Magnetic properties of Sr$_{3-x}$Ca$_x$Ru$_2$O$_7$

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Abstract. We report the magnetization data of single crystalline Sr$_{3-x}$Ca$_x$Ru$_2$O$_7$ ($x = 1.5, 2.0, 3.0$) grown by a floating-zone method. In the magnetic phase diagram of this system, a phase with a ferromagnetic correlation ($0.5 \leq x \leq 1.2$) adjoins a two-dimensional (2D) metallic and antiferromagnetic phase ($1.2 \leq x \leq 3$). In the antiferromagnetic and 2D-metallic phase, the magnetic susceptibilities indicate that the magnetic easy axis changes continuously from the $ab$-plane to $c$-axis with increasing Sr content. Our results exhibit that the metamagnetic transition of Ca$_3$Ru$_2$O$_7$, which is on the basis of a tunneling magnetoresistance, shifts to lower field and the transition becomes broad with increasing Sr content. Moreover, the magnetization data at $T = 5$ K for $x = 1.5, 2.0$ show a hysteresis, which suggests that the magnetic ground state is a canted antiferromagnetic one in this phase.

1. Introduction
Ruddlesden-Popper (R-P) type perovskite ruthenates (Sr,Ca)$_{n+1}$Ru$_n$O$_{3n+1}$ have attracted many researchers since the discovery of the spin triplet superconductor Sr$_2$RuO$_4$[1]. These compounds show a wide variety of physical properties; e.g., ferromagnetic metal, antiferromagnetic insulator and superconductivity. In addition, these properties are very sensitive to small perturbations such as atomic substitution, magnetic field and pressure. In Sr$_{2-x}$Ca$_x$RuO$_4$, starting from Pauli paramagnetic Sr$_2$RuO$_4$, magnetic correlation is enhanced as increasing Ca substitution up to $x \sim 1.5$ with involving the distortion of RuO$_6$ octahedra[2, 3, 4]. In these R-P type ruthenates, four 4$d$-electrons are on the $t_{2g}$ orbital (low-spin state). The structural distortions, therefore, cause a split of the energy-level scheme of the threefold degenerated $t_{2g}$ orbital, which strongly affects magnetic and electronic properties of this system.

In the double-layered ($n = 2$) ruthenates, Sr$_3$Ru$_2$O$_7$ shows Fermi liquid behavior with a large electronic specific heat coefficient $\gamma = 110$ mJ/Ru mol K. This compounds is also known as an enhanced paramagnetic metal[5]. In a magnetic field near $8$ T, metamagnetic transitions take place and quantum criticality in the vicinity of this field has been recently discussed[6, 7].

On the other hand, Ca$_3$Ru$_2$O$_7$ shows an antiferromagnetic ordering below $T_N = 56$ K and a structural phase transition at $T_S = 48$ K. The latter transition was thought to accompany a metal-insulator transition[8]; however, a recent study reported that its ground state is a quasi-two-dimensional (2D) metal with a large anisotropic electrical resistivity[9]. In the antiferromagnetic state, the magnetic moments align ferromagnetically within the double layer and antiferromagnetically between the double layers[10, 11]. In a magnetic field parallel to the
double layer, a metamagnetic transition take places near 6 T accompanied by the tunneling magnetoresistance effect[12].

Very recently, we have succeeded to obtain single crystal of $\text{Sr}_{3-x}\text{Ca}_x\text{Ru}_2\text{O}_7$ (0 ≤ x ≤ 3) grown by a floating zone method. From the results of X-ray diffraction, magnetic susceptibility, specific heat and electrical resistivity, the $x-T$ phase diagram was constructed. With increasing Ca content, a ferromagnetically correlated phase appears for 0.5 ≤ x ≤ 1.2. This phase adjoins the two-dimensional metallic and antiferromagnetic phase. In the antiferromagnetic 2D-metallic phase, the magnetic easy axis changes continuously from the $c$-axis to the axis in the $ab$-plane with increasing Ca content[13].

In order to investigate magnetic properties, such as magnetic anisotropy and antiferromagnetic ground state, we measured the magnetic field ($H$) dependence of magnetization of $\text{Sr}_{3-x}\text{Ca}_x\text{Ru}_2\text{O}_7$ for $x = 1.5, 2.0, 3.0$. Both $x = 1.5$ and 2.0 samples show an antiferromagnetic ordering in those ground states. The transition temperature $T_N$ is 35 K for $x = 1.5$ and 47 K for $x = 2.0$, respectively.

2. Experiments

Single crystals with different Sr content were grown using a floating-zone method with an image furnace. The magnetization measurements were carried out in $H$ increase and decrease sequences up to 7 T using a commercial SQUID magnetometer (Quantum Design, MPMS).

3. Results and discussion

Figure 1 shows the magnetization data of the samples with $x = 1.5, 2.0$, and 3.0 for the field along $b$-axis at 5 K. A metamagnetic transition accompanied with a hysteresis was observed for both samples. It is derived from spin reorientation as observed in $\text{Ca}_3\text{Ru}_2\text{O}_7$ ($x = 3.0$) at $H = 6$ T. With increasing Sr content, the transition shifts to lower field, i.e., 4.5 T for $x = 2.0$ and 1.7 T for $x = 1.5$ amounted in $H$ increase sequence. Above the transition fields, the values of the magnetization for both $x = 1.5$ and 2.0 are about 1.2 $\mu_B$, which is 60 % of expected ones for Ru$^{4+}$ ion.

Figure 2 shows the magnetization data of the samples with $x = 1.5, 2.0$, and 3.0 for the field along $c$-axis at 5 K. Taking account of the fact that the $c$-axis is magnetic hard axis for $\text{Ca}_3\text{Ru}_2\text{O}_7$, it is natural that any transition was not observed. Note that the values of magnetization increase with increasing Sr content in contrast with the results in $H/ a$.

Figure 3 and 4 show the magnetization data of the $x = 1.5, 2.0$ samples in $H/b$ at several temperatures with the differential coefficient $dM/dH$, respectively. The measurements were carried out at $T = 5$ K, just below $T_N$, and above $T_N$. The transition fields, which are defined by the maximum of $dM/dH$, decrease with increasing temperature and then no transition was observed above $T_N$.

According to our previous results, Sr substitution to $\text{Ca}_3\text{Ru}_2\text{O}_7$ causes the suppression of strong 2D-metallic character, i.e. $c$-axis conduction changes from insulative one to nearly metallic one[13]. This has an influence on the magnetic properties. In other words, localized character of the magnetic moments in $\text{Ca}_3\text{Ru}_2\text{O}_7$ may approach itinerant with increasing Sr substitution. As a result, the magnetization above the metamagnetic transition in $H/a$ has only about 1.2 $\mu_B$, which does not reach the full moment of 2 $\mu_B$ for the Ru$^{4+}$ ion, and the transition becomes broad (, which are also influenced by a randomness effect). Regarding with the results in $H/c$, the value of magnetization increase with increasing Sr content. This indicates the $c$-axis components of the magnetic moments emerge with increasing Sr content. Taking into account the fact that the hysteresis were observed in $H/a$ measurements, a canted antiferromagnetic state probably occurs in $x = 1.5$ and 2.0 samples. Sr substitution may affect the structural distortion of RuO$_6$ octahedra such as rotation and tilting, and then spin orientation changes. Detail
structural analyses like neutron diffraction will clarify the relationship between the magnetic properties and the structural distortions in this system.

4. Conclusion
We report the magnetization data of single crystalline $\text{Sr}_{3-x}\text{Ca}_x\text{Ru}_2\text{O}_7$ ($x=1.5, 2.0$) grown by a floating-zone method. The results exhibit that the metamagnetic transition of $\text{Ca}_3\text{Ru}_2\text{O}_7$, which is on the basis of a tunneling magnetoresistance, shifts to lower field and the transition becomes broad with increasing Sr content. Moreover, the magnetization data at $T=5$ K for $x=1.5, 2.0$
show a hysteresis, which suggests that the magnetic ground state is a canted antiferromagnetic one in this phase.

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