Possible observation of quantum ferromagnetic fluctuations in $La_4Ru_6O_{19}$

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We report electrical and magnetotransport measurements on $La_4Ru_6O_{19}$ that was found previously to feature metal-metal bonding and non-Fermi-liquid behavior. Our measurements showed that the transverse and longitudinal magnetoresistance grew rapidly below 30 K. Moreover, the longitudinal magnetoresistance is larger than the transverse magnetoresistance measured at the same temperatures (T) and the sign of the magnetoresistance is negative, suggesting the presence of ferromagnetic fluctuations in $La_4Ru_6O_{19}$. However, as T was lowered further to below $T^*=4$ K, the magnetoresistance was found to change its sign from negative to positive. The Hall coefficient, which is negative and strongly temperature dependent, reaches a maximum in its absolute value near T^*. Most importantly, the resistivity ρ was found to follow the non-Fermi-liquid dependence of $\rho \sim T^{3/2}$ below T^* in zero magnetic field and the Fermi-liquid behavior $\rho \sim T^2$ in a high magnetic field. We suggest that these observations can be explained by the existence of ferromagnetic quantum criticality in $La_4Ru_6O_{19}$ near ambient pressure.

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The discovery of the Cu-free layered perovskite superconductor Sr_2RuO_4 (Ref. 1) and subsequent experiments[2] including recent phase-sensitive measurements[3] confirming the prediction for a p-wave pairing symmetry in Sr_2RuO_4,[4,5] have led to intensive interests in ruthenates. Interestingly, Sr_2RuO_4 is the only compound found to be superconducting among all ruthenates that have been measured down to low temperatures thus far. This result is particularly striking given that many ruthenates, including those with nonperovskite structures, show metallic behavior down to low temperatures.[6–11] On the other hand, interesting phenomena have been found for many of these nonsuperconducting metallic ruthenates, revealing some striking relationships between the structure and physical properties. A dramatic example is $BaRuO_3$, which shows very different properties when it adopts its four known structures.[6,12–15]

Another example of unusual structure-property relationships was found in $La_4Ru_6O_{19}$, which was shown previously to feature non-Fermi-liquid behavior at low temperatures.[9] The most dominant structural feature of $La_4Ru_6O_{19}$ is the dimer of two octahedra with an unusually short Ru-Ru distance of 2.49 Å. The short Ru-Ru distance appears to alter the orbital states of Ru, leading to the proposal of the formation of the metal-metal bonding.[16] The formation of such orbital states appears to give rise to a very narrow band found right above the Fermi energy in band-structure calculation.[17] An interesting question is whether the formation of this narrow band is an indication of localized electronic states emerging from the metal-metal bonding and if metal-metal bonding is responsible to the non-Fermi-liquid behavior observed previously in this material. Here we report electrical and magnetotransport measurements, suggesting the presence of quantum critical point (QCP) in $La_4Ru_6O_{19}$ even under ambient pressure.

Single crystals of $La_4Ru_6O_{19}$ were synthesized by solid-state chemical reactions as described previously.[9] The residual resistivity ratio (RRR) was found to vary greatly from crystal to crystal even within the same batch, suggesting that the physical properties of this material is sensitive to even a small change in disorder. The RRR ratio for the highest-quality crystal was found to be 192, as reported previously.[9] Electrical-transport and magnetoresistance measurements were performed by standard four-point method in a Quantum Design physical property measurement system, a ^{3}He cryostat, or a dilution refrigerator. The Hall coefficient was measured in five-point probes with the two Hall-voltage leads arranged to be as symmetric as possible. The Hall voltage as a function of magnetic field was found to be linear up to the highest field (8 T) used in our measurements.

The electrical resistivity as a function of temperature from 300 K down to the base temperature at zero magnetic field is shown in the main panel of Fig. 1. Linear temperature dependence of resistivity was found below 30 K, which was taken previously as an indication of non-Fermi-liquid behavior.[9] Interestingly, magnetoresistance measured at 6 T was found to become significant only below 30 K (Fig. 1 inset), which suggests that the linear temperature dependence in resistivity may have a magnetic origin.

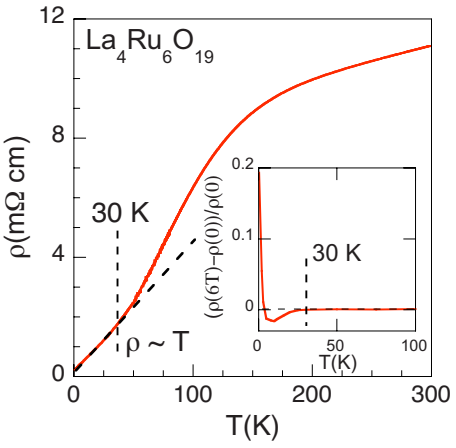

FIG. 1. (Color online) Temperature (T) dependence of electrical resistivity (ρ) of $La_4Ru_6O_{19}$. The RRR for this crystal is 110. Inset: T-dependent magnetoresistance taken at $\mu_0 H=6$ T.

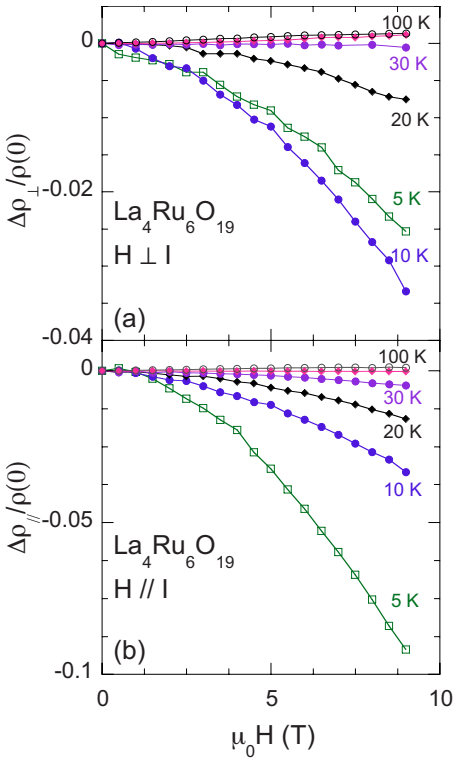

FIG. 2. (Color online) (a) Magnetoresistance $\Delta\rho_\perp/\rho(H=0)$ for $H \perp I$ from 5 to 100 K; (b) Magnetoresistance $\Delta\rho_\parallel/\rho(H=0)$ for $H \| I$ from 5 to 100 K.

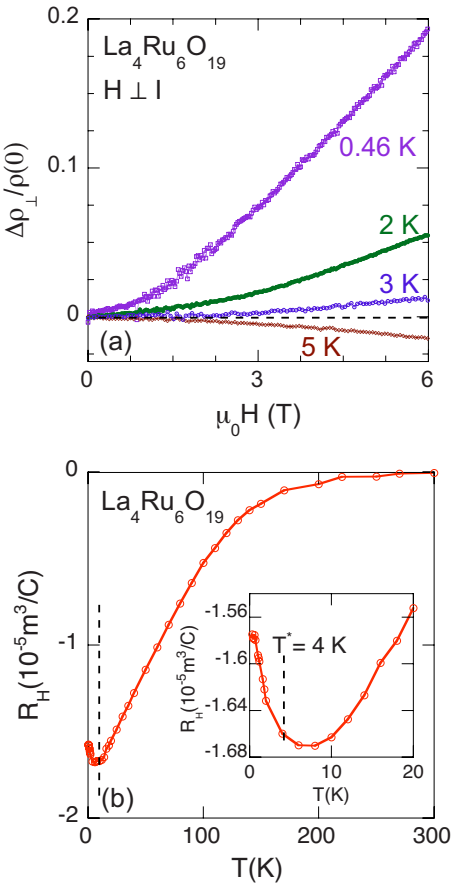

FIG. 3. (Color online) (a) $\Delta\rho_\perp/\rho(H=0)$ for $H \perp I$ at low temperatures; (b) Hall coefficient R_H as a function of T. Inset: Low-temperature part of Hall coefficient.

Detailed behavior seen in magnetoresistance measured in both transverse and longitudinal configuration provide further support that magnetic fluctuations may be responsible for the non-Fermi-liquid behavior of $La_4Ru_6O_{19}$. As shown in Fig. 2, both transverse and longitudinal magnetoresistances are negative, rising rapidly in magnitude below 30 K. Furthermore, the longitudinal magnetoresistance $\Delta\rho_\parallel$ is seen to be larger than the transverse magnetoresistance $\Delta\rho_\perp$ at each temperature, suggesting that the contribution to the quasiparticle scattering from magnetic fluctuations is important. A magnetic field tends to align the spins and reduce the magnetic fluctuations above the T_c of a ferromagnetic (FM) ordering. Therefore, the observation of negative magnetoresistance suggests that the magnetic fluctuations in $La_4Ru_6O_{19}$ are FM in nature.

As the temperature is decreased further, however, a sign change in the transverse magnetoresistance from being negative ($\Delta\rho_\perp<0$) to positive ($\Delta\rho_\perp>0$) was found around 4 K [Fig. 3(a)]. The change in the sign of magnetoresistance seems to suggest that the magnetic fluctuations change from being FM to antiferromagnetic (AFM). However, this is not necessarily true. The connection between the nature of magnetic fluctuations and the sign of the magnetoresistance is actually subtle. While thermal FM fluctuations are known to lead to negative magnetoresistance, whether quantum FM fluctuations will result in negative magnetoresistance is not clear (see below). On the other hand, the positive magnetoresistance showed quadratic dependence on magnetic field in low magnetic fields and linear magnetic field dependence in high magnetic fields, the latter of which, the linear magnetoresistance, is highly unusual. In fact, only a few physical mechanisms for this behavior have been identified so far, including the extreme quantum limit in which only one Landau band is partially filled[18] or a coherent state formed at low temperatures.[19] The extreme quantum limit requires unique pockets of Fermi surface with a small carrier effective mass, which was not found,[17] apparently excluding the extreme quantum limit as the origin of the observed linear magnetoresistance. Alternatively, linking the observed linear magnetoresistance to the emergence of a coherent state would require further evidence.

Behavior observed in the temperature dependence of the Hall coefficient R_H of $La_4Ru_6O_{19}$ suggests that not only the magnetic fluctuations but also the electronic state as well, may be changing as the temperature is lowered below 4 K. Indeed, R_H was found to be negative and strongly temperature dependent over the entire temperature range we used in our measurement (0.3–300 K). The absolute value of R_H grows monotonically as the temperature is lowered. $|R_H|$ reaches a maximum around 7 K, below which it decreases [Fig. 3(b)]. The rise in magnitude of R_H appears to be correlated with the growth in FM fluctuations. Such a phenomenon was observed previously in heavy Fermion systems.[20] The general trend seen in $\chi(T)$ and $\rho(T)$ of $La_4Ru_6O_{19}$ obtained previously[9] suggests that the growth of R_H as a function of decreasing temperature may be attributed to magnetic

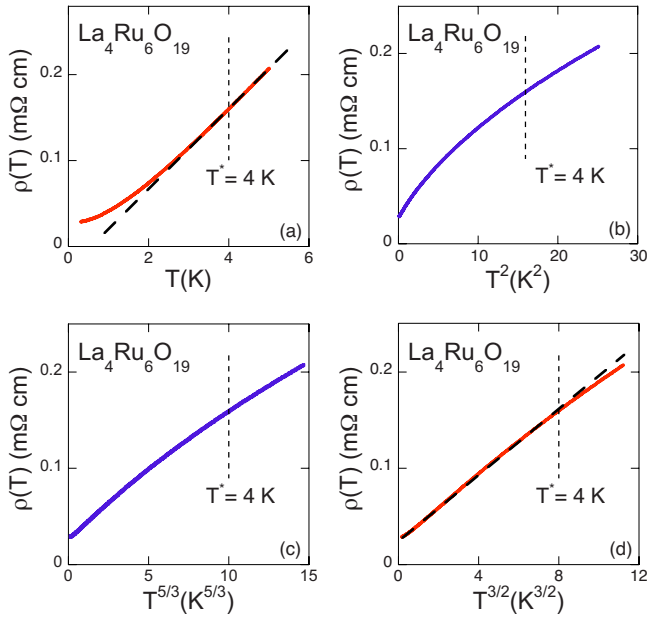

FIG. 4. (Color online) $\rho(T)-\rho(0)$, where $\rho(0)$ is a constant, as a function of (a) T, (b) T^2, (c) $T^{5/3}$, and (d) $T^{3/2}$ at low temperatures. Departures from the respective temperature are indicated.

fluctuations. In this regard, the most telling observation is the presence of a peak in $|R_H|$ and a minimum in the temperature-dependent specific heat[9] around 4 K, which clearly indicates that the system enters a different state below this characteristic temperature (T^*).

Physical insight into the nature of the electronic state below T^* can be obtained by noting that the specific heat below T^* follows the form, $C/T \sim \ln(T_0/T)$, where C is the specific heat and T_0 is a constant.[9] Such temperature dependence is expected near a quantum critical point. Analysis of our data (Fig. 4) shows that $\rho \sim T^{3/2}$ below T^*, providing further support for the presence of a quantum critical point in $La_4Ru_6O_{19}$ under ambient pressure. This has been observed recently in the heavy Fermion system β-$YbAlB_4$.[21] However, the existing theoretical predictions of three-dimensional (3D) QCP (Ref. 22) as discussed in more detail below, summarized in Table I, are inconsistent with our experimental results.

Similar issues were encountered previously in itinerant-electron ferromagnet MnSi (Ref. 23) and epitaxial films of $CaRuO_3$,[24] both of which undergo a quantum phase transition between FM and paramagnetic (PM) ground states tuned by pressure or chemical doping. In these cases, $\rho \sim T^{3/2}$ clearly fits the data best. Particularly, a sufficiently strong magnetic field appears to destroy non-Fermi-liquid behavior

TABLE I. Theoretical predictions on quantum critical behavior in 3D.

Model	$\rho(T)$	$C(T)/T$
AFM[a]	$\sim T^{3/2}$	$\sim T^{1/2}$
FM[a]	$\sim T^{5/3}$	$\sim \ln(T_0/T)$

[a]Reference 22.

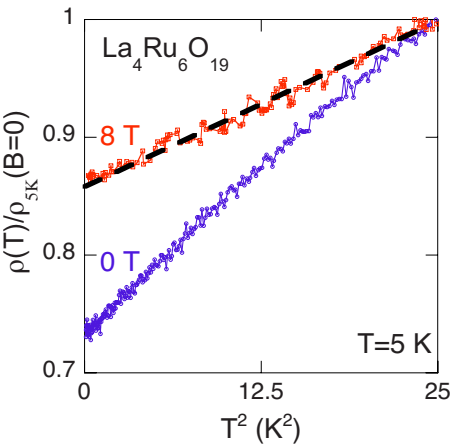

FIG. 5. (Color online) Low-temperature electrical resistivity at 0 and 8 T, normalized by $\rho_{5\ K}(0\ T)$.

in $La_4Ru_6O_{19}$, recovering the $\rho \sim T^2$ behavior (Fig. 5), as in the case of MnSi. Therefore, even though the $\rho \sim T^{3/2}$ behavior seen in $La_4Ru_6O_{19}$ does not fit the theoretical prediction for the 3D FM model, the experimental similarities between $La_4Ru_6O_{19}$ and MnSi (Table II) as well as $CaRuO_3$ (Ref. 24) suggest that $La_4Ru_6O_{19}$ is close to an FM QCP.

It should be emphasized that having FM fluctuations is different from having an FM long-range order. In the former case, the magnetic susceptibility as a function of magnetic field can be linear even at high magnetic fields and no hysteresis with respect to field ramping is expected, as seen experimentally in $La_4Ru_6O_{19}$. Furthermore, the Curie-Weiss fit to the magnetic-susceptibility data can yield a negative Curie-Weiss temperature even when the magnetic fluctuations are dominated by FM fluctuations, as seen in $Sr_{1-x}Ca_xRuO_3$, which features temperature-dependent magnetic susceptibility[25] similar to that of $La_4Ru_6O_{19}$. Force fitting the latter to Curie-Weiss behavior also yields a negative Curie-Weiss temperature.[9] Interestingly, a recent paper reported results on nuclear magnetic resonance (NMR) as well as bulk magnetic-susceptibility and specific-heat measurements on polycrystalline (as opposed to our single crystalline) $La_4Ru_6O_{19}$.[26] Their magnetic-susceptibility and specific-heat data, including a rapid rise in magnetic susceptibility as the temperature is lowered, agree well with our results obtained previously on single-crystal samples in overlapping ranges of the temperature. No field dependence of the magnetic susceptibility was observed, as seen previously. Most strikingly, the value of the ^{99}Ru Knight shift[26] was found to increase significantly as the temperature is lowered, consistent with the low-temperature rise of the magnetic susceptibility.[9,26] This suggests that the increasing bulk mag-

TABLE II. Experimental results observed in MnSi and $La_4Ru_6O_{19}$.

Material	$\rho(T)$	$C(T)/T$
MnSi[a]	$\sim T^{3/2}$	$\sim \ln(T_0/T)$
$La_4Ru_6O_{19}$	$\sim T^{3/2}$	$\sim \ln(T_0/T)$

[a]Reference 23.

netic susceptibility observed in $La_4Ru_6O_{19}$ is intrinsic rather than due to impurity contributions since the NMR measurements probe magnetic response on Ru sites only. The authors of the paper suggested that the magnetic fluctuations below 20 K in $La_4Ru_6O_{19}$ are AFM rather than FM in nature by fitting their data to a 3D itinerant AFM model near a QCP. However, the fitting involved several parameters that cannot be determined independently and the range of the fitting is limited, especially for the specific-heat data. Therefore, further experiments, especially neutron-diffraction measurements, are needed to resolve this issue.

The possible quantum critical behavior in $La_4Ru_6O_{19}$ suggests that both thermal and quantum FM fluctuations may be present. While thermal FM fluctuations lead to negative magnetoresistance as observed in $La_4Ru_6O_{19}$ at modestly low temperatures, quantum FM fluctuations, which can lead to $\rho \sim T^{3/2}$ behavior as seen in MnSi (Ref. 23) and $CaRuO_3$,[24] may have dominated at temperatures below T^*. The sign of magnetoresistance in systems dominated by quantum FM fluctuations can be either positive or negative, as seen near the quantum critical point of MnSi tuned by pressure.[23]

It is interesting to ask how the possible quantum FM fluctuations emerge in $La_4Ru_6O_{19}$. As pointed out above, metal-metal bonding in $La_4Ru_6O_{19}$ appears to result in molecular-orbital states and the narrow band. These molecular-orbital states will interact with one another as well as with conduction electrons. We speculate that interactions between the molecular-orbital states drive the system toward an FM ordering. On the other hand, interactions between the molecular-orbital states and the conducting electrons work to screen out the magnetic moments of the molecular-orbital state to form a nonmagnetic state, similar to heavy fermion materials[27] described theoretically by Kondo-lattice model.[28] It appears that these two interactions happen to be similar in magnitude even under ambient pressure, giving rise to the possible quantum FM fluctuations. The corresponding quantum phase transition between an FM and a PM ground state should be tunable by pressure or doping.

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