Anisotropy in the magnetization and resistivity of the metallic triangular-lattice magnet PdCrO$_2$

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Abstract. We report results of our magnetization and resistivity measurements using single crystals of the conductive antiferromagnet PdCrO$_2$ with a layered structure, consisting of alternating stacks of a triangular lattice of Pd$^{1+}$ and of Cr$^{3+}$ along the c axis. We confirmed that the magnetic susceptibility is nearly isotropic above $T_N$ but becomes slightly anisotropic below $T_N$ ($\chi_{ab} > \chi_c$). These results, combined with previously known facts, indicate that PdCrO$_2$ is a Heisenberg spin system, and the spins lie in a plane containing the c axis below $T_N$ (an “easy-axis type” 120$^\circ$ structure). We also found that the resistivity exhibits a highly two-dimensional metallic behavior in the whole measured temperature range with an anisotropy ratio $\rho_c/\rho_{ab} \geq 150$. Interestingly, despite such a strongly anisotropic conductivity, the inter-Pd-layer hopping and the intra-Pd-layer conductivity are both affected by the localized Cr spins in comparable magnitude. The present results make PdCrO$_2$ a promising candidate for the emergence of the unconventional anomalous Hall effect.

1. Introduction
Recent studies on geometrically frustrated spin systems have generated increasing interest for roles of special spin configurations mediated by the frustration among spins. For metallic systems, such nontrivial spin structure may lead to an unconventional anomalous Hall effect (AHE), in which the Hall resistivity $\rho_{\text{Hall}}$ does not obey the empirical relation [1, 2]: $\rho_{\text{Hall}} = R_0 H + 4\pi R_S M$, where $R_0$ and $R_S$ are the ordinary and conventional anomalous Hall coefficients, and $M$ is the magnetization. In order to extract unconventional contribution to the AHE, it is thus essential to obtain precise information of $M$. In addition, the resistivity needs to be investigated, since it is expected to be intimately related to the coefficient $R_S$ [3].

As a promising material for the observation of the unconventional AHE, we have been studying the metallic two-dimensional triangular-lattice magnet PdCrO$_2$ [4, 5]. This oxide has been known to exhibit an antiferromagnetic transition with a 120$^\circ$ spin order at $T_N \approx 38$ K [5, 6]. Because of its layered crystal structure, it is important to study anisotropy of the physical properties using single crystals. However, such study has not been reported yet. Here, we report the results of magnetization and resistivity studies on single crystals of PdCrO$_2$. We confirmed a small anisotropy between the magnetic susceptibility along the c axis ($\chi_c$) and in the ab plane ($\chi_{ab}$) above $T_N$. Below $T_N$, in contrast, a distinct anisotropy, $\chi_{ab} > \chi_c$, develops. These results indicate that PdCrO$_2$ is a Heisenberg spin system above $T_N$, and once temperature decreases below $T_N$, the spins lie in a plane which is parallel to the c axis. We also found that the localized
spins in the Cr layer influences both the inter- and intra-Pd-plane conductivity with almost the same magnitude, although the electrical resistivity is highly anisotropic ($\rho_c/\rho_{ab} \geq 150$).

2. Experimental

Single crystals of PdCrO$_2$ were grown through a flux method. Powder samples were obtained with a solid state reaction [5]. The samples were characterized by using powder x-ray diffraction (XRD) with CuK$_{α1}$ radiation and energy dispersive x-ray (EDX) analysis. The XRD pattern confirmed that the samples crystallize in the delafossite structure with the $R3m$ symmetry. The difference of the unit-cell volume between single crystals and powder samples is less than 1%. The EDX analysis confirmed the homogeneity of samples and a composition ratio of Pd and Cr to be Pd/Cr = 1 ± 0.1, indicating stoichiometry within the experimental resolution. The dc magnetization $M$ along the $c$ axis and in the $ab$ plane were measured with a SQUID magnetometer (Quantum Design, MPMS) from 1.8 K to 300 K in magnetic fields $\mu_0H$ between 0.01 and 7 T in both field-cooled (FC) and zero field cooled (ZFC) conditions. We selected approximately one hundred crystals and aligned them on a sample holder plate for the measurements. The field dependence of the dc magnetization was measured from $-7$ T to 7 T. The electrical resistivity was measured on a single crystal with both an ac or dc four-probe method from 300 K to 0.32 K with a commercial equipment (Quantum Design, PPMS) and a $^3$He refrigerator (Oxford Instruments, Heliox).

3. Results and Discussion

Temperature dependence of $\chi_c(=M_c/H)$ and $\chi_{ab}(=M_{ab}/H)$ are shown in figure 1 (a) and (b). We observed a strong field dependence in both $\chi_c$ and $\chi_{ab}$. However, for any fields, $\chi_c$ is nearly equal to $\chi_{ab}$ above $T_N$, whereas $\chi_c$ becomes smaller than $\chi_{ab}$ below $T_N$. This behavior is similar to the magnetic susceptibility of the same structural compound CuCrO$_2$ [7]. The result implies that PdCrO$_2$ is a Heisenberg spin system, and below $T_N$ the spins order in a plane that is parallel to the $c$ axis forming a 120° spin structure, i.e., an “easy-axis type” 120° structure as

![Figure 1](image-url)

**Figure 1.** Temperature dependence of the magnetic susceptibility in the applied magnetic fields (a) along the $c$ axis ($\chi_c$) and (b) in the $ab$ plane ($\chi_{ab}$). Both exhibit a strong field dependence especially at low temperatures below $T_N \approx 38$ K. Figures (c) and (d) represent the field dependence of the magnetization at 2 K in the low field region. Figure (e) is the temperature dependence of the magnetic susceptibility of a powder sample at $\mu_0H = 0.01$ T.
in CuCrO$_2$ [7].

In low fields below 0.05 T, $\chi_c$ and $\chi_{ab}$ are strongly enhanced at temperatures below 60 K with a splitting of the ZFC and FC curves. The peak temperature of $\chi(T)$ in the ZFC curves is approximately 20 K for 0.01 T and approximately 12 K for 0.05 T. The antiferromagnetic transition at $T_N \simeq 38$ K is not very clear in these low-field data. Corresponding to the splitting of the ZFC and FC curves, the field dependence of $M_c$ and $M_{ab}$ exhibit a slight hysteresis at 2 K (figures 2(c) and (d)). The enhancement of the susceptibility is suppressed in higher magnetic fields, where both $\chi_c$ and $\chi_{ab}$ exhibit a broad peak around 60 K and sudden decrease at $T_N$ with decreasing temperatures. Interestingly, for powder samples, the enhancement of the susceptibility in low fields is not observed (figure 2(e)), but a splitting of the ZFC and FC curves around 12 K was reproducibly observed. The origin of the low-field behavior is yet unclear. Possibly, it can be attributed to a change in the spin structure induced by the frustration; e.g., realization of a canted spin structure [8] or spin-glass-like freezing [9].

Temperature dependence of the electrical resistivity along the $c$ axis ($\rho_c$) and in the $ab$ plane ($\rho_{ab}$) is shown in figures 2(a) and (b). Both exhibit metallic temperature dependence down to 0.32 K. The resistivity has a large anisotropy, $\rho_c/\rho_{ab} \gtrsim 150$, in the whole measurement temperature range, supporting the fact that the conductivity is mainly governed by the Pd layers. The residual resistivity $\rho_0$ is 16.5 $\mu$Ωcm for $\rho_c$ and 0.05 $\mu$Ωcm for $\rho_{ab}$: these small values of $\rho_0$ lead to a large residual resistivity ratio (RRR $\equiv \rho(300K)/\rho(0.32K)$) of 103 for $\rho_c$ and 200 for $\rho_{ab}$ indicating a good quality of the crystals. The resistivity due to the magnetic scattering $\rho_m$ along the $c$ axis and in the $ab$ plane is also plotted in figures 2(a) and (b). Here, $\rho_m$ is estimated from the relation $\rho_m = \rho_{total} - \rho_0 - \rho_{ph}$, where $\rho_{total}$ is the total resistivity and $\rho_{ph}$ represents the resistivity due to the phonon scattering. We here assumed that $\rho_{ph}$ is equal to that of the isostuctural non-magnetic PdCoO$_2$ [10]. As temperature decreases, $\rho_m$ starts to decrease from temperatures well above $T_N$ and suddenly drops at $T_N$. These results are attributed to the reduction of a randomness of the magnetic spins, associated with the development of the short-range spin correlation above $T_N$ and the long-range antiferromagnetic order at $T_N$ [5]. The temperature derivative of the resistivity $d\rho/dT$ divided by $\rho$ exhibit a clear peak at $T_N$ with almost the same magnitude in both $\rho_c$ and $\rho_{ab}$ (the inset of figure 2(a) and (b)). This fact indicates that the frustrated Cr spins indeed affects the out-of-plane as well as the in-plane
motion of the conduction electrons in the Pd layer, in spite of the fact that the conductivity and magnetism are separately governed by different layers, Pd layers and Cr layers.

We confirmed that there is substantial interaction between the conduction electrons and the frustrated spins. In addition, the observed enhancement of the magnetic susceptibility and its suppression in higher magnetic fields implies that the magnetic spin configuration can be controlled by the applied magnetic field. Measurements of the Hall resistivity are underway to uncover the unconventional aspects of the AHE in this two dimensional triangular-lattice system.

4. Conclusion
In conclusion, we have investigated the magnetization and resistivity of single crystals of the metallic two-dimensional triangular-lattice magnet PdCrO$_2$, which exhibits an antiferromagnetic transition at $T_N \simeq 38$ K with the 120$^\circ$ spin order. The small anisotropy between $\chi_c$ and $\chi_{ab}$ above $T_N$ confirms that PdCrO$_2$ is a Heisenberg spin system, as expected from the electronic configuration of 3d$^3$ of Cr$^{3+}$ ions. Below $T_N$, a distinct anisotropy associated with a sharp drop in $\chi_c$ develops, indicating an easy plane parallel to the c axis (an “easy-axis type” 120$^\circ$ structure). Both $\chi_c$ and $\chi_{ab}$ in low fields show strong enhancement at low temperatures below 60 K. This behavior is qualitatively different from $\chi$ of the powder samples. Small hysteresis loops are observed in the field dependence of both $M_c$ and $M_{ab}$. These results may be attributed to a slight canting of the spins.

The resistivity measurements revealed that PdCrO$_2$ is a highly anisotropic metal with the ratio $\rho_c/\rho_{ab} \gtrsim 150$. In spite of this large anisotropy, the relative magnitude of the anomaly at $T_N$ for $\rho_{ab}$ is as large as that for $\rho_c$. This fact indicates that the localized spins on the Cr layer strongly affect the conduction electron in the Pd layer. The substantial coupling between the frustrated spins and the conduction electrons realized in the triangular-lattice magnet PdCrO$_2$ will provide an excellent opportunity for the investigation of unconventional anomalous Hall effects.

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[1] Taguchi Y, Oohara Y, Yoshizawa H, Nagaosa N and Tokura Y 2001 Science 291 2573
[2] Machida Y, Nakatsuji S, Maeno Y, Tayama T, Sakakibara T and Onoda S 2007 Phys. Rev. Lett. 98 057203
[3] Hurd C M 1972 The Hall effect in metals and alloys (New York: Plenum Press)
[4] Takatsu H, Yoshizawa H and Maeno Y 2009 J. Phys.: Conf. Ser. 145 012046
[5] Takatsu H, Yoshizawa H, Yonezawa S and Maeno Y 2009 Phys. Rev. B 79 104424
[6] Mekata M, Sugino T, Oohara A, Oohara Y and Yoshizawa H 1995 Physica B 213 221
[7] Kimura K, Nakamura H, Ohgushi K and Kimura T 2008 Phys. Rev. B 78 140401(R)
[8] Sugiyama J, Ikedo Y, Mukai K, Brewer J H, Ansald E J, Morris G D, Chow K H, Yoshida H and Hiroi Z 2006 Phys. Rev. B 73 224437
[9] Miyoshi K, Nishimura Y, Honda K, Fujiwara K and Takeuchi J 2000 J. Phys. Soc. Jpn. 69 3517
[10] Takatsu H, Yonezawa S, Mouri S, Nakatsuji S, Tanaka K and Maeno Y 2007 J. Phys. Soc. Jpn. 76 104701