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Ground-state instability of the Mott insulator Ca_2RuO_4 : Impact of slight La doping on the metal-insulator transition and magnetic ordering

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Ca_2RuO_4 is a Mott system with a structurally driven metal-insulator transition at $T_{\text{MI}}=357$ K and Néel temperature at $T_N=110$ K. Slight substitution of trivalent La for divalent Ca in Ca_2RuO_4 drastically reduces T_{MI} and the electrical resistivity, simultaneously precipitating robust ferromagnetism in the antiferromagnetic host. T_C is conspicuously and consistently lower than T_{MI} , suggesting that the metal-insulator transition is not driven by the magnetic instability. The La substitution also results in a rapid increase in both the Pauli susceptibility and electronic specific heat coefficient, and a crossover from hopping conductivity to disordered metallic behavior at low temperatures. These dramatic changes underline the subtlety of the competition between the antiferromagnetic and ferromagnetic coupling and a near degeneracy of the ground state in Ca_2RuO_4 .

In transition metal oxides, the intra-atomic Coulomb interaction, U , competes with the bandwidth, W , in determining the ground state. This competition becomes particularly intricate in $4d$ electrons characterized by their largely extended orbitals. This extended characteristic suggests a weak U , yet at the same time, an enhanced electron-lattice interaction which very often precipitates structural distortions, ultimately narrowing W . It is not surprising, given such a complex competition between U and W , that many $4d$ transition metal oxides are delicately poised near a metallic to nonmetallic boundary with $U/W \sim 1$, and that small perturbations, such as slight alterations of crystal structures, dilute doping, disorder, etc., can readily tip the balance across the metal-nonmetal borderline with pronounced changes in physical properties and ground states. In no other isomorphous systems is this better illustrated than in the quasi-two-dimensional ruthenates of Ca_2RuO_4 and Sr_2RuO_4 . They have the same K_2NiF_4 layered structure, yet completely different physical properties.¹⁻⁶ Ca_2RuO_4 , being more distorted than Sr_2RuO_4 due to the smaller ionic radius $r_{\text{Ca}} < r_{\text{Sr}}$, is a Mott insulator below 357 K with an antiferromagnetic ground state at $T < T_N=110$ K,²⁻⁴ whereas Sr_2RuO_4 is a superconductor be-

low 1.5 K and a paramagnet with a tendency toward ferromagnetism.^{1,5} The fundamental differences in physical properties between these two isostructural compounds reflect a strong competition between ferromagnetic and antiferromagnetic coupling and an extraordinarily high sensitivity of the ground state to distortions of the crystal structure.

We have recently reported a structurally driven insulator-to-“near” metal transition, T_{MI} , above room temperature ($T_{\text{MI}}=357$ K) in Ca_2RuO_4 , the transition being simultaneous with a low temperature orthorhombic to high temperature tetragonal structural transition.⁴ It is also known that Ca_2RuO_4 in the insulating phase has a narrow gap of about 0.2 eV, determined from both transport and optical measurements.^{2,7} Its magnetic moment at 30 T is anomalously low ($\sim 0.4\mu_B/\text{Ru}$),² compared to those of the other Ca- and Sr-based ruthenates, which have moments consistent with the $2.0\mu_B/\text{Ru}$ expected for the low spin ($S=1$) state of the $\text{Ru}^{4+}(4d^4)$ configuration.⁸ Most remarkably, the resistivity of Ca_2RuO_4 in the basal plane changes by an astonishing ten orders of magnitude, from $10^9 \Omega \text{ cm}$ at $T=70$ K to $10^{-1} \Omega \text{ cm}$ at $T=580$ K, and obeys the Efros-Shklovskii mechanism (ES) for $T \leq 300$ K.²

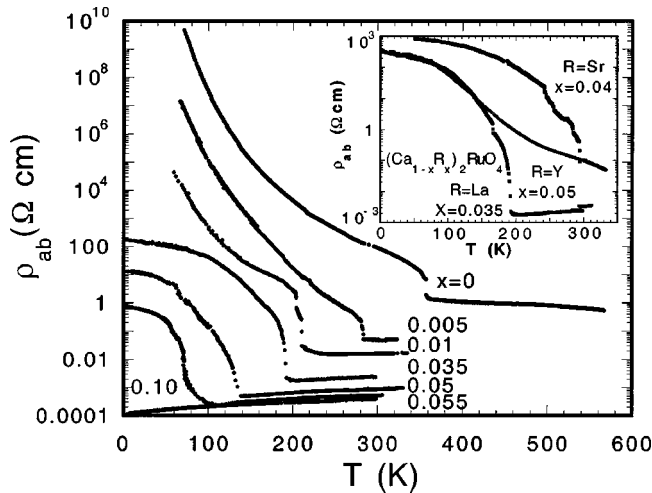


FIG. 1. Electrical resistivity $\rho(T)$ for the basal plane as a function of temperature T for $x=0, 0.005, 0.01, 0.035, 0.050, 0.055,$ and 0.10 . Inset: $\rho(T)$ for Sr-, Y-, and La-doped crystals with comparable x .

Some progress has been made in bridging the disparate physical properties of Sr_2RuO_4 and Ca_2RuO_4 by forming single crystal $(\text{Ca}_{1-x}\text{Sr}_x)_2\text{RuO}_4$ at least to $x=0.04$. As expected, the resistivity decreases and the system approaches a metallic ground state, however, the antiferromagnetic ordering remains, showing a broader transition in the vicinity of $T=100$ K for $x \leq 0.04$.² In this paper, we take an alternate approach in understanding the properties of the Mott insulator Ca_2RuO_4 , namely, with controlled substitution of the divalent Ca by trivalent La, which has only a slightly larger ionic radius (1.03 \AA vs 1.00 \AA). While this approach offers an advantage in essentially retaining the original lattice structure, and thus the Coulomb interaction U , the slight substitution of La for Ca is believed to effectively increase the t_{2g} bandwidth W by lowering the highly distorted Ru-O-Ru bond angle (151° for $x=0$),⁶ and simultaneously filling the t_{2g} bands with the electron added from the La ion. These two approaches, known as bandwidth control and filling control, are commonly seen in perovskitelike oxides, but rarely as drastic and distinct as in Ca_2RuO_4 . Here, we report the results of our study on transport and thermodynamic properties of single crystal $(\text{Ca}_{1-x}\text{La}_x)_2\text{RuO}_4$ along with comparisons drawn from Ca_2RuO_4 doped with other impurities (such as Sr, Y, etc.).

Single crystals of $(\text{Ca}_{1-x}\text{La}_x)_2\text{RuO}_4$ were grown in Pt crucibles using a flux technique described elsewhere.² X-ray diffraction was performed on powdered single crystals using a Siemens Θ - 2Θ diffractometer. The La concentration was determined by energy dispersion x-ray (EDX) analysis, and results of x-ray diffraction and EDX indicated that the crystals studied were single phase with a uniform La distribution. Resistivity, $\rho(T)$, was measured with a standard four probe technique and magnetization, $M(T,H)$, with a commercial superconducting quantum interference device (SQUID) magnetometer. The heat capacities, $C(T)$, were measured in a low mass heat capacity cryostat using a quasiadiabatic heat pulse relaxation technique. All measurements were performed on several single crystals for each La concentration to ensure the reproducibility.

In Fig. 1 we show $\rho(T)$ in the ab plane of $(\text{Ca}_{1-x}\text{La}_x)_2\text{RuO}_4$ for $0 < x < 0.10$. For $x=0$, an abrupt first

order transition from a low temperature insulating phase to a nearly metallic phase occurs at $T_{\text{MI}}=357$ K, simultaneous with the orthorhombic to tetragonal transition, as recently reported.⁴ The sudden decrease in $\rho(T)$ by a factor of 3.5 is unambiguously first order, as the samples sometime suffer irreversible structural damage, the volume change being 1.3% between 90 and 400 K.⁴ Upon La doping, both $\rho(T)$ and T_{MI} decrease dramatically. For $x=0.005$ (0.5%), the most lightly doped sample, T_{MI} drops from 357 to 280 K, and $\rho(T)$ decreases by more than two orders of magnitude throughout the entire measured temperature range. With a further increase in La concentration, $\rho(T)$ and T_{MI} continue to decrease, and for $x=0.10$ the metallic phase is retained down to at least $T=2$ K, and $\rho(T)$ decreases to $10^{-4} \Omega \text{ cm}$, suggesting that the gap is fully closed. For all samples with $x > 0$, a metallic phase at $T > T_{\text{MI}}$ is well established and $\rho(T)$ is linear in T over a wide range of temperature. As seen in Fig. 1, $\rho(T)$ for $T > T_{\text{MI}}$ shows clear metallic behavior with *decreasing* temperature, and for any subsequent *increase* in temperature, $\rho(T)$ is hysteretic at the transition, showing weaker temperature dependence due to large strains associated with the transition.

The behavior of the low temperature $\rho(T)$ for $x \leq 0.01$ and $x \geq 0.035$ is fundamentally different, reflecting a clear deviation in the conduction process from the variable-range hopping-Efros-Shklovskii mechanism (ES), $\rho(T) = A \exp[T_0/T]^{1/2}$, to excitation to extended states characterized by a much weaker temperature dependence (see Fig. 1). The characteristic temperature T_0 , a measure of the localization length, shows a rapid decrease with increasing x , vanishing in the vicinity of $x=0.015$, indicating a rapid divergence of the localization length. Consistently, the conductivity $\sigma (\approx 1/\rho)$ extrapolated to $T=0$ exhibits an abrupt rise around $x=0.035$, suggesting that electrons start to populate extended states in the upper Hubbard band, and the system accordingly approaches a delocalized state [see also Fig. 3(a)]. The density of states, $N(E)$, near the Fermi level E_F is substantially enhanced at this crossover, as the electronic specific heat coefficient, γ , rapidly rises from 16 mJ/mole K^2 for $x=0.01$ to 90 mJ/mole K^2 for $x=0.035$. This is further supported by a similar enhancement in the Pauli susceptibility (see below). Such a distinct change in low temperature ρ is rare,⁹ and unambiguously defines a continuous transition from a strictly insulating phase to a regime with low yet finite conductivity σ [$\rho(0 \text{ K})=180 \Omega \text{ cm}$ for $x=0.035$]. The low conductivity for $0.035 \leq x \leq 0.055$ is believed to be due to disorder or the structural distortion that is persistent up to $x=0.055$. It is known that under the strong influence of the metal-insulator transition, electrons can be readily localized by randomness and electron-lattice coupling.⁹

The impact of La doping on $\rho(T)$ is much stronger than for other dopants such as Sr or Y. This is illustrated in the inset of Fig. 1, which shows $\rho(T)$ for crystals comparably doped with La, Y, and Sr. The effect of doping on Ca_2RuO_4 is dramatic in all cases, but with quite dissimilar impacts. La doping (3.5%) results in the largest decrease in $\rho(T)$ and $T_{\text{MI}}=175$ K compared to $T_{\text{MI}}=280$ K for the 4% Sr-doped sample. The 5% Y-doped sample shows no well-defined T_{MI} , though $\rho(T)$ is largely reduced. As in other perovskite-like systems, the bandwidth W in this system depends criti-

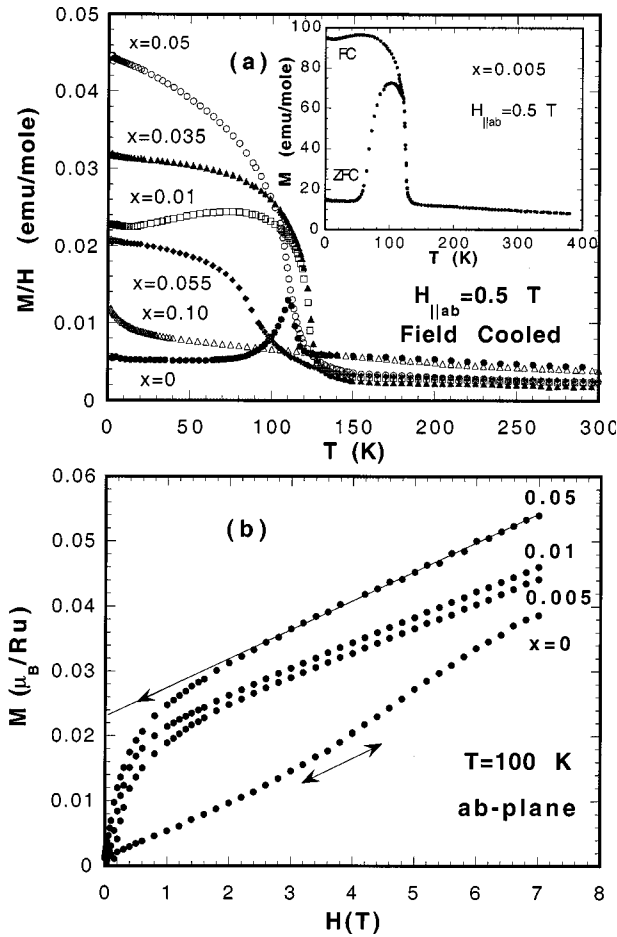


FIG. 2. (a) Magnetic susceptibility defined as M/H vs temperature T at $H_{||ab}$ plane for $x = 0, 0.01, 0.035, 0.050, 0.055$, and 0.10 . Inset: magnetization M vs T for $x = 0.005$. (b) Magnetization M as a function of magnetic field H at $H_{||ab}$ for $x = 0, 0.005, 0.010$, and 0.05 .

cally on the Ru-O-Ru bond angle distortion, which can be controlled by varying the tolerance factor through changing the ionic radius r of cations, a method known as bandwidth control. W is expected to be broadened as the bond angle increases when the small divalent Ca ($r_{Ca} = 1.00$ Å) is partially replaced by the much larger divalent Sr ($r_{Sr} = 1.18$ Å). It is surprising, however, that the trivalent La doping has a stronger impact than divalent Sr doping, given that $r_{La} = 1.03 \ll r_{Sr}$. The distinct behavior points out the importance of the electron added by the La ion, i.e., filling control. On the other hand, the sizable, yet weaker, response of $\rho(T)$ to the Y dopant ($r_Y = 0.90$ Å) implies once again a crucial role of bandwidth control. It is clear that the transport properties of Ca_2RuO_4 are highly sensitive to the combined effect of bandwidth and filling control, which is rare among almost all metal-insulator transition systems known to date.⁹

Closely associated with the anomalies in resistivity of $(Ca_{1-x}La_x)_2RuO_4$, the magnetic instability ($T_N = 110$ K for $x = 0$) undergoes abrupt changes with La doping of Ca_2RuO_4 . Figure 2(a) shows the magnetic susceptibility, $\chi(T)$, defined as M/H vs temperature for the field applied, $H = 0.5$ T, along the ab plane. (In all cases, the measuring field was small enough so that M/H represents “zero field” susceptibility.) Upon La doping, the systems show an immediate transition from clear nonhysteretic antiferromagnetic behavior to ferromagnetic behavior. To clarify this, the mag-

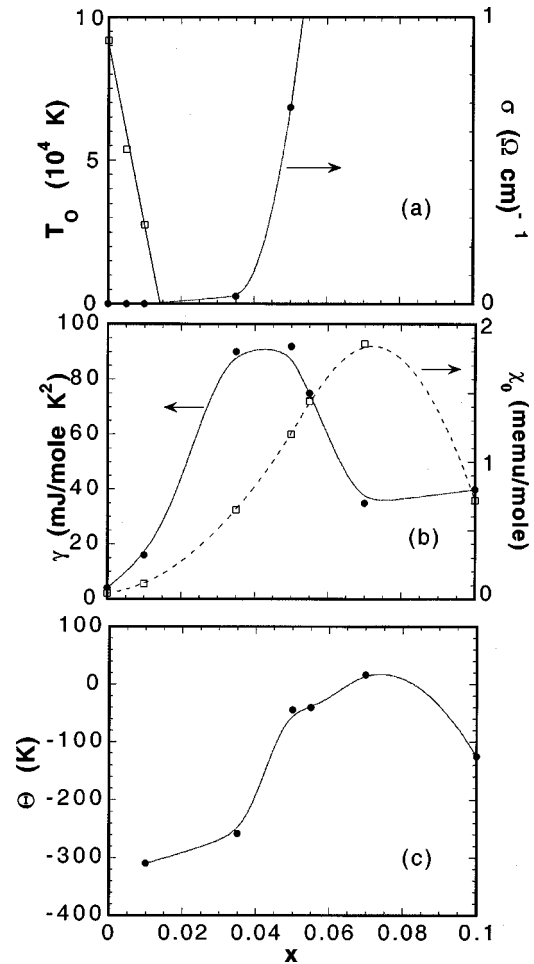


FIG. 3. x dependence of T_0 (left) and conductivity σ (a), γ (left) and χ_0 (b), and the Curie-Weiss temperature Θ (c).

netization, $M(T)$, of the $x = 0.005$ (0.5%) sample is shown in the inset of Fig. 2(a). Not only is the hysteresis obvious, but ferromagnetic behavior is also indicated by the sharpness of the transition at $T_c = 125$ K. The ferromagnetism is evident as well in Fig. 2(b) where $M(H)$ rises rapidly with a sizable hysteresis at $H < 2$ T, expected for the domain rotation in a ferromagnet. The moment μ_s extrapolated from $M(H)$ at higher fields increases with La doping, indicating an increase in the ferromagnetic coupling. In contrast, the Curie temperature T_C shows only a weak La concentration dependence for $0 \leq x \leq 0.055$, but eventually vanishes for the fully metallic $x = 0.10$ composition.

The $\chi(T)$ for $x = 0$ and $x = 0.005$ is effectively linear in temperature for $140 < T < 360$ K—clearly not Curie-Weiss-like [see inset of Fig. 2(a)]. This anomalous behavior is attributed to the unstable lattice structure, and the concomitant change in the band structure, as discussed in Refs. 2 and 4. However, as the La concentration increases, $\chi(T)$ for $x > 0.005$ follows a modified Curie-Weiss law, $\chi(T) = \chi_0 + C/(T - \Theta)$. The fitting parameters derived from $\chi(T)$ combined with the results of heat capacity $C(T)$ and $\rho(T)$ provide the following important features, summarized in Fig. 3. Figure 3(a) shows T_0 and σ vs x as discussed above. Shown in Fig. 3(b) is the x dependence of χ_0 and γ . The temperature independent term χ_0 increases by an order of magnitude as x approaches $x = 0.07$, and then decreases at higher concentrations [Fig. 3(b)]. Since the Van Vleck con-

tribution to χ_0 is expected to be two to three orders of magnitude smaller than the measured χ_0 , the enhancement in χ_0 is believed to be due mainly to an increase in the density of states. This point is also supported by the trend of γ . Essentially following χ_0 , γ initially rises, peaks at $x=0.05$, and then decreases at $x>0.05$ [Fig. 3(b)], implying a widened W and a lower $N(E)$ near E_F . The peak of γ seen at $0.035 \leq x \leq 0.05$ indicates a large enhancement of the effective mass m^* of the charge carriers, which is a generic feature of the filling control in the vicinity of the Mott-Hubbard insulating phase.¹⁰ It is apparent that the behavior of both χ_0 and γ fully reflects the change in $\rho(T)$.

Remarkably, the Curie-Weiss temperature, Θ , shows a general trend from negative to positive and then back to negative with a peak at $x=0.07$ as x increases [see Fig. 3(c)]. This signals an increase in ferromagnetic coupling for $x<0.07$ and an evolution from a nearly ferromagnetic state at $x=0.07$ to a paramagnetic ground state at $x=0.10$. Furthermore, the x dependence of χ_0 on the La concentration traces that of Θ , confirming a robust crossover of the magnetic ground state. The disappearance of the magnetic ordering at $x=0.10$ is not unexpected, given the appearance of the metallic ground state.

We note that $M(H)$ displayed in Fig. 2(b) shows a pronounced field dependence at $H>2$ T, seemingly indicating a possible coexistence of both ferromagnetic and antiferromagnetic order. $M(T)$ at $H>2$ T can be described by $M = M_0 + \chi_A H$, where M_0 increases with x , but χ_A is essentially the same for all samples with $x<0.07$, implying the antiferromagnetic background. The phenomenon appears to be somewhat similar to that observed in $\text{Gd}_{1-x}\text{V}_x\text{S}_4$ where the existence of randomly placed vacancies, V , leads to the formation of ferromagnetic polarons as evidenced by local ferromagnetic alignment in an antiferromagnetic background and large magnetoresistivity.¹¹ However, in $(\text{Ca}_{1-x}\text{La}_x)_2\text{RuO}_4$ for all x , measurements of ρ performed at H up to 12 T yield no significant magnetoresistivity. We have also found that slight substitutions (<2%) by other trivalent dopants, such as Y, Ce (mixed-valent), and Pr, all uniformly result in ferromagnetic coupling with T_C varying from 120 to 200 K,¹² suggesting that the electron added by the trivalent ions tends to ferromagnetically align Ru spins. In contrast, slight divalent Sr doping does not precipitate a ferromagnetic phase as rapidly as the trivalent ion doping. In fact, the antiferromagnetic phase persists to at least 4% Sr doping.²

It seems apparent that there exist some common trends in oxides, notably competition between ferromagnetic and antiferromagnetic states, which may lead to phase segregated regions, as observed in manganites, for example. Recent computer simulations have shown that the spins-canted state is unstable, and the ground state, with extended Coulomb interactions, is found to have small islands of one phase embedded in the other.¹³ This point may also be valid for the compound discussed here and other ruthenates where magnetic inhomogeneities are suggested.⁸ This issue is to be thoroughly pursued in our studies of the ruthenates.

All results presented above lead to the following conclusions:

(i) The system for $x<0.07$ undergoes a strong first order transition from a paramagnetic metallic state to a *paramag-*

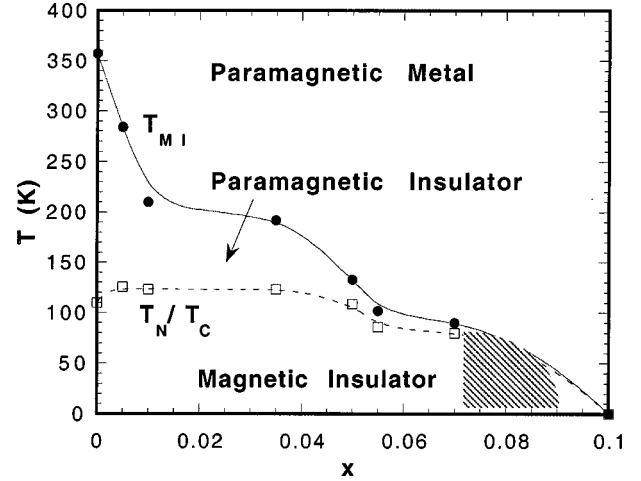


FIG. 4. Néel/Curie temperature T_N/T_C and metal-insulator transition T_{MI} vs x .

netic insulating state at T_{MI} , which is then followed by a magnetic transition to a *magnetic* insulating state at T_N (for $x=0$) or T_C (for $x>0$). The system finally becomes a paramagnetic metal at $x=0.10$. Figure 4 summarizes these phase transitions. The shaded area represents a regime that is not well defined due to limited availability of crystals. (ii) T_{MI} is primarily structurally driven. That $T_{MI}>T_C$ further confirms that T_{MI} is not influenced by the magnetic ordering instability. (iii) The dramatic suppression of both $\rho(T)$ and T_{MI} due to dilute La doping suggests an unstable electronic structure that is unusually sensitive to the *combined* effect of the bandwidth and band filling control. (iv) The slight La doping largely enhances $N(E)$ near E_F , resulting in strongly correlated electrons. This enhancement is intimately accompanied by a striking change in the conduction process at $T \ll T_{MI}$, i.e., the system evolves from a Mott insulator to a disordered metal and finally to a fully metallic ground state. (v) The magnetic ordering in Ca_2RuO_4 is highly unstable due to the strong competition between antiferromagnetic and ferromagnetic coupling. This observation is consistent with *some* results of a recent theoretical study using local density approximation calculations. The results of the calculations indicate that the antiferromagnetic ordering induced by a nesting effect is degenerate with a ferromagnetic ordering in Ca_2RuO_4 and that the magnetic instability depends on $N(E)$, or the Stoner criterion, $IN(E)$, where I is the exchange interaction between two parallel-spin electrons. Based on the calculations, $IN(E_F)>1$ favors an antiferromagnetic solution whereas $IN(E)>1$ favors a ferromagnetic one.¹⁴ Indeed, almost all layered ruthenates possess an unstable ground state characterized by pronounced changes in physical properties due to small perturbations.¹⁵ But Ca_2RuO_4 , given its low dimensionality and unusual ground-state instability, is a rare model system for investigating questions of metal-insulator transitions in particular and the interplay of charge, spin, and orbital degrees of freedom in transition metal oxides in general.

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- ¹Y. Maeno *et al.*, Nature (London) **372**, 532 (1994).
- ²G. Cao *et al.*, Phys. Rev. B **56**, R2916 (1997).
- ³S. Nakatusji *et al.*, J. Phys. Soc. Jpn. **66**, 1868 (1997).
- ⁴C. S. Alexander *et al.*, Phys. Rev. B **60**, R8422 (1999).
- ⁵Y. Maeno *et al.*, J. Phys. Soc. Jpn. **66**, 1035 (1997).
- ⁶M. Braden *et al.*, Phys. Rev. B **58**, 847 (1998); M. Braden *et al.*, *ibid.* **57**, 1236 (1998).
- ⁷A. V. Puchkov *et al.*, Phys. Rev. Lett. **81**, 2747 (1998).
- ⁸G. Cao *et al.*, Phys. Rev. Lett. **78**, 1751 (1997); G. Cao *et al.*, Phys. Rev. B **55**, R672 (1997); **56**, R5740 (1997); G. Cao *et al.*, *ibid.* **56**, 321 (1997); G. Cao *et al.*, *ibid.* **56**, 5387 (1997); G. Cao *et al.*, Physica B **259-261**, 951 (1999).
- ⁹M. Imada *et al.*, Rev. Mod. Phys. **70**, 1039 (1998).
- ¹⁰N. Furukawa and M. Imada, J. Phys. Soc. Jpn. **61**, 3331 (1992).
- ¹¹S. von Molnar and T. Penney, in *Localization and Metal-Insulator Transition*, edited by H. Frizsche and D. Adler (Plenum, New York, 1985), p. 183.
- ¹²G. Cao *et al.* (unpublished).
- ¹³For example, A. Moreo, S. Unoki, and E. Dagatto, Science **283**, 2034 (1999).
- ¹⁴I. I. Mazin and D. J. Singh, Phys. Rev. Lett. **82**, 4324 (1999). We note that experimental results obtained by us (Refs. 2, 4, 8) and others (Refs. 3, 6) differ significantly from some conclusions of this theoretical study. This, however, should not invalidate the other points made in the paper that are consistent with experiments.
- ¹⁵G. Cao *et al.*, Mater. Sci. Eng., B **B63**, 76 (1999), and references within.