. M. Kusters, J. Singleton, D. A. Keen, R. McGreevy, and W. Hayes, Physica (Amsterdam) **155B**, 362 (1989).
[20] P. Schiffer, A. P. Ramirez, W. Bao, and S-W. Cheong (unpublished).
[21] J. B. A. A. Elemans, B. vanLaar, K. R. vanderVeer, and B. O. Loopstra, J. Solid State Chem. **3**, 238 (1971).