Magnetic and Transport Properties in Ba$_{1-x}$Sr$_x$RuO$_3$ Single Crystals

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Abstract. We have investigated the magnetic and the electrical transport properties in Ba$_{1-x}$Sr$_x$RuO$_3$ single crystals. In BaRuO$_3$, which has a nine-layer rhombohedral (9R) structure, the magnetic susceptibility has two components; a Curie-Weiss component ($\chi_{cw}$) and a Pauli paramagnetic-like one ($\chi_{pp}$). $\chi_{pp}(T)$ increases monotonically with increasing temperature up to 400 K, suggesting an exchange enhanced Pauli paramagnetism by the spin fluctuation. The temperature dependence of the resistivity ($\rho$) shows a minimum around 130 K. In the whole temperature region, the positive magnetoresistance was observed, which cannot be scaled by Kohler rule. The Hall resistivity ($\rho_H$) is positive and decreases with increasing temperature.

In Ba$_{0.7}$Sr$_{0.3}$RuO$_3$, which has a four-layer hexagonal (4H, $P6_3/mmc$ group) structure, the increment of $\chi_{pp}(T)$ above $\sim$100 K and the minimum of $\rho(T)$ were not observed, though $\chi_{cw}(T)$ is almost the same as that of 9R BaRuO$_3$. The magnetoresistance was negative suggesting the suppression of the spin fluctuation scattering of the conduction electrons. $\rho_H$ is negative at low temperatures, and changes its sign around 100 K. We infer that the difference of the Fermi surface resulting from the different layered-structure yields the distinct magnetic and transport properties.

Barium ruthenium oxide BaRuO$_3$ has a nine-layer rhombohedral (9R) structure with the space group $R\bar{3}m$ [1, 2, 3, 4]. The crystal structure changes by Sr-substitution in Ba site. With increasing Sr content $x$, the structure of Ba$_{1-x}$Sr$_x$RuO$_3$ changes from 9R to a four-layer hexagonal (4H, $P6_3/mmc$ group) at around $x = 0.1$, and from 4H to a six-layer monoclinic (6M) structure at around $x = 0.4$ [5]. For $x >$~0.9, the perovskite (P) structure, which can be regarded as a three-layer (3L) structure, with the orthorhombic $Pnma$ symmetry is realized [6]. For 9R, 4H and 6M phases, the face-shared RuO$_6$ octahedra make a pillar and the pillars are connected with the corner-shared RuO$_6$ bonding along the c-axis. The ratio of the number of the corner-shared bonding ($N_{\text{corner}}$) to that of the face-shared one ($N_{\text{face}}$) increases with increasing Sr content. The ratio $N_{\text{corner}}/N_{\text{face}}$ is 3/6, 2/2 and 4/2 for 9R, 4H and 6M structures, respectively.

It is expected that the different layered-structure yields the distinct band structure, leading to the characteristic magnetic and electrical transport properties [4]. In order to investigate the difference of such properties, we performed the measurements of the magnetization, the resistivity and the Hall effect on the same sample and geometry on the single crystals of BaRuO$_3$ with 9R structure and Ba$_{0.7}$Sr$_{0.3}$RuO$_3$ with 4H structure.

Polycrystalline samples of BaRuO$_3$ and Ba$_{0.7}$Sr$_{0.3}$RuO$_3$ were synthesized by a solid-state reaction of predried BaCO$_3$, SrCO$_3$ and RuO$_2$ at 1300°C. Single crystals were grown by the flux method using BaCl$_2$ or the mixture of BaCl$_2$ and SrCl$_2$ as a flux. Laue photographs confirmed
that each sample is a proper single crystal. The chemical composition and homogeneity of the crystals were characterized using JEOL JXA-8900 electron-probe microanalyzer. The structure of the crystals was confirmed by x-ray powder diffraction after being ground.

The magnetization measurements were performed with a Quantum Design SQUID magnetometer under a magnetic field up to 7 T. The Hall and the resistivity measurements were performed by a conventional dc four-probe method under a magnetic field up to 9 T.

Figure 1 shows the temperature dependence of the magnetic susceptibility ($\chi$), the resistivity ($\rho$), and the Hall resistivity ($\rho_H$) of BaRuO$_3$ and Ba$_{0.7}$Sr$_{0.3}$RuO$_3$ single crystals. In Fig. 1, we show the data for the current direction parallel to [001]$_H$ of the hexagonal lattice and the applied magnetic field in (001)$_H$ plane.

In BaRuO$_3$, which has a nine-layer rhombohedral structure, $\chi(T)$ has two components; a Curie-Weiss component $\chi_{cw} = C/(T - \theta)$ and a Pauli paramagnetic-like one ($\chi_{pp}$) as shown in Fig. 1(a). In $\chi_{cw}$, the Curie constant $C$ and the Weiss temperature $\theta$ are obtained as 0.11 emu K/mol and -2.9 K, respectively. The anisotropy in $\chi(T)$ between for the field in (001)$_H$ plane and perpendicular to the plane was very small. The magnitude of $\chi_{pp}(T)$ is several times larger than that of the ordinary transition metals [7]. $\chi_{pp}(T)$ increases monotonically with increasing temperature up to 400 K. In several materials exhibiting an exchange enhanced Pauli paramagnetism such as YCo$_2$, the magnitude of $\chi(T)$ is several times larger than that of the ordinary Pauli paramagnets and $\chi(T)$ shows a maximum [8]. The characteristics of $\chi_{pp}(T)$ suggest that BaRuO$_3$ is an exchange enhanced Pauli paramagnet where the ferromagnetic spin fluctuation is large. According to the Curie constant $C$ of $\chi_{cw}$, about 10 % of Ru$^{4+}$ ions have the spin 1, which seems to be too large to attribute $\chi_{cw}$ to the impurity magnetization. The observation suggests that the characteristics of the magnetism of BaRuO$_3$ is an intermediate between the localized and the itinerant electron magnetism.

As shown in Fig. 1(b), the resistivity $\rho$ of 9R BaRuO$_3$ shows a metallic behavior at higher temperatures, but increases with decreasing temperature below around 130 K, as previously reported [4]. The increment of $\rho$ at low temperatures was not suppressed by applied magnetic field 9 T, which implies that the increment of $\rho(T)$ is not due to the Kondo effect. The measurements of $\rho(H)$ revealed the positive magneto-resistance (MR) between 2 and 300 K as shown in the inset of Fig. 1(b), suggesting the ordinary MR [9]. The magnitude of MR $[(\rho - \rho_0)/\rho_0]$ at 9 T is less than 0.5% below 30 K or above 250 K. MR shows a maximum value about 2% at around 130 K where the minimum of $\rho(T)$ is observed. It is natural that the ordinary MR is larger for smaller $\rho$. However, $\rho(H)$ cannot be scaled by the Kohler rule as shown in the inset of Fig. 1(b) [9], which implies that the observed positive MR cannot be explained solely by the ordinary MR. The deviation of MR from the Kohler rule suggests a non-Fermi liquid-like behavior resulting from some quantum fluctuation.

The Hall resistivity $\rho_H$ of BaRuO$_3$ was almost proportional to $H$ in the whole temperature region investigated. The value of $\rho_H$ is positive in sign and decreases in magnitude with increasing temperature (see Fig. 1(c)). $\rho_H(T)$ cannot be reproduced by $\rho_H(T) = R_0 H + a_0 + a_p(T)\chi(T)H$ assuming that the ordinary Hall coefficient $R_0$ and the coefficient of the skew scattering $a$ are constant [10]. The observation suggests that the temperature dependence of $\rho_H(T)$ cannot be explained by the temperature dependence of the extraordinary Hall effect. In the present $\rho_H$, it is expected that the ordinary Hall coefficient $R_0$ is largely temperature dependent. The increment of both $\rho_H$ and $\rho$ with decreasing temperature at low temperatures suggests the decrease of the area of the Fermi surface due to a pseudo-gap formation on some part of the Fermi surface.

In Ba$_{0.7}$Sr$_{0.3}$RuO$_3$, which has a four-layer hexagonal 4H structure, $\chi(T)$ is reproduced by the sum of the $\chi_{cw}(T)$ and constant $\chi_{pp}$ as shown in Fig. 1(d). The magnitude of $\chi_{pp}$ is less than half of that of BaRuO$_3$ at 400 K, and the increment of $\chi_{pp}$ was not observed, suggesting that the spin fluctuation associated with the exchange enhanced Pauli paramagnetism is suppressed.
Figure 1. Temperature dependence of (a) and (d) the magnetic susceptibility ($\chi$) measured at 0.5 T, (b) and (e) the resistivity ($\rho$) at 0 T, and (c) and (f) the Hall resistivity ($\rho_H$) at 9 T of BaRuO$_3$ and Ba$_{0.7}$Sr$_{0.3}$RuO$_3$ single crystals. In Figs. 1(a) and (d), the dotted and the solid lines represent a Pauli paramagnetic-like component ($\chi_{pp}$) and a Curie-Weiss one ($\chi_{cw}$), respectively. The insets in Figs. 1(b) and (e) show the field dependence of $\rho$. The current direction was parallel to [001]$_H$ of the hexagonal axis. The magnetic field was applied in (001)$_H$ plane.

in 4H Ba$_{0.7}$Sr$_{0.3}$RuO$_3$. On the other hand, $\chi_{cw}(T)$ is almost the same as that of BaRuO$_3$.

As shown in Fig. 1(e), the resistivity of 4H Ba$_{0.7}$Sr$_{0.3}$RuO$_3$ shows metallic behavior in the whole temperature region investigated, and shows no minimum in $\rho(T)$ around 130 K observed in 9R BaRuO$_3$. $\rho(T)$ tends to saturate at higher temperatures, which suggests the contribution of the spin fluctuation scattering of the conduction electrons on $\rho$ of Ba$_{0.7}$Sr$_{0.3}$RuO$_3$. The MR is negative above 10 K, suggesting the suppression of the spin fluctuation scattering. Below 10 K, $\rho(H)$ decreases at lower fields but increases at higher fields with increasing field, which is due to the smaller spin fluctuation scattering and the larger ordinary MR (see the inset of Fig. 1(e)).
Also in Ba$_0.7$Sr$_{0.3}$RuO$_3$, $\rho_H(H)$ was almost proportional to $H$. The Hall resistivity $\rho_H(T)$ of $4H$ Ba$_0.7$Sr$_{0.3}$RuO$_3$ is negative at low temperature, and changes its sign around 100 K, as shown in Fig. 1(f). This behavior of $\rho_H(T)$ is remarkably different from that of BaRuO$_3$. $\rho_H(T)$ of Ba$_0.7$Sr$_{0.3}$RuO$_3$ also cannot be explained by the extraordinary Hall effect, suggesting that the observed $\rho_H(T)$ reflects mainly the temperature dependence of the ordinary Hall coefficient $R_0$.

As described above, $\chi$, $\rho$ and $\rho_H$ exhibit distinct characteristics between 9R BaRuO$_3$ and 4H Ba$_0.7$Sr$_{0.3}$RuO$_3$. Taking into account the difference in the layered-structure between the materials, it is expected that the difference of the Fermi surface and/or the band structure yields such the distinct magnetic and transport properties between these materials. The remarkable difference of $\rho_H(T)$ strongly supports the different Fermi surface, since $\rho_H(T)$ in the present experiment arises from the difference of the ordinary Hall coefficient. The anomalous increment of $\chi(T)$ with increasing temperature above $\sim$100 K and the increment of $\rho(T)$ with decreasing temperature at low temperatures suggest that 9R BaRuO$_3$ is more anomalous metal than 4H Ba$_0.7$Sr$_{0.3}$RuO$_3$. It is expected that the Fermi surface of 9R BaRuO$_3$ is more one-dimensional, which might be the origin of the anomalous magnetic and transport properties such as the exchange enhance Pauli paramagnetism and the pseudo-gap formation in 9R BaRuO$_3$.

In conclusion, we have investigated the magnetic and the electrical transport properties in Ba$_{1-x}$Sr$_x$RuO$_3$ single crystals. In both BaRuO$_3$ and Ba$_0.7$Sr$_{0.3}$RuO$_3$, the magnetic susceptibility has two components; a Curie-Weiss component $\chi_{cw}$ and a Pauli paramagnetic-like one $\chi_{pp}$. In 9R BaRuO$_3$, $\chi_{pp}(T)$ increases monotonically with increasing temperature up to 400 K, suggesting an exchange enhanced Pauli paramagnetism. The temperature dependence of $\rho$ shows a minimum around 130 K. In the whole temperature region, the positive magnetoresistance was observed, which cannot be scaled by Kohler plot. The Hall resistivity $\rho_H$ is positive and decreases with increasing temperature. In 4H Ba$_0.7$Sr$_{0.3}$RuO$_3$, the increment of $\chi_{pp}(T)$ above $\sim$100 K and the minimum of $\rho(T)$ were not observed, though $\chi_{cw}(T)$ is almost the same as that of 9R BaRuO$_3$. The magnetoresistance was negative, suggesting the suppression of the spin fluctuation scattering of the conduction electrons. $\rho_H$ is negative at low temperature, and changes its sign around 100 K. We infer that the difference of the Fermi surface due to the different layered-structure yields the distinct magnetic and transport properties.

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