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We report an unusual nearly ferromagnetic heavy-mass state with a surprisingly large Wilson ratio R_w (e.g., $R_w \sim 700$ for $x=0.2$) in double layered ruthenates (Sr₁₋ₓCaₓ)₃Ru₂O₇ with $0.08 < x < 0.4$. This state does not evolve into a long-range ferromagnetically ordered state despite considerably strong ferromagnetic correlations, but it freezes into a cluster-spin glass at low temperatures. In addition, evidence of non-Fermi-liquid behavior is observed as the spin-freezing temperature of the cluster-spin glass approaches zero near $x \approx 0.1$. We discuss the origin of this unique magnetic state from the Fermi-surface information probed by Hall-effect measurements.

The Ruddlesden-Popper (RP) series of ruthenates (Sr,Ca)$_{n+1}$Ru$_n$O$_{3n+1}$ have attracted widespread attention with their exceptionally rich physical properties, such as unconventional spin-triplet superconductivity,[1] itinerant magnetism,[2] orbital ordering,[3,4] Mott insulator behavior of purely electronic origin,[5] and field-tuned electronic nematic phases.[6,7] The close proximity of these exotic states testifies to the delicate balance among the charge, spin, lattice, and orbital degrees of freedom in ruthenates, and it provides a remarkable opportunity to tune the system to quantum criticality and/or new exotic states using nonthermal parameters such as chemical composition, pressure, and magnetic field.

The double layered ruthenates (Sr₁₋ₓCaₓ)₃Ru₂O₇ are of particular interest to explore the composition-tuned exotic phenomena because the end members, Sr₃Ru₂O₇ and Ca₃Ru₂O₇, show distinct properties. Sr₃Ru₂O₇ has a paramagnetic (PM) Fermi-liquid (FL) ground state.[8] It exhibits a field-tuned metamagnetic quantum critical end point near which non-FL behavior and an electronic nematic phase have been observed.[6,7] In contrast, Ca₃Ru₂O₇ orders antiferromagnetically at 56 K and then experiences a metal-insulator transition (MIT) at 48 K; [9,10] giant magnetoresistance was observed and attributed to a bulk spin-valve effect.[11–13] The (Sr₁₋ₓCaₓ)₃Ru₂O₇ solid solution series has been previously studied using polycrystalline and flux-grown single-crystalline samples.[14,15] Those experiments show that the antiferromagnetic (AFM) state of Ca₃Ru₂O₇ is suppressed for $x < 0.4$, and the ferromagnetic (FM) order becomes stable even without an external magnetic field.[14,15] However, there exists a remarkable difference between the reported Curie temperatures: $T_c \approx 3$ K for the polycrystalline samples[14] and $T_c \approx 100$ K for the single-crystalline samples.[15] This discrepancy may originate from an impurity phase since the RP series easily involves the intergrowth of members of different n.[16–18]

In this Rapid Communication, we report results of mag-netization, specific heat, and Hall effect for (Sr₁₋ₓCaₓ)₃Ru₂O₇ single-crystalline samples grown by the floating-zone technique. A magnetic phase diagram, which reveals unusual phenomena, has been obtained due to the improved sample quality. In contrast with previous results,[14,15] no spontaneous FM order is found for any Ca content. We find an unusual nearly-ferromagnetic (NFM), heavy-mass state with an extremely large Wilson ratio in the composition region $0.08 < x < 0.4$ (e.g., $R_w \sim 700$ for $x=0.2$), where the FM phase was previously reported.[14,15] This state does not evolve into a long-range FM-ordered state despite considerably strong FM fluctuations, but it freezes into a cluster-spin-glass (CSG) phase at low temperatures. In addition, evidence of non-FL behavior is observed when the CSG phase is suppressed near $x \approx 0.1$.

All samples used in this study were screened carefully by x-ray diffraction and a superconducting quantum interference device (SQUID) magnetometry to ensure they are highly pure and untwinned. Since SQUID magnetometry has an extremely high sensitivity to ferromagnetic materials, it guarantees that the selected samples do not contain any FM impurity phases such as (Sr,Ca)₄Ru₃O₁₀.[18] SQUID magnetometry is also used for systematic magnetization measurements on selected samples. Specific-heat measurements were performed using a thermal relaxation method, and the Hall effect was measured using a conventional four-probe method with the $B \| c$ axis (the longitudinal resistivity component was eliminated by reversing the field direction).

The phase diagram of (Sr₁₋ₓCaₓ)₃Ru₂O₇ from our study is shown in Fig. 1. It consists of three regions at low temperatures. (I) $0 \le x < 0.08$, which is metamagnetic. A reversible itinerant metamagnetic transition occurs at moderate magnetic fields below T_M, the peak temperature in $M(T)/B$ [see Fig. 2(a)]. T_M and the metamagnetic transition field B_{MM} decrease with Ca substitution for Sr, down to zero when x is
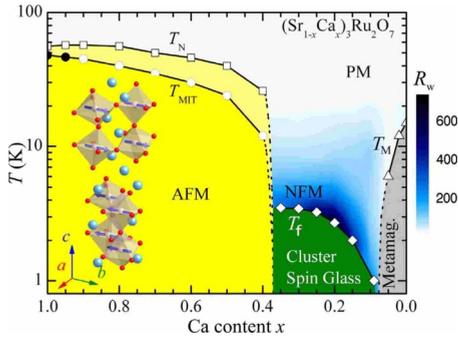
FIG. 1. (Color online) Magnetic phase diagram of $(Sr_{1-x}Ca_x)_3Ru_2O_7$. AFM, antiferromagnetic; T_N, the Néel temperature; and T_{MIT}, the metal-insulator transition temperature. The closed and open circles represent first- and second-order transitions, respectively. Metamag., itinerant metamagnetic and T_M, the temperature of the peak in the susceptibility, below which the metamagnetic transition occurs. PM: paramagnetic, represented by the contour plot of the Wilson ratio R_w. NFM: unusual nearly FM heavy-mass state. T_f: the frozen temperature of the CSG phase. Inset: the magnetic structure of $Ca_3Ru_2O_7$ below T_{MIT} determined by neutron scattering (Ref. 13).

increased to ~0.08. Such itinerant metamagnetism has generally been interpreted as a field-tuned Stoner transition into a highly polarized magnetic state.[6] (II) $0.4 \leq x \leq 1$, which is antiferromagnetic. The system first orders antiferromagnetically at the Néel temperature T_N and then experiences a MIT at T_{MIT}. T_N and T_{MIT} can be identified by anomalies in magnetization as shown in Fig. 2(a), and they are consistent with previous results.[14,15] The magnetic structures of $Ca_3Ru_2O_7$ were recently determined by neutron-scattering measurements;[10,13] the structure below T_{MIT} is shown in the inset of Fig. 1. (III) $0.08 < x < 0.4$, which is an unusual nearly ferromagnetic heavy mass. We will focus on this region below since it is the phase revealed in this study.
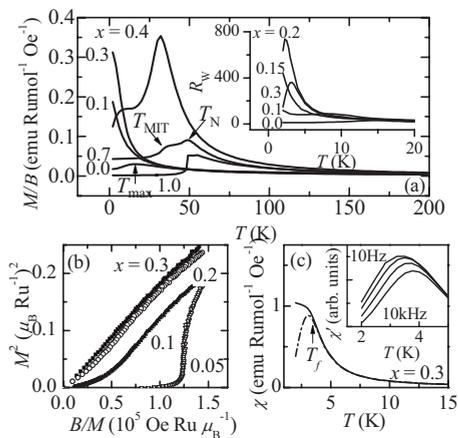

FIG. 2. Magnetic properties for $(Sr_{1-x}Ca_x)_3Ru_2O_7$. (a) Magnetization divided by field M/B vs T under $B(\|a)=0.3$ T. Inset: the temperature dependence of Wilson ratio R_w of typical compositions. (b) The Arrott plot of $M(B)$ at $T=2$ K. (c) $\chi(T)$ measured under $B=5$ mT with FC (solid line) and ZFC (dotted line) histories for $x=0.3$. Inset: ac susceptibility measured at various frequencies for $x=0.3$.

As shown in Fig. 2(a), M/B is enhanced drastically with increasing Ca content for $0.08 < x < 0.4$ and $T < 10$ K, suggesting enhanced magnetic fluctuations. We have estimated the Wilson ratio $R_w = (\pi^2 k_B^2 / 3\mu_B^2)(\chi / \gamma_e)$ for these samples using the susceptibility χ measured with 5 mT and zero-field-cooling (ZFC) histories and the electronic specific heat. R_w generally measures the FM correlation strength. For $x=0$, R_w is ~10 at 2 K, consistent with the previous result;[8] it increases significantly with increasing Ca content. R_w also strongly depends on temperature and tends to diverge with decreasing temperature. It reaches surprisingly large values at low temperatures; e.g., $R_w \sim 700$ for $x=0.2$ at ~2.5 K [see the inset of Fig. 2(a) and the R_w contour plot of Fig. 1]. This divergent tendency is cut off due to the formation of the CSG phase (see below), resulting in a maximum of R_w around $x=0.2$. Such a large Wilson ratio far surpasses that of any nearly ferromagnetic material such as Pd ($R_w \approx 6-8$), Ni_3Ga ($R_w \approx 40$),[19] and $Ca_{0.5}Sr_{1.5}RuO_4$ ($R_w \approx 40$),[20] indicating that the FM fluctuations in the $0.08 < x < 0.4$ range are considerably stronger.

Nevertheless, such strong FM fluctuations do not evolve into a long-range FM-ordered state; this is evidenced by the Arrott plot of magnetization shown in Fig. 2(b). The hallmark of a long-range FM state is the presence of a spontaneous magnetization, which manifests itself as a positive intercept on the M^2 axis in an Arrott plot. The Arrott plots for $0 < x < 0.4$ exhibit no positive M^2 intercept, indicating the absence of long-range FM order even for the samples with the strongest FM fluctuations. We note that the intercept for the samples with $x=0.2$ and 0.3 approximately equals to zero, indicating that the system is extremely close to a long-range FM order.

This unusual nearly FM state freezes into a CSG phase at low temperatures. For all of the samples in the $0.08 < x < 0.4$ range, we observed irreversibility in $\chi(T)$ measured at 5 mT between ZFC and field-cooling (FC) histories, as well as a strong frequency dependence of the ac susceptibility peak occurring at the frozen temperature T_f, which are typical signatures of a glassy state. Figure 2(c) presents the typical data for these observations.

All unusual magnetic properties described above can be well understood by assuming that the system is in close proximity to a two-dimensional (2D) ferromagnet with $T_c = 0$ K. This scenario allows the existence of strong FM fluctuations without forming a long-range-ordered state at finite temperatures since the long-range FM order in 2D on a square lattice is not stable according to the Mermin-Wagner theorem.[21] The formation of the CSG is the way the system releases the entropy at $T>0$ K when disorder unavoidably exists in the solid solution.

Our observation of magnetic properties for $x<0.4$ differs from early results as pointed out above.[14,15] The $T_c \approx 3$ K weak FM phase observed in polycrystalline samples is probably due to the CSG phase being driven to a long-range FM state by the intergrowth of the FM $(Sr,Ca)RuO_3$ which was indeed found in their samples.[2,14] The $T_c \approx 100$ K FM state seen in flux-grown single crystals is likely due to the intergrowth of the FM $(Sr,Ca)_4Ru_3O_{10}$ with $T_c \approx 100$ K.[15,18] We actually observed a similar FM feature in the impure crystals from our initial batches which were found to involve tiny amounts of $(Sr,Ca)_4Ru_3O_{10}$ intergrowth.
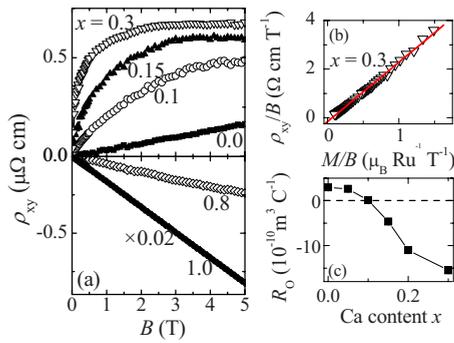
FIG. 3. (Color online) (a) Field dependence of the Hall resistivity $\rho_{xy}(B)$ of various compositions at $T=2$ K. (b) ρ_{xy}/B vs M/B plot for the sample with $x=0.3$, which is a typical sample showing AHE. The solid line represents the least-squares fitting to Eq. (1). (c) Normal Hall coefficient R_0 as a function of x. R_0 is determined by fitting the data to Eq. (1) for $0.1 \leq x < 0.4$.

The evolution of magnetic states with Ca content discussed above was also probed by Hall resistivity ρ_{xy}, which is summarized in Fig. 3. For the samples in the metamagnetic region, ρ_{xy} displays a linear field dependence with a positive slope, consistent with the previous report.[22] For the samples showing unusual nearly FM states, ρ_{xy} is strongly enhanced. An anomalous Hall effect (AHE) occurs and ρ_{xy} follows the empirical expression [see Fig. 3(b)]

$$\rho_{xy} = R_0 B + 4\pi R_S M, \quad (1)$$

which is usually observed in FM metals and semiconductors.[23] When the system becomes AFM for $x \geq 0.4$, ρ_{xy} recovers to a linear field dependence but changes its sign to negative. The linear field dependence in this region can be understood by considering the magnetic structure of the AFM state;[13] since the FM RuO_2 bilayers stack antiferromagnetically along the c axis, the anomalous contribution from the magnetization of FM bilayers cancels, leaving only the normal term $R_0 B$ in ρ_{xy}.

We further investigated the thermodynamic properties of these various magnetic states through specific-heat measurements. Figure 4 displays the electronic specific heat divided by temperature C_e/T of typical samples. Electron correlations are strongly enhanced for the samples with enhanced FM correlations. γ_e reaches large values for these samples,
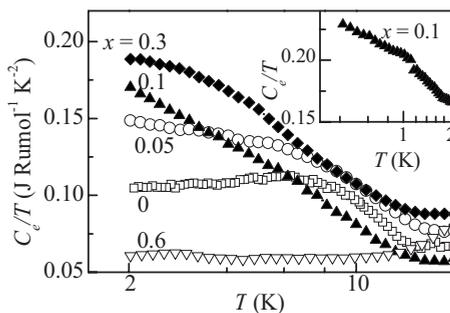

FIG. 4. Electronic specific heat divided by temperature C_e/T vs log T for typical samples of $(Sr_{1-x}Ca_x)_3Ru_2O_7$. Inset: C_e/T vs log T for $x=0.1$ down to 0.3 K.

e.g., $\gamma_e \sim 0.25$ J/Ru mol K^2 at 0.3 K for $x=0.1$, comparable to those seen in $Ca_{2-x}Sr_xRuO_4$ with $x \approx 0.5$,[20] indicating the formation of heavy-mass quasiparticles. Moreover, we observe an upturn anomaly for $0.08 < x < 0.40$ in sharp contrast with the FL behavior observed in $Sr_3Ru_2O_7$. For $x=0.1$, C_e/T increases logarithmically below ~ 10 K and this behavior continues even below T_f (≈ 1 K) where C_e/T shows a kink (see the inset of Fig. 4). This observation, together with the power-law temperature dependence of χ (data not shown), suggests the presence of non-FL behaviors at low temperatures in the vicinity of $x \approx 0.1$.

We now wish to discuss the possible origin of these magnetic phase transitions. In general, since Ca ions are smaller than Sr ions, Ca substitution for Sr is expected to introduce structure distortions; this would tune the electronic band structure and possibly induce a magnetic phase transition.[20] Our Hall-effect measurements suggest that orbital states are tuned as well. As shown in Fig. 3(c) the normal Hall coefficient R_0 changes sign from positive to negative near $x \approx 0.1$ when the system switches from the metamagnetic state to the CSG phase, suggesting that the charge carriers change from holelike to electronlike. This change might be associated with an evolution of a multiple-band effect. Band-structure calculations indicate the existence of competing magnetic correlations for $Sr_3Ru_2O_7$:[24] d_{xy} orbital gives rise to purely electronlike bands, which are close to a FM Stoner instability, while both electronlike and holelike bands can be derived from d_{xz} and d_{yz} orbitals, and they have nesting features and thus favor AFM fluctuations. Such a picture of orbital-dependent magnetic correlations is supported by recent experiments on $Sr_3Ru_2O_7$.[25,26] Under this circumstance, the natural interpretation for our observation of the sign change in R_0, as well as the enhancement of FM correlations, is that the d_{xy} bands become increasingly dominant with Ca/Sr substitution. For $x \geq 0.4$, the transition from the nearly FM heavy mass to the AFM state might be related to a structural phase transition since early angle resolved photoemission spectroscopy (ARPES) studies on this material system reveal a remarkable change in electronic structure near $x=0.4$.[27]

In summary, we have established the magnetic phase diagram of double layered ruthenates $(Sr_{1-x}Ca_x)_3Ru_2O_7$ using high-quality single crystals. The system approaches an unusual limiting magnetic state with heavy-mass quasiparticles for $0.08 < x < 0.4$. While FM correlations are extremely strong, the system does not form long-range FM order but forms a CSG phase at low temperatures; non-FL behavior occurs as the CSG phase is suppressed. These behaviors suggest that this state is in close proximity to a 2D ferromagnetic instability.

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