Unconventional Anomalous Hall Effect in the Metallic Triangular-Lattice Magnet PdCrO$_2$

Hiroshi Takatsu, Shingo Yonezawa, Satoshi Fujimoto, and Yoshiteru Maeno

Department of Physics, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

(Dated: August 17, 2010)

We experimentally reveal an unconventional anomalous Hall effect (UAHE) in a quasi-two-dimensional triangular-lattice antiferromagnet PdCrO$_2$. Using high quality single crystals of PdCrO$_2$, we found that the Hall resistivity $\rho_{xy}$ deviates from the conventional behavior below $T^* \approx 20$ K, noticeably lower than $T_N = 37.5$ K, at which Cr$^{3+}$ ($S = 3/2$) spins order in a 120° structure. In view of the theoretical expectation that the spin chirality cancels out in the simplest 120° spin structure, we discuss required conditions for the emergence of UAHE within Berry-phase mechanisms.

PACS numbers: 72.15.-v, 75.47.-m, 75.47.Lx

Recently, there has been a rapid progress in the study of unconventional magnetic phenomena which cannot be accounted solely in terms of the conventional order parameter, i.e., magnetization [1, 2]. One example of such phenomena is the unconventional anomalous Hall effect (UAHE) in frustrated spin systems [2–12], which cannot be accounted for by conventional AHE mechanisms based on spin-orbit interaction (SOI) to magnetization $M$ [13–15]. The Hall resistivity $\rho_{xy}$ violates the empirical relation expressed as a linear combination of terms proportional to the magnetic induction $B = H + 4\pi M$ and to $M$:

$$\rho_{xy}(H, T) = R_0(T)B + 4\pi R_S(T)M,$$

where $R_0$ and $R_S$ are the ordinary Hall coefficient and the anomalous Hall coefficient, respectively [16]. The first term originates from the Lorenz force and the second term is attributed to the orbital motion of the spin polarized electrons by SOI. For the origin of UAHE, various new mechanisms including those based on multiple spin order parameters, namely spin chiralities, have been proposed [7–10]. These mechanisms are based on the Berry phase theory [17] taking into account a finite phase gain of the wavefunction of a conduction electron as it circulates through the field of the nontrivial (i.e. non-collinear and non-coplanar) spin structure. The single-valuedness of the wavefunction enforces the conduction electrons to be subjected to a fictitious magnetic field, analogously to the Aharonov-Bohm effect [18], leading to UAHE [7,12].

Geometrically frustrated magnets are promising for investigating such UAHE, because they often exhibit nontrivial spin configurations with non-vanishing spin chiralities. However, the observation of UAHE has been limited to only a handful of bulk materials with the three-dimensional (3D) analogue to the triangular lattice (TL) [2,4]. Moreover, for the archetypal example of geometrically frustrated spin systems, an antiferromagnet with a two-dimensional (2D) TL, UAHE has not been experimentally reported nor theoretically expected [10]. It is thus important to find a conductive material with spins on a TL and investigate its Hall effect. In this context, we have studied the transport and magnetic properties of the metallic 2D-TL antiferromagnet PdCrO$_2$, which should provide a unique testing ground for the clarification of the unresolved mechanism of UAHE.

PdCrO$_2$ crystallizes in the delafossite structure with the $R3m$ symmetry consisting of layers of Pd triangles and Cr triangles stacking along the c axis. In this oxide, localized spins of the Cr$^{3+}$ ions ($S = 3/2$) exhibit an antiferromagnetic order at $T_N = 37.5$ K, forming a 120° spin structure [13,20]. This is one of the simplest spin structure among the structures with the $\sqrt{3} \times \sqrt{3}$ periodicity consisting of three magnetic sublattices. Metallic conductivity, maintained down to the lowest temperatures [20], is predominantly attributable to the Pd 4d$^9$ electrons, analogous to the isostructural non-magnetic metal PdCoO$_2$ [21,24]. Since majority of the known 2D-TL magnets are insulators or semiconductors, PdCrO$_2$ is envisaged to serve as a standard for the Hall effect in metallic 2D-TL magnets with the 120° spin structure. In this Letter, we report a clear observation of unexpected UAHE in PdCrO$_2$ from the single-crystalline study. We observed that $\rho_{xy}$ clearly deviates from the $H$–linear dependence and even changes its sign, although $M$ increase linearly with $H$. This behavior sharply contrasts with the empirical behavior expressed by Eq. (1).

Single crystals of PdCrO$_2$ were grown by a flux method and characterized with the powder x-ray diffraction and energy dispersive x-ray analysis [25]. The magnetoresistivity $\rho_{xx}$ and the Hall resistivity $\rho_{xy}$, evaluated by reversing the field direction, were simultaneously measured with a dc four-probe method with six contacts; the magnetic field $H$ was applied along the $c$ axis (001) direction and the current $I$ was applied in the $ab$ plane ($\langle 110 \rangle$ direction). In order to extract effects of the frustrated spins, the data for non-magnetic PdCoO$_2$ were compared. The dc magnetization $M$ of PdCrO$_2$ in fields along the $c$ axis and in the $ab$ plane were measured with a SQUID magnetometer (Quantum Design MPMS) for samples consisting of aligned crystals.

Figures 1(a) and (b) represent the field dependence of $\rho_{xy}$ of PdCrO$_2$ and PdCoO$_2$ measured at several temperatures. For PdCrO$_2$, $\rho_{xy}$ exhibits a linear field dependence above and near $T_N$ with a negative slope, indicating the dominance of electron-like carriers. With decreasing temperature below $T_N$, the slope rapidly changes with the magnetic phase transition. Curiously, an unusual non-linear field dependence with a hump around 10–30 kOe emerges at temperatures below $T^* \approx 20$ K. This behavior is reproducibly observed in differ-
In contrast, \( \rho_{xy} \) of non-magnetic PdCoO\(_2\) exhibits a linear field dependence without a slope change below 40 K. We note here that the slight non-linearity of \( \rho_{xy} \) of PdCoO\(_2\) at elevated temperatures (inset of Fig. 1(b)) is attributable to mechanisms such as multi-band effects or the scattering by optical phonons. These results clearly indicate that the localized Cr spins affect \( \rho_{xy} \) of PdCrO\(_2\).

Let us compare \( \rho_{xy} \) and \( M \) of PdCrO\(_2\) (Fig. 1(c)). Above \( T_N \), both \( \rho_{xy} \) and \( M \) exhibit a linear field dependence, and the relation (1) holds. Between \( T_N \) and \( T^* \), the relation (1) still holds. The slope change of \( \rho_{xy}(H, T) \) in these temperature regions can be interpreted within the conventional AHE behavior, i.e., the temperature dependence of \( R_S \). However, once the temperature decreases below \( T^* \), \( \rho_{xy} \) deviates from the linearity although \( M \) still varies linearly on the magnetic fields. This result manifests that UAHE appears at temperatures below \( T^* \).

Figure 2(a) compares the temperature dependence of the magnetic susceptibility \( \chi (= M/H) \) with applied magnetic fields along the \( c \) axis and in the \( ab \) plane. We confirmed that \( \chi \) is isotropic above \( T_N \) within the experimental precision of 5 \( \times \) 10\(^{-5} \) emu/mol between the measurements. This result indicates that PdCrO\(_2\) constitutes the Heisenberg spin system. In contrast, \( \chi \) becomes anisotropic below \( T_N \) with a sharp drop in \( \chi \) (Fig. 2(b)). Combined with the 120° spin structure determined from neutron diffraction, such anisotropy in PdCrO\(_2\) indicates that the spins order in a plane containing the \( c \) axis, and that they are coupled antiferromagnetically between the layers [24]. Interestingly, a broad maximum appears around \( T^* \) in \( d\chi_{ab}/dT \) (Fig. 2(c)). This implies a minute modification of the magnetic structure. It should be noted that the specific heat in our previous polycrystalline study [20], as well as in our recent single-crystalline study, also revealed a small anomaly around \( T^* \).

In order to express the unconventional nature of the AHE, let us extend Eq. (1) to allow the anomalous Hall coefficient \( R_S \) to depend on field as well as on temperature:

\[
R_S(H, T) = \{ \rho_{xy}(H, T) - R_0 B \}/4\pi M(H, T). \tag{2}
\]

Here we estimate the ordinary Hall resistivity \( R_0 B \) of PdCrO\(_2\) using \( R_0 \) of PdCoO\(_2\), since PdCoO\(_2\) is a good non-magnetic reference system to PdCrO\(_2\) for the following reasons: The values of the electronic specific heat coefficient [20, 21], of room-temperature in-plane resistivity [21, 27], and of the Hall resistivity above \( T_N \) are nearly the same for both compounds; the band structure calculation revealed similar electronic configurations and Fermi surfaces [28]. In the analysis, \( R_0 \) of PdCoO\(_2\) is represented by the value at 2 K, \( R_0 = -3.86 \times 10^{-4} \) cm\(^2\)/C, since it is indeed temperature independent below 40 K. Furthermore, \( B \) in PdCrO\(_2\) is approximated by the applied magnetic field, \( B = H + 4\pi M \approx H \), since \( 4\pi M \) is only about 0.1% of \( H \) in the measured field region. Figure 4 shows the temperature dependence of \( R_S \). It is clear that \( R_S \) indeed becomes field dependent only below \( T^* \), demonstrating the violation of Eq. (1).

For conventional clean magnetic conductors, \( R_S \) is known to diminish at low temperatures [16]. It is remarkable that \( R_S \) of PdCrO\(_2\) retains a large value at low temperatures, although it is a clean metal with the estimated mean free path of 30 \( \mu \)m [25]. This provides additional evidence for UAHE of PdCrO\(_2\). Such unconventional field and temperature dependence of \( R_S \) is also observed in conductive pyrochlore magnets with nontrivial spin structures [2, 4].

For theoretical analyses, a quantity of more fundamental physical significance is the Hall conductivity \( \sigma_{xy} \), evaluated from \( \rho_{xy} \) and \( \rho_{xx} \), through the relation \( \sigma_{xy} = \rho_{xy}/(\rho_{xx}^2 + \rho_{xy}^2) \). Figure 2(a) represents the overall field and temperature dependence of \( \sigma_{xy} \). This 3D plot clearly indicates a trench representing \( T^* \) and an island centered at about 15 kOe below 10 K. This island represents the main characteristic of UAHE, because, based on the chirality mechanism discussed below, such an island corresponds to the opposite direction of the fictitious field with respect to the applied field direction. The
field dependence at low temperatures is more clearly shown in Fig. 2(b). The negative initial slope representing the Lorentz force term is taken over by the unconventional contribution.

We have revealed that the 2D-TL magnet PdCrO$_2$ exhibitsUAHE, which cannot be ascribed solely by the conventional mechanism based on the spin-orbit coupling to the magnetization. To the best of our knowledge, this is the first UAHE report among the TL systems. Moreover, the observed anomalies in $d\chi_{ab}/dT$ and the magnetic specific heat, as well as the comparison with $\rho_{ij}$ of non-magnetic PdCoO$_2$, indicate that the unconventional behavior below $T^*$ is not related to Fermi surface effects such as the magnetic breakdown [16]. Instead, the observed unconventional feature is similar to those reported in other 3D geometrically frustrated spin systems [2-4]. It is therefore promising to pursue the connection with various Berry-phase mechanisms in this 2D-TL system as well.

The scalar spin chirality mechanism is one of the candidates to explain UAHE in frustrated magnets. Let us consider the local exchange field acting on Pd sites and the scalar spin chirality $\chi_{ijk}^{Pd} = s_i \cdot (s_j \times s_k)$. Here, $s_i$ is the conduction electron spin at the Pd site $i$; we assumed that $s_i$ tends to align in the direction of the local exchange field $I_i = \sum_{l=1}^{6} J S_{l}$, created by Cr spins in the layers below and above the Pd site. $J$ is the coupling between the hopping Pd $d$-electrons and the localized Cr $d$-electrons, and $S_{l}$ is a Cr$^{3+}$ spin at a site $l$ surrounding the Pd ion at the site $i$ (Fig. 3(a)). Such a model has also been used for the pyrochlore Pr$_2$Ir$_2$O$_7$ [3]. In this model, $\chi_{ijk}^{Pd}$ is zero for the simple 120° spin structure of Cr spins because $I_i = 0$ everywhere. In order to give rise to finite $\chi_{ijk}^{Pd}$, it is necessary that a modification of the spin structure occurs at $T^*$. Such a modification is in fact anticipated by the observed weak anomalies in the susceptibility and specific heat.

With the limited size of the single crystals currently available, it is technically difficult to determine the subtle spin modification below $T^*$. Nevertheless, we can provide a few prerequisites for the actual spin modification. Under a magnetic field, $I_i$ becomes non-zero because of the polarization of the Cr spins surrounding a Pd ion. As a first prerequisite, for $\chi_{ijk}^{Pd}$ not to vanish, $I_m (m = i, j, k)$ should be non-coplanar. This requires that the Cr-spin configuration should be non-coplanar and moreover break the $\sqrt{3} \times \sqrt{3}$ periodicity. Secondly, $\chi_{ijk}^{Pd}$ after averaged over the entire lattice should not vanish. By analogy with the Berry-phase theory of magnetic nanostructures [29], one can deduce that both $\Delta \theta_{ij} = \theta_i - \theta_j$ and $\Delta \phi_{ij} = \phi_i - \phi_j$ should not vanish for the appearance of a net non-vanishing $\chi_{ijk}^{Pd}$. Here, $(\theta_i, \phi_i)$ specifies the polar-coordinate direction of $I_i$. These conditions require a somewhat complicated modulation of the Cr-spin configuration.

Based on these prerequisites, let us examine possible modifications of the spin structure in PdCrO$_2$. We should first note that as long as the $\sqrt{3} \times \sqrt{3}$ periodicity is maintained, simple modifications such as a change from antiferromagnetic to ferromagnetic interlayer coupling and a spin flop to the so-called “up-up-down” structure [30] do not satisfy the first prerequisite. Such a spin flop is indeed inconsistent with the absence of a magnetization plateau in Fig. 1(c). A simple illustrative example satisfying both prerequisites is a spin structure in which the normal vector of the 120° spin plane precesses with the secondary propagation vector $q_1 = (1/3, 2/3, 0)$. In zero field, and in the case of an antiferromagnetic inter-Cr-layer stacking indicated by the susceptibility data, the total chirality averages to zero in the magnetic unit cell. However, additional Cr spin polarization under a c-axis magnetic field leads to a non-vanishing net chirality through a breaking of symmetry between the two Cr layers, as shown in Fig. 3(b). We note that the orbital Berry phase mechanism [12] may be additionally relevant because of the multi-band conductivity of PdCrO$_2$ [28].

In summary, the anomalous Hall effect in a 2D-TL antifer-
FIG. 4: (a) 3D representation of the overall field and temperature dependence of the the Hall conductivity $\sigma_{xy}$. (b) Field dependence of $\sigma_{xy}$ at temperatures below 40 K. From a point of view based on the scalar spin chirality mechanism, the fictitious field has the opposite sign to the applied magnetic field in the red region in (a).

FIG. 5: (a) Positions of Pd and Cr ions in PdCrO$_2$. The arrows represent Cr spins in a 120° spin structure with the antiferromagnetic interlayer coupling. (b) Calculated spin chirality $\chi_{Pd}$ mapping in the Pd-TL net for the modulated Cr spin structure in which the normal vector of the 120° plane precesses. The arrows indicate the exchange field $I$ on Pd ions; the red and blue colorings of triangles represent plus and minus values of $\chi_{Pd}$, respectively. Slight tilt of spins due to the magnetic field leads to overall non-zero chirality. The parameters used in this figure are the precession angle of 5° and the magnetic field strength of 70 kOe. The chirality values are nonlinear in these parameters.

romagnet PdCrO$_2$ becomes unconventional below 20 K, substantially lower than $T_N$. It is remarkable that such UAHE indeed emerges in a simplest geometrically frustrated system, namely the Heisenberg spins on a 2D-TL interacting with conduction electrons. For this reason, it is expected that PdCrO$_2$ serves as an archetypal system toward clarification of the unresolved mechanism of UAHE. Detailed studies on the magnetic and crystal structure below $T^*$ are important in the future for deeper understandings of the origin of UAHE.

We acknowledge K. Ishida, M. Kriener, C. Michioka, Y. Nakai, S. Kittaka, J. Sobota and Z. X. Shen for their supports and H. Kontani, T. Tomizawa, G. Tatara, T. Shishidou and T. Oguchi for fruitful discussion. This work was supported by the Grant-in-Aid for the Global COE Program “The Next Generation of Physics, Spun from Universality and Emergence” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan and a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS). H.T. is financially supported as a JSPS research fellow.

[1] S.-W. Cheong and M. Mostovoy, Nat. Mater. 6, 13 (2007).
[2] Y. Taguchi, Y. Oohara, H. Yoshizawa, N. Nagaosa, and Y. Tokura, Science 291, 2573 (2001).
[3] Y. Yasui, T. Kageyama, T. Moyoshi, M. Sada, M. Sato, and K. Kukurai, J. Phys. Soc. Jpn. 75, 084711 (2006).
[4] Y. Machida, S. Nakatsuji, Y. Maeno, T. Tayama, T. Sakakibara, and S. Onoda, Phys. Rev. Lett. 98, 057203 (2007).
[5] Y. Machida, S. Nakatsuji, S. Onoda, T. Tayama, and T. Sakakibara, Nature 463, 210 (2009).
[6] P. Matl, N. P. Ong, Y. F. Yan, Y. Q. Li, D. Studebaker, T. Baum, and G. Doubinbin, Phys. Rev. B 57, 10248 (1998).
[7] J. Ye, Y. B. Kim, A. J. Millis, B. I. Shraiman, P. Majumdar, and Z. Tasanovic, Phys. Rev. Lett. 83, 3737 (1999).
[8] K. Ohgushi, S. Murakami, and N. Nagaosa, Phys. Rev. B 62, 6065 (2000).
[9] G. Tata and H. Kawamura, J. Phys. Soc. Jpn. 71, 2613 (2002).
[10] N. Nagaosa, J. Phys. Soc. Jpn. 75, 042001 (2006).
[11] D. Xiao, M.-C. Chang, and Q. Niu, arXiv:0907.2021v1.
[12] T. Tomizawa and H. Kontani, Phys. Rev. B 80, 100401 (2009).
[13] R. Karplus and J. M. Luttinger, Phys. Rev. 95, 1154 (1954).
[14] J. Smit, Physica 21, 877 (1955).
[15] L. Berger, Phys. Rev. B 2, 4559 (1970).
[16] C. M. Hurd, The Hall effect in metals and alloys (Plenum Press, New York, 1972).
[17] M. V. Berry, Proc. R. Soc. London Ser. A 392, 45 (1984).
[18] Y. Aharonov and D. Bohm, Phys. Rev. 115, 485 (1959).
[19] M. Mekata, T. Sugino, A. Oohara, Y. Oohara, and H. Yoshizawa, Physica B 213, 221 (1995).
[20] H. Takatsu, H. Yoshizawa, S. Yonezawa, and Y. Maeno, Phys. Rev. B 79, 104424 (2009).
[21] H. Takatsu, S. Yonezawa, S. Mouri, S. Nakatsuji, K. Tanaka, and Y. Maeno, J. Phys. Soc. Jpn. 76, 104701 (2007).
[22] V. Eyert, R. Fréasard, and A. Maignan, Chem. Mater. 20, 2370 (2008).
[23] H.-J. Noh, J. Jeong, J. J. E.-J. Cho, S. B. Kim, K. Kim, B. I. Min, and H. D. Kim, Phys. Rev. Lett. 102, 256404 (2009).
[24] K. Kim, H. Chul, and B. I. Min, Phys. Rev. B 80, 035116 (2009).
[25] H. Takatsu and Y. Maeno, (unpublished).
[26] T. Hirose and K. Adachi, J. Phys. Soc. Jpn. 12, 156 (1957).
[27] H. Takatsu, S. Yonezawa, C. Michioka, K. Yoshimura, and Y. Maeno, J. Phys. Conf. Ser. 200, 012198 (2010).
[28] T. Shishidou and T. Oguchi, presented at the 65th annual meeting of the Physical Society of Japan (2010) 23aGI-14.
[29] P. Bruno, V. K. Dugaev, and M. Taillufumier, Phys. Rev. Lett. 93, 096806 (2004).
[30] H. Kawamura and S. Miyashita, J. Phys. Soc. Jpn 54, 4530.
(1985).