Quantum Phase Transition in Quasi-One-Dimensional $BaRu_6O_{12}$

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We report the first systematic study of the electrical transport and magnetic properties of $BaRu_6O_{12}$, which has a quasi-one-dimensional (quasi-1D) hollandite structure. We show that $BaRu_6O_{12}$ is quasi-1D electronically as well. Its physical properties were found to be extremely sensitive to disorder. Furthermore, a transition from being metallic with a resistance drop around 2 K to being weakly insulating as the applied magnetic field was increased was also found. We propose that these two features are related to the possible presence of a quantum phase transition in this material system.

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The search for exotic collective electronic phenomena in ternary compounds of ruthenium and oxygen has been extremely fruitful in recent years, as evidenced by the discoveries of spin-triplet superconductivity in Sr_2RuO_4 [1,2], metamagnetism in $Sr_3Ru_2O_7$ [3], non-Fermi-liquid behavior in $La_4Ru_6O_{19}$ [4], and pseudo gap formation in $BaRuO_3$ [5–7]. The remarkably rich properties displayed by ruthenates derive from both the electronic characteristics and the great structural variety. One-dimensional (1D) ruthenates would be of particular interest in this pursuit because of the inherent instability of low-temperature ground states in 1D, but detailed studies of any 1D ruthenate have not yet been reported. Here we present electrical and magnetic measurements on $BaRu_6O_{12}$, showing that electronically it is quasi-1D, with physical properties extremely sensitive to disorder. In addition, we found strong evidence for the existence of two ground states and an associated quantum phase transition (QPT) [8,9] in this quasi-1D ruthenate.

$BaRu_6O_{12}$ has the tetragonal hollandite structure [10] (Fig. 1). Hollandites are well known 1D materials due to the edge sharing of octahedra in one direction and corner sharing in the other direction. In $BaRu_6O_{12}$, the double chains of edge sharing RuO_6 octahedra run parallel to the crystallographic c axis. This structure is not similar to other ternary ruthenates presently under study — it is highly 1D in character. The 1D metals are an important paradigm of contemporary condensed matter physics. Electron-electron interactions in 1D lead to a breakdown of the Fermi liquid theory, resulting in a Luttinger-Tomonaga liquid state [11,12]. In addition, the presence of multiple competing instabilities, typical for 1D or quasi-1D systems, has been found to give rise to greatly enhanced quantum fluctuations which, in turn, lead to novel physical phenomena, as demonstrated in organic conductors [13]. $BaRu_6O_{12}$ provides the first opportunity to study these unusual 1D phenomena in ruthenates, in which electrons in the $4d$ orbitals dominate the physical properties of the material.

Single crystals of $BaRu_6O_{12}$ were prepared by flux and vapor-transport methods. In the flux method, RuO_2, BaO_2, and Ru were mixed stoichiometrically, added to $BaCl_2$ and heated in alumina crucibles placed in evacuated quartz tubes at 1200 °C for 5 d. In the vapor-transport method, the starting materials were elemental Ru placed in an alumina boat at 1275 °C, and a $BaCl_2$, $BaCO_3$ mixture placed in another alumina boat at 1100 °C. The distance between the two crucibles was about 10 cm. Flowing oxygen was used as the carrier gas. Needlelike single crystals of $BaRu_6O_{12}$ were grown in the boat containing the Ba source. The typical size of the crystals used for resistivity measurements was $1\,\text{mm} \times 0.1\,\text{mm} \times 0.1\,\text{mm}$. Electrical transport measurements were carried out in either ^{3}He cryostats with a base

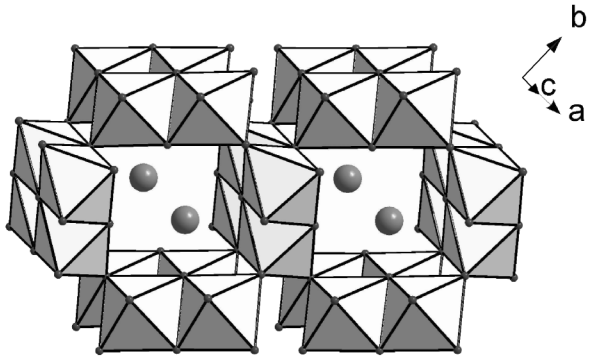

FIG. 1. Crystal structure of $BaRu_6O_{12}$, which consists of double chains (along c axis) of edge-sharing RuO_6 octahedra (Ru in the center of the octahedron and O at the corners). The chains of RuO_6 octahedra are linked by sharing corner oxygens, forming square tunnels in which the Ba ions are located. The crystals grew along the c axis, forming needlelike single crystals with a nearly square cross section.

temperature of 0.3 K or a dilution refrigerator that can reach 20 mK. Magnetic susceptibility measurements were performed in a dc superconducting quantum interference device magnetometer with a base temperature of 1.8 K.

Figure 2 shows the temperature (T) dependences of the resistivity parallel and perpendicular to the ruthenium-oxygen chains (c axis), denoted by $\rho_{\parallel}$ and $\rho_{\perp}$, respectively. $\rho_{\parallel}(T)$ was found to be metallic over the whole temperature range [0.03–300 K; see also the inset of Fig. 5(b) below]. It is interesting to note that both $\rho_{\parallel}$(300 K) and the T dependence of $\rho_{\parallel}$ are similar to the in-plane resistivity of superconducting Sr_2RuO_4 [1]. On the other hand, $\rho_{\perp}(T)$ exhibited incoherent behavior ($d\rho_{\perp}/dT < 0$) for $T > 210$ K, followed by a crossover to coherent behavior ($d\rho_{\perp}/dT > 0$), also similar to the $\rho_c(T)$ of Sr_2RuO_4 [1]. On several samples we measured both $\rho_{\perp}$ and $\rho_{\parallel}$ (on the same crystal). For all samples measured, the ratio of $\rho_{\perp}/\rho_{\parallel}$ was found to be around 6 at 300 K and 13 at 4.2 K. Although the resistivity anisotropy $\rho_{\perp}/\rho_{\parallel}$ is not very large in $BaRu_6O_{12}$, the temperature dependences of $\rho_{\parallel}$ and $\rho_{\perp}$ are significantly different, which indicates $BaRu_6O_{12}$ is quasi-1D electronically.

Figure 3(a) shows the magnetic susceptibility of $BaRu_6O_{12}$ measured on a collection of single crystals. The temperature dependence of magnetic susceptibility $\chi(T)$ was found to be highly unusual. A monotonic decrease was found down to 30–40 K, followed by a slight increase as the temperature is lowered further. The physical origin for the rise in $\chi(T)$ at low-temperature has not been identified. We have also measured the field dependence of magnetization at 2 and 10 K, which shows a linear behavior [see the inset of Fig. 3(a)], indicating that no long-range magnetic ordering occurs in $BaRu_6O_{12}$ down to 2 K.

Figure 3(b) shows the Hall coefficient R_H of $BaRu_6O_{12}$. It is seen that R_H depends strongly on T, showing a change in sign at a temperature near the incoherent-coherent crossover in $\rho_{\perp}(T)$. The Hall voltage is linear as a function of the magnetic field at low fields, showing a small nonlinearity at high fields and low temperatures. The carrier density of $BaRu_6O_{12}$ derived from the mea sured R_H is $n = 1.7 \times 10^{22}$ cm^{-3} at room temperature, comparable to that of $SrRuO_3$ which is a ferromagnetic metal [14].

The resistivity of $BaRu_6O_{12}$ at low temperatures was found to be sensitive to disorder, as shown in Fig. 4(a). The disorder level may be quantified by the value of room temperature to residual resistivity ratio [RRR = $\rho_{\parallel}$(300 K)/$\rho_{\parallel}$(4.2 K)]. The value of RRR was found to vary from crystal to crystal, ranging from 11.3 to 2.6 among over 50 crystals we measured. All samples measured down to 0.3 K (> 10 crystals) showed a drop in $\rho_{\parallel}(T)$ below 2 K, with metallic behavior down to the lowest temperature at which the sample was measured,

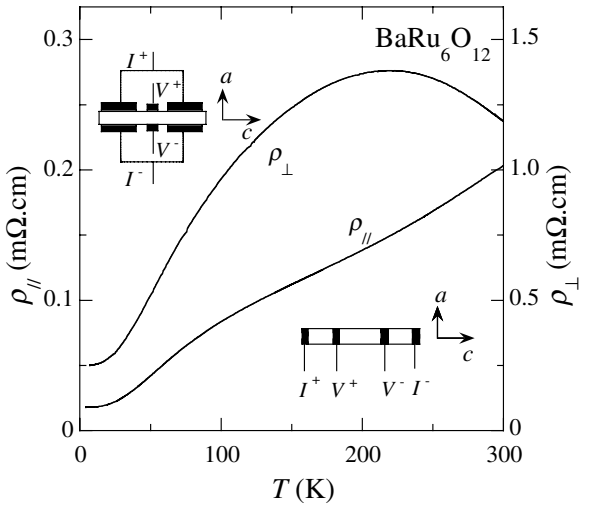

FIG. 2. Resistivities of $BaRu_6O_{12}$ along and perpendicular to the chains ($\parallel$ and $\perp$ c axis) of RuO_6 octahedra, $\rho_{\parallel}(T)$ and $\rho_{\perp}(T)$, respectively. $\rho_{\parallel}(T)$ was measured by sending a current along the c axis while $\rho_{\perp}(T)$ was measured using a six-lead configuration with current flowing perpendicular to the chain direction (inset).

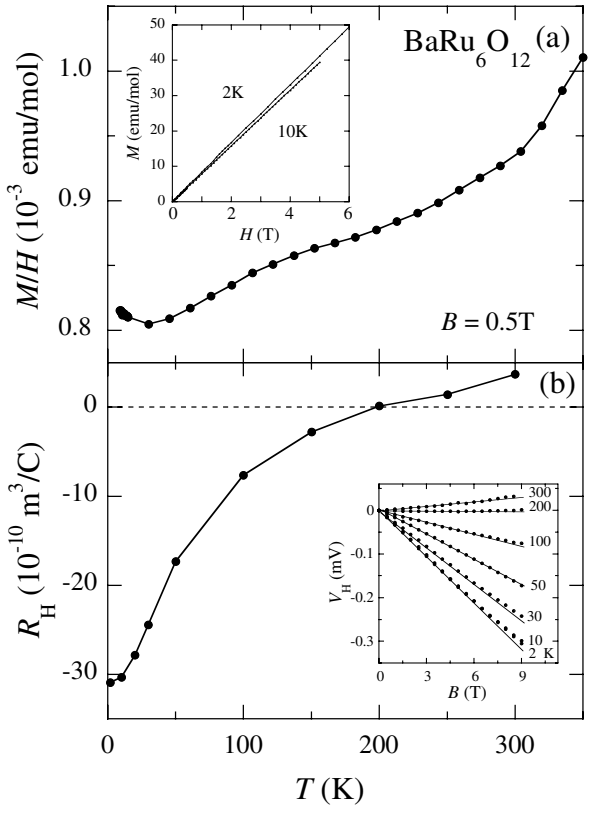

FIG. 3. (a) Temperature dependence of magnetic susceptibility, $\chi(T)$, measured at $B = 0.5$ T for a collection of $BaRu_6O_{12}$ single crystals, aligned randomly. Inset: The magnetic field dependence of magnetization, $M(H)$ measured at 2 and 10 K, respectively. (b) Hall coefficient as a function of temperature, $R_H(T)$, for $BaRu_6O_{12}$. Inset: The Hall voltage (V_H) vs H at various temperatures as indicated.

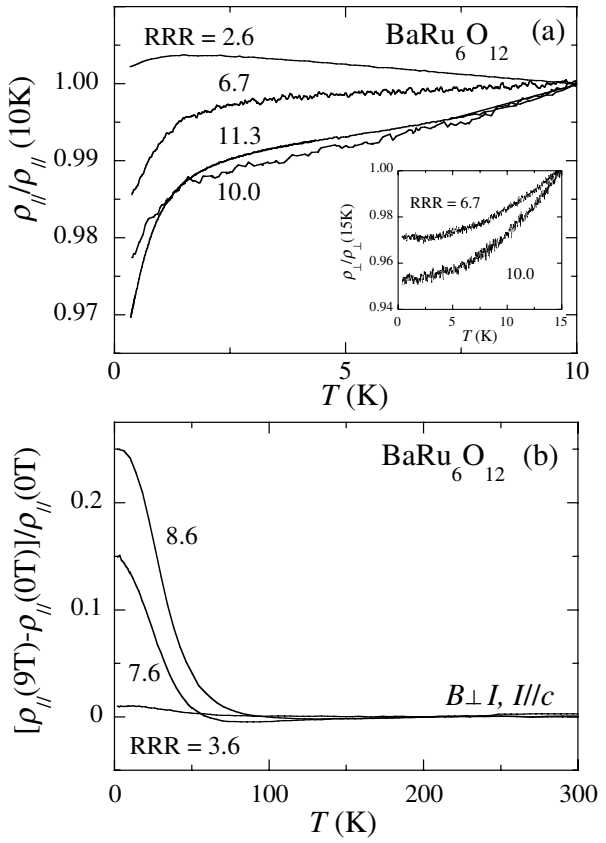

FIG. 4. (a) Normalized $\rho_{\parallel}(T)$ at low temperatures for $BaRu_6O_{12}$ samples with different RRR [$= \rho_{\parallel}(300\ \mathrm{K})/\rho_{\parallel}(4.2\ \mathrm{K})$]. The values of $\rho_{\parallel}$ at 10 K for four samples are, from top to bottom, 58.0, 30.7, 19.6, and 18.1 $\mu\Omega \cdot$ cm. Inset: Normalized $\rho_{\perp}(T)$ for two samples shown in the main panel with RRR = 6.7 and 10.0, respectively; (b) c-axis transverse magnetoresistance $\Delta\rho_{\parallel}(H_{\perp})/\rho_{\parallel}\{= [\rho_{\parallel}(H_{\perp}) - \rho_{\parallel}(0)]/\rho_{\parallel}(0)\}$ as a function of temperature for three $BaRu_6O_{12}$ samples with different RRRs.

30 mK [inset of Fig. 5(b)]. The sharpness and the relative size of the drop, as well as the slope above the drop, depend sensitively on RRR. A negative $d\rho_{\parallel}/dT$ was found in the most disordered sample (RRR = 2.6) for $2\ \mathrm{K} < T < 13\ \mathrm{K}$. For all samples on which both $\rho_{\perp}$ and $\rho_{\parallel}$ were measured, $\rho_{\perp}$ did not exhibit any drop below 2 K [inset of Fig. 4(a)] while $\rho_{\parallel}$ did. This makes it difficult to associate the drop in $\rho_{\parallel}$ with the occurrence of superconductivity.

The sensitivity of the low-temperature electronic and magnetic states in $BaRu_6O_{12}$ to disorder is also evident in the RRR dependence of the size of the magnetoresistance (MR). Figure 4(b) shows the temperature dependence of the c-axis transverse MR $\Delta\rho_{\parallel}(H_{\perp})/\rho_{\parallel}$, measured at $H =$ 9 T, for several samples. For those with a high RRR, $\Delta\rho_{\parallel}(H_{\perp})/\rho_{\parallel}$ was found to be large at low temperatures. For samples with a low RRR, on the other hand, $\Delta\rho_{\parallel}(H_{\perp})/\rho_{\parallel}$ is quite small over the entire temperature range. Indeed, $\Delta\rho_{\parallel}(H_{\perp})/\rho_{\parallel}$ at 4 K and 9 T is about 25% for the sample with RRR = 8.6, but for the sample with RRR = 3.6 it is about 1%. The disorder effect on both the 2 K resistivity drop and the MR makes it clear that the physical properties of $BaRu_6O_{12}$ are extremely sensitive to disorder.

Sensitivity to disorder has been noted for $Sr_3Ru_2O_7$ previously [15], for which a 60% in-plane transverse MR at 5 K and 7 T was found for samples with RRR = 75, and 14% for samples with RRR = 12 [16]. In comparison, $BaRu_6O_{12}$ appears to be even more sensitive to disorder than $Sr_3Ru_2O_7$. The physical origin for such sensitivity has not been identified for $Sr_3Ru_2O_7$. However, given that $Sr_3Ru_2O_7$ is near a metamagnetic quantum phase transition (QPT) [3], the extremely high sensitivity to disorder seen in $Sr_3Ru_2O_7$ is likely due to its proximity to a QPT.

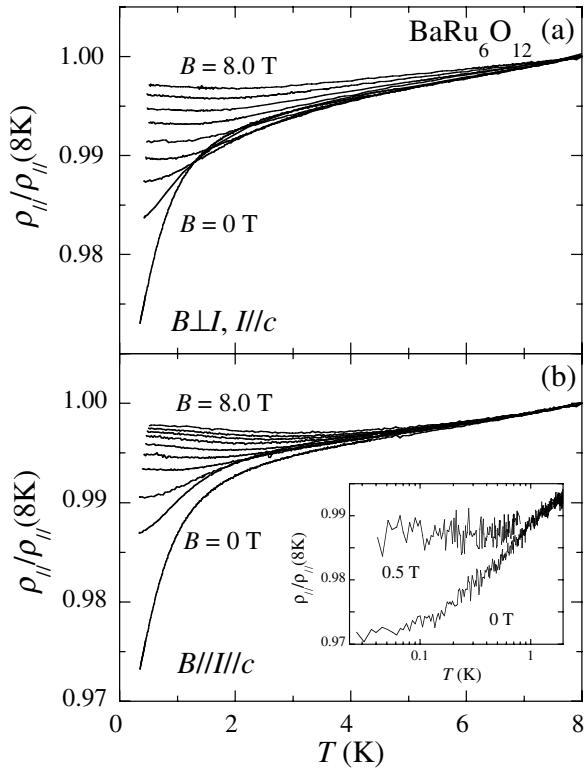

FIG. 5. Normalized c-axis resistivity, $\rho_{\parallel}(T)/\rho_{\parallel}(8\ \mathrm{K})$, of the cleanest sample available, with RRR = 11.3, measured under (a) transverse and (b) longitudinal magnetic fields with values of the field as indicated. The top curve corresponds to the highest field. The values of resistivity at 8 K used for the normalization, which are field dependent, are 18.00, 18.13, 18.38, 18.76, 19.22, 19.78, 20.36, 21.03, and 21.71 $\mu\Omega \cdot$ cm for the transverse fields of 0, 1, 2, 3, 4, 5, 6, 7, and 8 T; 18.00, 18.00, 18.00, 18.02, 18.03, 18.05, 18.07, 18.10, 18.15, and 18.20 $\mu\Omega \cdot$ cm for the longitudinal fields of 0, 0.5, 1, 2, 3, 4, 5, 6, 7, and 8 T, respectively. Inset: Semilog plot of the normalized c-axis resistivity as a function of temperature, $\rho_{\parallel}(T)/\rho_{\parallel}(8\ \mathrm{K})$, of a sample with RRR = 7.5, measured down to dilution refrigerator temperatures. (Lower-temperature data for the sample shown in the main panel is not available.)

Similarly, the sensitivity to disorder seen in $BaRu_6O_{12}$ may also be related to a QPT.

Is there a QPT in $BaRu_6O_{12}$? The slightly increasing resistivity seen in the RRR = 2.6 sample above the 2 K resistivity drop [Fig. 4(a)] suggests that a weakly localized ground state might be present in this material. In Fig. 5, curves of $\rho_{\|}(T)$ at various magnetic fields, applied perpendicular to [Fig. 5(a)] and along [Fig. 5(b)] the c axis, are shown for the sample with RRR = 11.3. Independent of the field orientation, an increasing low-temperature resistivity was found to persist down to the lowest temperature for $B > 1$–2 T, demonstrating that a competing, weakly localized ground state indeed exists in $BaRu_6O_{12}$. The characteristic temperature below which the resistance shows an upturn goes up as the field increases, further supporting that the field leads to, and stabilizes, the electron localization. In addition, since both the parallel and the transverse fields lead to a similar crossover, the spin degrees of freedom must be important for the formation of the weakly localized ground state.

It might be possible that simple enhancement in carrier confinement (to the chain) in the presence of a sufficiently high magnetic field led to a relatively weak upturn in resistivity as temperature was lowered. In this scenario, however, we would not have seen the localized behavior for the perpendicular field. It should also be pointed out that the quantum interference and/or the interaction effects in weakly disordered, diffusive electrons [17] are not relevant here as in that physical regime, the resistivity in zero field should be weakly insulating ($d\rho/dT < 0$) down to the lowest temperatures. In our experiment, however, no insulating behavior was observed in $\rho_{\|}$ in zero field at any temperatures for all samples with reasonably high values of RRR. Therefore results shown in Fig. 5 should be due to the existence of two fundamentally different ground states, namely, a metallic and a weakly localized state, in $BaRu_6O_{12}$. The observed coherent-incoherent crossover tuned by a magnetic field should be a true QPT between two ground states. Such QPT can apparently be tuned by disorder as well [Fig. 4(a)]. This also explains the observed sensitivity of MR to disorder.

As we pointed out above, the 2 K drop in $\rho_{\|}(T)$ [Fig. 4(a)] does not seem to be related to the occurrence superconductivity. We noticed that the presence of the drop is tunable by magnetic field, and that it is sensitive to disorder in a similar manner as the magnetoresistance. Both facts suggest that this resistance drop may be related to magnetic correlation. Although our current magnetic susceptibility measurements did not reveal any magnetic ordering down to 2 K, further magnetic property studies below 2 K, like NMR measurement, would be necessary to clarify this interesting metallic ground state.

The magnetic field induced weakly localized ground state in $BaRu_6O_{12}$ found in the present work appears to be unique among ruthenates. The discovery of a ruthenate that is so close to a quantum phase transition, with such a unique ground state, may provide a new arena for studying itinerant magnetism in low dimensions and opportunities for seeking out novel collective phenomena, such as unconventional superconductivity that may occur under suitable conditions (e.g., a hydrostatic pressure).

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