Unconventional Anomalous Hall Effect in the Metallic Triangular-Lattice Magnet $PdCrO_2$

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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 ρ_{xy} deviates from the conventional behavior below $T^* \simeq 20$ 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.

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Recently, there has been rapid progress in the study of unconventional magnetic phenomena which cannot be described 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 ρ_{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:

$$\rho_{xy}(H, T) = R_0(T)B + 4\pi R_S(T)M, \tag{1}$$

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 wave function of a conduction electron as it circulates through the field of the nontrivial (i.e., noncollinear and noncoplanar) spin structure. The single-valuedness of the wave function 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 nonvanishing spin chiralities. However, the observation of UAHE has been limited to only a handful of bulk materials with the three-dimensional analogue to the triangular lattice (TL) [2,4]. Moreover, for the archetypal example of geometrically frustrated spin systems, an antiferromagnet with a two-dimensional 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 $R\bar{3}m$ 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 [19,20]. This is one of the simplest spin structures 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 nonmagnetic metal $PdCoO_2$ [21–24]. Since the 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 ρ_{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 ρ_{xx} and the Hall resistivity ρ_{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 ($\langle 001 \rangle$ 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 nonmagnetic $PdCoO_2$ 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 for samples consisting of aligned crystals.

Figures 1(a) and 1(b) represent the field dependence of ρ_{xy} of $PdCrO_2$ and $PdCoO_2$ measured at several temperatures. For $PdCrO_2$, ρ_{xy} exhibits a linear field dependence

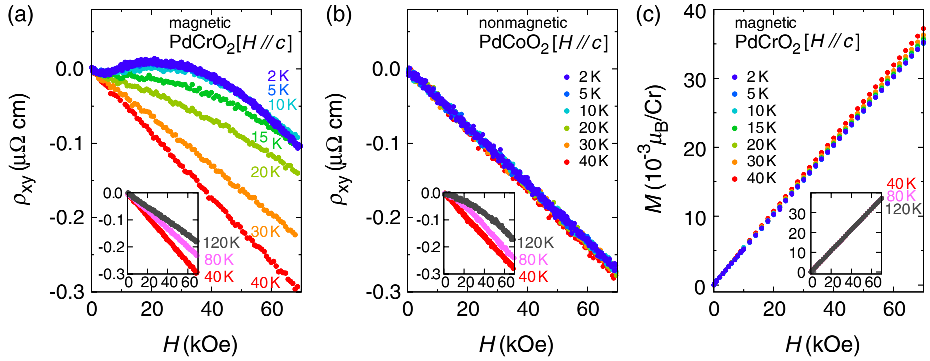

FIG. 1 (color online). Field dependence of the Hall resistivity ρ_{xy} for (a) $PdCrO_2$ ($T_N = 37.5$ K) and for (b) nonmagnetic $PdCoO_2$. (c) Field dependence of the magnetization M for $PdCrO_2$. Insets represent data at temperatures above 40 K. On cooling below $T^* \simeq$ 20 K, ρ_{xy} of $PdCrO_2$ strongly deviates from the linearity and exhibits a hump to positive values at around 10–30 kOe.

above and near T_N with a negative slope, indicating the dominance of electronlike carriers. With decreasing temperature below T_N, the slope rapidly changes with the magnetic phase transition. Curiously, an unusual nonlinear field dependence with a hump around 10–30 kOe emerges at temperatures below $T^* \simeq 20$ K. This behavior is reproducibly observed in different crystals we investigated. In contrast, ρ_{xy} of nonmagnetic $PdCoO_2$ exhibits a linear field dependence without a slope change below 40 K. We note here that the slight nonlinearity of ρ_{xy} of $PdCoO_2$ at elevated temperatures [inset of Fig. 1(b)] is attributable to mechanisms such as multiband effects or the scattering by optical phonons. These results clearly indicate that the localized Cr spins affect the behavior of ρ_{xy} of $PdCrO_2$.

Let us compare ρ_{xy} and M of $PdCrO_2$ [Fig. 1(c)]. Above T_N, both ρ_{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^*, ρ_{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 χ ($= M/H$) with applied magnetic fields along the c axis and in the ab plane. We confirmed that χ is isotropic above T_N within the experimental precision of 5×10^{-5} emu/mol between the measurements. This result indicates that $PdCrO_2$ constitutes the Heisenberg spin system. In contrast, χ becomes anisotropic below T_N with a sharp drop in χ_c [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 [26]. 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:

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

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 nonmagnetic 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^3/C, since it is indeed temperature independent below 40 K. Furthermore, B in $PdCrO_2$ is approximated by the applied magnetic field, $B = H + 4\pi M \simeq H$, since $4\pi M$ is only about 0.1% of H in the measured field region. Figure 3 shows the temperature dependence of R_S. It is clear that R_S indeed

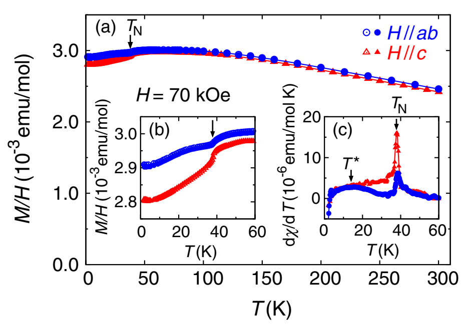

FIG. 2 (color online). (a) Temperature dependence of the magnetic susceptibility of single-crystalline $PdCrO_2$ for fields along the c axis ($\chi_c = M_c/H$) and in the ab plane ($\chi_{ab} = M_{ab}/H$) at 70 kOe. (b) Details of the anisotropy below T_N. Open (closed) symbols represent data in the field cooling (zero-field cooling) condition. (c) Temperature derivative of χ_c and χ_{ab}.

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 μm [25]. This provides additional evidence for UAHE of $PdCrO_2$. Such unconventional H and T 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 σ_{xy}, evaluated from ρ_{xy} and ρ_{xx} through the relation $\sigma_{xy} = \rho_{xy}/(\rho_{xx}^2 + \rho_{xy}^2)$. Figure 4(a) represents the overall field and temperature dependence of σ_{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. 4(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 $PdCrO_2$ exhibits UAHE, 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 ρ_{xy} of nonmagnetic $PdCoO_2$, 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 $\chi_{ijk}^{\mathrm{Pd}} = \boldsymbol{s}_i \cdot (\boldsymbol{s}_j \times \boldsymbol{s}_k)$. Here, $\boldsymbol{s}_i$ is the conduction electron spin at the Pd site i; we assumed that $\boldsymbol{s}_i$ tends to align in the direction of the local exchange field $\boldsymbol{I}_i = \sum_{l=1}^{6} J\boldsymbol{S}_l$, 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 $\boldsymbol{S}_l$ is a Cr^{3+} spin at a site l surrounding the Pd ion at the site i [Fig. 5(a)]. Such a model has also been used for the pyrochlore $Pr_2Ir_2O_7$ [4]. In this model, χ_{ijk}^{Pd} is zero for the simple 120° spin structure of Cr spins because $\boldsymbol{I}_i = 0$ everywhere. In order to give rise to finite χ_{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, $\boldsymbol{I}_i$ becomes nonzero because of the polarization of the Cr spins surrounding a Pd ion. As a first prerequisite, for χ_{ijk}^{Pd} not to vanish, $\boldsymbol{I}_m$ ($m = i, j, k$) should be noncoplanar. This requires that the Cr-spin configuration should be noncoplanar and moreover break the $\sqrt{3} \times \sqrt{3}$ periodicity. Secondly, χ_{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 nonvanishing χ_{ijk}^{Pd}. Here, (θ_i, ϕ_i) specifies the polar-coordinate direction of $\boldsymbol{I}_i$. These conditions require a somewhat complicated modulation of the Cr-spin configuration.

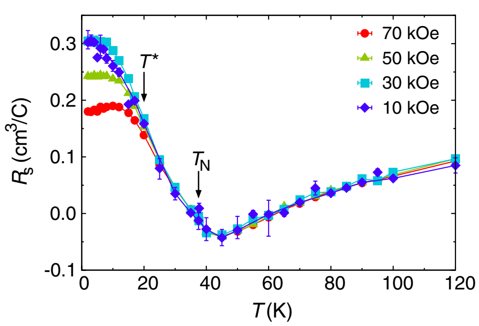

FIG. 3 (color online). Temperature dependence of $R_S(H, T)$ represented by Eq. (2). $R_S(H, T)$ does not depend on the magnetic field at temperatures above $T^* \simeq 20$ K, whereas below T^* it is field dependent, indicating the appearance of UAHE.

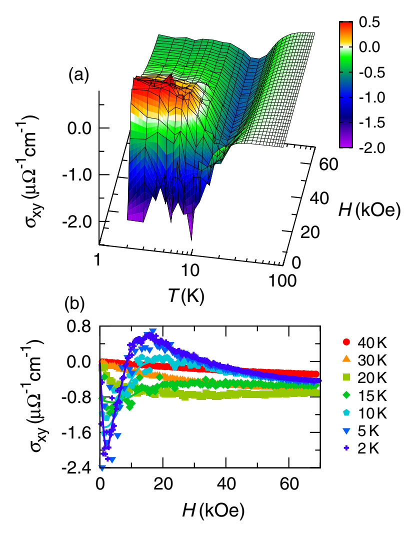

FIG. 4 (color online). (a) 3D representation of the overall field and temperature dependence of the Hall conductivity σ_{xy}. (b) Field dependence of σ_{xy} at temperatures below 40 K. From a point of view based on the scalar spin chirality mechanism, the fictitious field has the opposite sign to the applied magnetic field in the red region in (a).

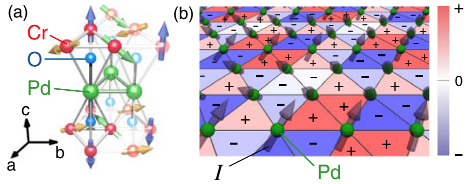

FIG. 5 (color online). (a) Positions of Pd and Cr ions in $PdCrO_2$. The arrows represent Cr spins in a 120° spin structure with the antiferromagnetic interlayer coupling. (b) Calculated spin chirality χ_{ijk}^{Pd} mapping in the Pd-TL net for the modulated Cr spin structure in which the normal vector of the 120° plane processes. The arrows indicate the exchange field $\boldsymbol{I}$ on Pd ions; the + and − symbols, as well as the red and blue colorings, indicate plus and minus values of χ_{ijk}^{Pd} of a triangle, respectively. Slight tilt of spins due to the magnetic field leads to overall nonzero 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.

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 $\boldsymbol{q}_1 = (1/3, 2/3, 0)$. 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 nonvanishing net chirality through a breaking of symmetry between the two Cr layers, as shown in Fig. 5(b). We note that the orbital Berry-phase mechanism [12] may be additionally relevant because of the multiband conductivity of $PdCrO_2$ [28].

In summary, the anomalous Hall effect in a 2D-TL antiferromagnet $PdCrO_2$ 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.

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Note added in proof.—We recently noticed theoretical reports on the Hall effect in the TL system, which suggest finite scalar-spin-chirality contribution to UAHE by considering a noncoplanar spin configuration with a four-site magnetic unit cell [31–33].

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