Field-tuned collapse of an orbitally ordered and spin-polarized state: Colossal magnetoresistance in the bilayered ruthenate $Ca_3Ru_2O_7$

G. Cao,[1] L. Balicas,[2] X. N. Lin,[1] S. Chikara,[1] E. Elhami,[1] V. Duairaj,[1] J. W. Brill,[1] R. C. Rai,[1] and J. E. Crow[2]
[1]*Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506, USA*
[2]*National High Magnetic Field Laboratory, Tallahassee, Florida 32310, USA*
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$Ca_3Ru_2O_7$ with a Mott-like transition at 48 K and a Néel temperature at 56 K features different in-plane anisotropies of the magnetization and magnetoresistance. Applying a magnetic field along the magnetic easy-axis precipitates a spin-polarized state via a first-order metamagnetic transition, but does not lead to a full suppression of the Mott state, whereas applying a magnetic field along the magnetic hard axis does, causing a resistivity reduction of three orders of magnitude. The colossal magnetoresistivity is attributed to the collapse of an orbitally ordered and spin-polarized state. This phenomenon is striking in that the spin polarization, which is a fundamental driving force for all other magnetoresistive systems, is detrimental to the colossal magnetoresistence in this $4d$-based electron system. Evidence of a density wave is also presented.

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The physics of magnetoresistance has generated enormous interest in recent years. While this quantum mechanical phenomenon is in general associated with the spin scattering process of conduction electrons, the origins of various kinds of magnetoresistance are vastly different. The giant magnetoresistance observed in magnetic metallic multiplayer structures can be qualitatively explained using the two current model, corresponding to up-spin and down-spin electrons.[1] Tunneling magnetoresistance, often seen in magnetic tunnel junctions separated by an insulating spacer layer, is a consequence of spin-polarization. On the other hand, colossal magnetoresistance (CMR), seen only in the mixed-valence manganites so far, originates from a metal-insulator transition in the vicinity of the Curie temperature driven primarily by double exchange due to the hopping of e_g electrons of Mn^{3+} ions and the Jahn-Teller effect.[2]

The novelty of the bilayered $Ca_3Ru_2O_7$, as presented in this paper, is that *the colossal magnetoresistivity is a result of the collapse of the orbitally ordered state that is realized by demolishing the spin-polarized state*. This phenomenon is striking in that the spin polarization, which is a fundamental driving force for all other magnetoresistive systems, is detrimental to the colossal magnetoresistence in this $4d$-based electron system. Indeed, the electron kinetic energy hinges on the spin-orbital-lattice coupling in such a way that applying magnetic field, B, along the magnetic easy axis (a axis) precipitates a spin-polarized state via a first-order metamagnetic transition, but does not lead to a full suppression of the Mott state, whereas applying B along the magnetic hard axis (b axis) does, giving rise to a resistivity reduction of three orders of magnitude. Our previous work indicated the puzzling anisotropic behavior observed in the field dependence of the resistivity at temperatures below 0.6 K,[3] but it alone could not establish the existence and consequences of the orbital ordering. The results presented here reveal critical information complementary to the previous work. These results include the temperature dependence of the Mott state with $B \| a$ and b axes for a wide range of magnetic field ($0 \leqslant B \leqslant 28$ T), the field dependence of the resistivity with $B \| a$ and b axes for $0.6 \leqslant T \leqslant 80$ K, and nonlinear transport for various temperatures and magnetic fields. It is these results coupled with some previous data that provide coherent and comprehensive evidence of the role of the orbital ordering, which has never been addressed in our previous work. It is now clear that the orbital and spin degrees of freedom are intimately coupled so that polarizing spins stabilizes the orbitally ordered state that forbids the electron hopping, and thus the destruction of the spin-polarized state naturally leads to a ''quantum melting'' of the orbitally ordered state that in turn brings about the colossal magnetoresistance. This conclusion is also supported by evidence for the formation of a density wave along the a axis.

The bilayered $Ca_3Ru_2O_7$ belongs to the Ruddlesden-Popper series with lattice parameters of $a = 5.3720(6)$ Å, $b = 5.5305(6)$ Å, and $c = 19.572(2)$ Å.[4] The crystal structure is severely distorted by tilting of RuO_6. The tilt projects primarily onto the ac plane (153.22°) while only slightly impacting the bc plane (172.0°).[4] These are crucial bond angles defining anisotropic spin-orbital-lattice coupling within the basal plane. $Ca_3Ru_2O_7$ undergoes an antiferromagnetic ordering at $T_N = 56$ K while remaining metallic[6] and then undergoes a Mott-like transition at $T_{MI} = 48$ K (Refs. 3–11) with the formation of a charge gap of 0.1 eV that bears a resemblance to a Mott system.[7,10] Shown in Fig. 1 is the temperature dependence of magnetization, $M(T)$, for the a and b axes at $B = 0.5$ T along with temperature dependence of the lattice parameters of the c axis (a) and $M(T)$ for the two orientations at $B \geqslant 6.5$ T (b). Although similar data were shown previously, Fig. 1 presented here is meant to emphasize two major features that are critically linked to later discussions. First, the low field $M(T)$ for the a axis, the magnetic easy axis, features two phase transition temperatures, $T_N = 56$ K and $T_{MI} = 48$ K. In contrast, $M(T)$ for the b axis exhibits no anomaly corresponding to T_{MI} but a sharp peak at T_N as shown in Fig. 1(a). In addition, the precipitous decrease of M for the a axis at T_{MI} is accompanied by a simultaneous collapse of the c-axis lattice parameter, indicating the importance of magnetoelastic interactions and a Jahn-

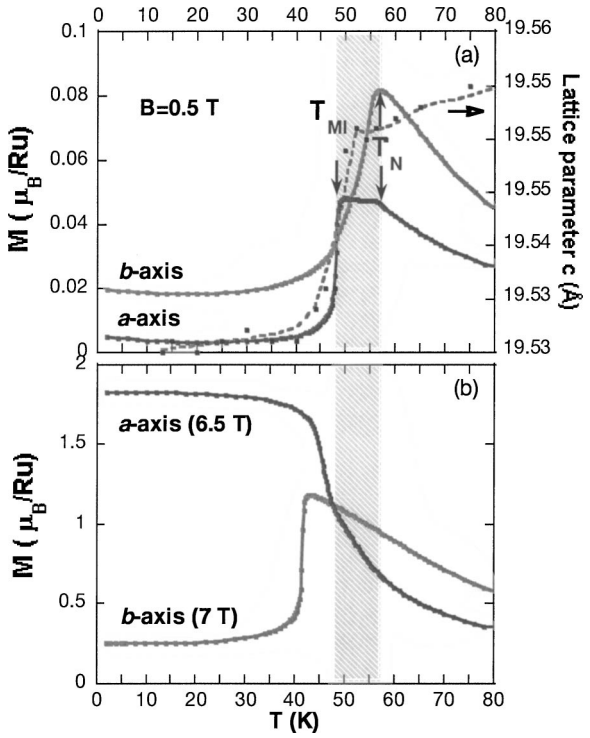

FIG. 1. Temperature dependence of the magnetization, M, for the a and b axes at $B=0.5$ T (a) and $B>6.5$ T (b). The lattice parameter c axis (right scale) vs temperature is also shown in (a). The shaded area is the temperature range between T_{MI} and T_N.

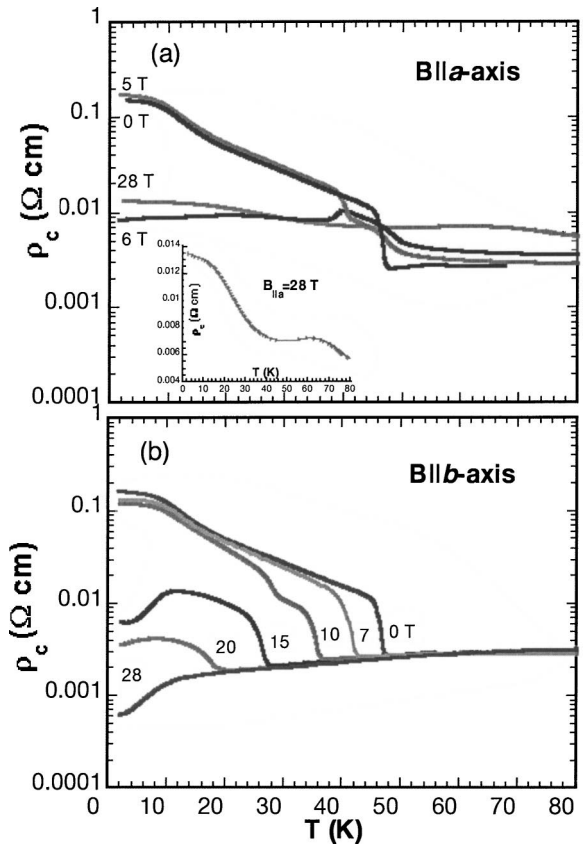

FIG. 2. Temperature dependence of the c-axis resistivity, ρ_c, at a few representative B up to 28 T applied along the a axis (a) and the b axis (b) for $1.2\ \mathrm{K}<T<80\ \mathrm{K}$. Inset: ρ_c vs T for $B_{\|a}=28$ T. The temperature dependence of the a-axis resistivity ρ_a is identical to that of ρ_c presented here, and therefore not shown.

Teller distortion of RuO_6.[3,5] Second, as B applied parallel to the a axis increases, T_{MI} shifts slightly, whereas T_N remains essentially unchanged initially and becomes rounded eventually. At $B>6$ T, the first-order metamagnetic transition leads to a *spin-polarized or ferromagnetic* (FM) state with a saturation moment $M_s=1.73\mu_B$/Ru along the a axis, suggesting more than 85% of a hypothetical saturation magnetization $2\mu_B$/Ru expected for an $S=1$ system. On the other hand, when B is parallel to the b axis, T_N decreases with increasing B at approximately a rate of 2 K/T. Markedly, the magnetic ground state for $B\|b$ axis *remains antiferromagnetic*, entirely different from that for $B\|a$ axis as shown in Fig. 1(b). This anisotropic behavior reflects the anisotropic spin-orbit coupling that only favors the spin-stabilized orbital ordering along the a axis below T_{MI}. The absence of the anomaly at T_{MI} in the b axis $M(T)$ confirms such an anisotropic spin-orbit coupling. As can be seen below, applying B along the b axis effectively destabilizes the spin-polarized state, and consequently causes the collapse of the orbital ordered state, which in turn drastically increases the electron mobility.

Shown in Fig. 2 is the temperature dependence of the c-axis resistivity, ρ_c, at a few representative B, which is applied along the a axis [Fig. 2(a)] and the b axis [Fig. 2(b)], respectively. [Note that the same log scale is used for both Figs. 2(a) and 2(b) for comparison.] For $B\|a$ axis, ρ_c at low temperatures increases slightly with increasing B when $B<6$ T, and decreases abruptly by about an order of magnitude when $B\geqslant 6$ T, at which the first order metamagnetic transition lead to the spin-polarized state [also see Fig. 3(a)]. Further increasing B only results in slightly higher resistivity at low temperatures. The reduction of ρ_c is attributed to a tunneling effect facilitated by a field-induced coherent motion of spin-polarized electrons between Ru-O planes separated by insulating (I) Ca-O planes. This situation is similar to an array of FM/I/FM junctions where the probability of tunneling and thus electronic conductivity depend on the angle between spins of adjacent ferromagnets. It is astonishing that the spin-polarized state generates no fully metallic state in spite of the pronounced impact of the tunneling effect on ρ_c. In fact, the behavior of ρ_c at $B=28$ T suggests a still nonmetallic state (see the inset). What is entirely unexpected is that when $B\|b$ axis, the magnetic hard axis, the Mott state starts to collapse at approximately the rate of 2 K/T, and vanishes at $B>24$ T, as clearly shown in Fig. 2(b).

Such an anisotropy is further illustrated in Fig. 3 where ρ_c as a function of B is plotted for $B\|a$ axis [Fig. 3(a)] and $B\|b$ axis [Fig. 3(b)], respectively, for a few representative temperatures. M at 5 K for the a axis and the b axis is also shown in Fig. 3(a) (right scale) for the discussion. When $B\|a$ axis, ρ_c shows a first order transition in the vicinity of 6 T, apparently driven by the first order metamagnetic transition which leads to the spin-polarized state with a saturation moment, $M_s=1.73\ \mu_B$/Ru. This metamagnetic transition decreases slightly with increasing temperature and disappears com-

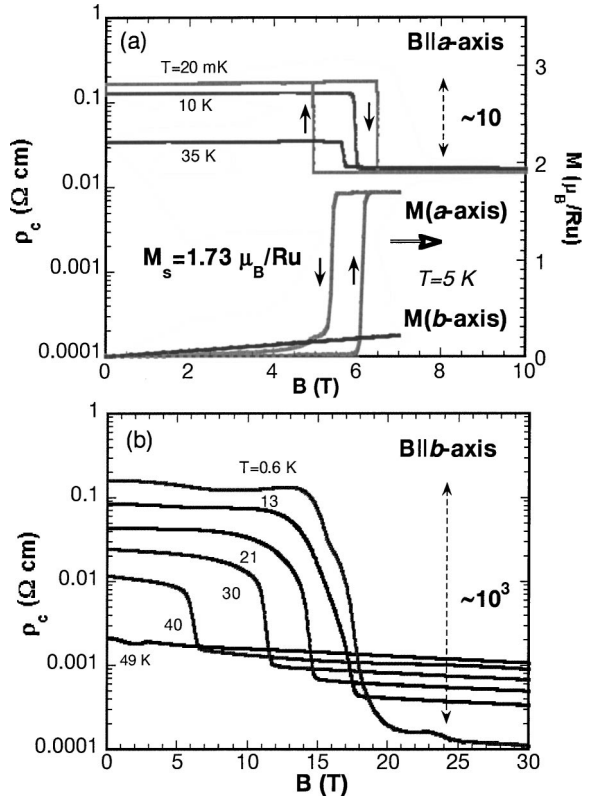

FIG. 3. Field dependence of ρ_c for $B\|a$ axis (a) and $B\|b$ axis (b) for a few representative temperatures from 0.6 to 49 K. M at 5 K for the a axis and the b axis is shown in (a) (right scale).

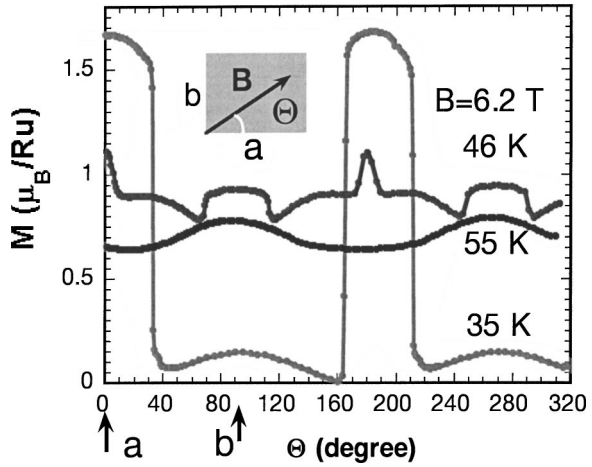

FIG. 4. M as a function of angle, Θ, between the a axis ($\Theta=0$) and B at $B=6.2$ T for temperatures indicated. Note that M decreases abruptly when B rotates away from the a axis at $T<40$ K and that the easy-axis starts to rotate to the b axis ($\Theta=90°$) with increasing temperature when $T>42$ K. The field dependence of the a-axis resistivity ρ_a is nearly identical to that of ρ_c presented here.

pletely when T approaches T_{MI} (=48 K).[6] Further increasing B to 30 T only results in a linear increase of the resistivity with B. When $B\|b$ axis, the magnetic state remains antiferromagnetic as shown in M (b axis), completely different from M (a axis) due to a strong anisotropy field of 22.4 T,[11] and ρ_c rapidly decreases at a critical field by as much as three orders of magnitude shown in Fig. 3(b). The temperature and field dependence of the a-axis resistivity ρ_a is nearly identical to that of ρ_c presented here, therefore not shown.[12]

While the abrupt, simultaneous transitions in both M and ρ shown in Fig. 3(a) suggest a strong spin-charge coupling when $B\|a$ axis, it is clear that the spin-polarized state can at most lower the resistivity by one order of magnitude evident in both Figs. 2(a) and 3(a). Then, *what is the origin that reduces the resistivity by three orders of magnitude when $B\|b$ axis and when the spin-polarized state is destabilized*? It is this issue that reflects the physics fundamentally different from that driving other magnetoresistive materials including the manganites where a spin-polarized state is essential for CMR.[2]

It becomes increasingly clear that the behavior observed in the ruthenate is predominantly associated with the role of the orbital degree of freedom and its coupling to the spin and lattice degrees of freedom. The orbital degeneracy can be lifted by both the Jahn-Teller distortion and the spin-orbit coupling. As shown in Fig. 1, the abrupt decrease in the c-axis lattice parameter at T_{MI} suggests the Jahn-Teller distortion that lifts the degeneracy of the t_{2g} orbitals by lowering the energy of the d_{xy} orbital relative to that of the d_{yz} and d_{xz} orbitals[3,5] and facilitates the orbital ordering. On the other hand, the orbital degeneracy can be also lifted by the spin-orbit interaction, which is accompanied by simultaneous spin symmetry breaking evidenced by the occurrence of the magnetic ordering at T_{MI} in M for the a axis [see Fig. 1(a)]. This anisotropic magnetic behavior illustrated in Figs. 1–3 can be attributed to the existence of the orbital ordering along the a axis below T_{MI} that is stabilized by the spin-polarized state via the spin-orbit interaction. Loosely speaking, spin ferromagnetism must be accompanied by antiferrorbital order, and vice versa. Therefore, applying B along the a axis in effect strengthens the orbital-ordered state by inducing the ferromagnetism. The magnetoresistive behavior for $B\|a$ axis shown in Figs. 2(a) and 3(a) is thus due entirely to the spin polarization or reduction of spin scattering, while the still nonmetallic behavior arises from the orbital ordering that forbids neighbor hopping between orbitals. Conversely, applying B along the b axis effectively destabilizes the ferromagnetic state, thus the orbital-ordered state. The field-tuned collapse of the orbital-ordered state systematically and drastically increases the electron hopping amplitude or kinetic energy, leading to the colossal magnetoresistivity as it is unequivocally illustrated in Figs. 2(b) and 3.

In line with the argument, the magnetic easy axis starts to rotate away from the a-axis in the vicinity of T_{MI} and becomes parallel to the b axis at T_N with the saturation moment M_s being only $0.8\mu_B$/Ru, as shown in Fig. 4. This rotation driven by the collapse of the c axis shown in Fig. 1 effectively destabilizes the spin-orbit coupling favorable for the orbital ordering, resulting in the rare antiferromagnetic *metallic* state intermediate between T_{MI} and T_N (the shaded area in Fig. 1).[6] The itinerancy in turn leads to the reduced M_s, which is about a half of the saturation moment below 42 K.

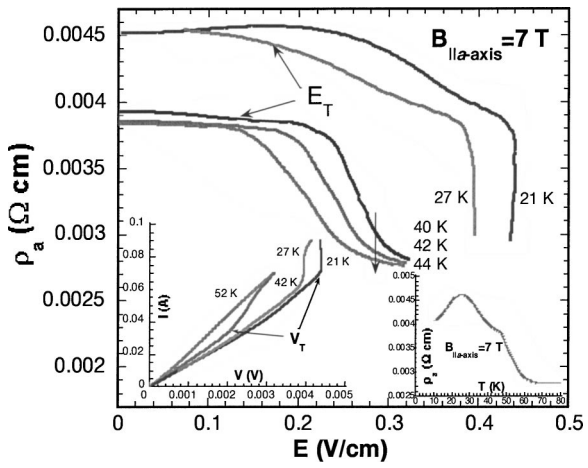

FIG. 5. Resistivity for the *a* axis, ρ_a, as a function of dc electric field, *E*, at $B=7$ T applied along the *a* axis for a few temperatures indicated. Inset 1: *I*-*V* curves for temperatures indicated. Inset 2: Temperature dependence of ρ_a at $B=7$ applied along the *a* axis. Note that ρ_a shows a peak near 25 K. That the nonlinear transport behavior below and above 25 K is characteristically the same indicates the self-heating effect, if any, is not dominant.

The orbital ordered state might also be manifested by a possible density wave below T_{MI}. Shown in Fig. 5 is the resistivity for the *a* axis, ρ_a, as a function of dc electric field, *E*, at $B=7$ T applied along the *a* axis. The nonohmic behavior above the threshold field, E_T, suggests sliding density wave transport.[13] The onset of the nonlinear conduction is also evidenced by the current-voltage (*I*-*V*) characteristic shown in the inset. As S-shaped nonlinear behavior is also observed at $B=0$, but the rapidly increasing resistivity with decreasing temperature below T_{MI} creates ambiguity due to possible self-heating. As discussed above, applying *B* larger than 6 T along the *a* axis drastically reduces the magnitude of ρ_a with the nonmonotonic temperature dependence (see inset 2). Should the nonlinear behavior be due to the self-heating effect, the *E* dependence of ρ_a and the *I*-*V* curve would be characteristically different when measured below and above the peak at 25 K seen in ρ_a (*T*) at 7 T shown in inset 2. Nevertheless, the formation of the density wave below T_{MI}, although subject to a thorough investigation,[14] provides additional evidence for the existence of the orbital-ordered state brought about by the highly anisotropic spin-lattice-orbital coupling.

Recently, a theoretical study using the Hubbard model with Coulombic and phononic interactions predicts the existence of a ferromagnetic orbital ordered state and colossal magnetoresistance in the ruthenates.[15] The phase diagram generated in this study shows that the ferromagnetic orbital ordered state is stabilized when both the interorbital Coulomb interaction and the phonon self-trapping energy are sufficiently strong.[15] The study also suggests a possible colossal magnetoresistive behavior due to a strong competition between ferromagnetic and antiferromagnetic states. The general agreement between the theoretical and experimental results further validates the crucial role of the orbital ordering driving the phenomena.

In conclusion, the colossal magnetoresistance reported here is due to the collapse of the orbital ordering through destabilizing the spin-polarized state. The physics involved is fundamentally different from that governing all other magnetoresistive materials.

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