Comparative study of conductive delafossites with and without frustrated spins on a triangular lattice, PdMO$_2$ ($M = \text{Cr, Co}$)

H. Takatsu$^1$, H. Yoshizawa$^2$ and Y. Maeno$^1$

$^1$Department of Physics, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan
$^2$Neutron Science Laboratory, Institute for Solid State Physics, The University of Tokyo, Tokai Ibaraki 319-1106, Japan

E-mail: takatsu@scphys.kyoto-u.ac.jp

Abstract. We report a comparative study of the conductive oxides PdMO$_2$ ($M = \text{Cr, Co}$) consisting of a layered structure with a triangular lattice of $M^{3+}$ ions: PdCrO$_2$ ($S = 3/2$) is magnetically active showing an antiferromagnetic (AF) transition at $T_N \simeq 37.5$ K, whereas PdCoO$_2$ ($S = 0$) is not magnetically active. Both compounds exhibit metallic conductivity down to low temperatures, but the temperature dependence of the resistivity is quite different reflecting the difference in their magnetic properties. Especially, the resistivity of PdCrO$_2$ exhibits strong sub-linear temperature dependence in a wide temperature range above $T_N$. Such dependence is markedly different from that of ordinary magnetic metals with non-frustrated localized spin moments. The estimated entropy at $T_N$ is substantially smaller than that expected for a system with $S = 3/2$, suggesting that the spin correlations still remain much above $T_N$. These facts indicate that it is the short-range correlations of frustrated spins that leads to the unusual sub-linear temperature dependence of the resistivity.

1. Introduction

Antiferromagnetic (AF) Heisenberg spins on a two-dimensional (2D) triangular lattice (TL) offer one of the simplest systems to examine novel spin states under geometrical frustration. Since the majority of the 2D-TL Heisenberg antiferromagnets are insulators or semiconductors, a conductive member provides a rare and important opportunity to study an interplay between geometrically frustrated spins and the conduction electrons.

Recently, we found that the 2D-TL magnetic compound PdCrO$_2$ ($Cr^{3+}$, $S = 3/2$) exhibits metallic conductivity down to low temperatures without chemical doping [1]. We also confirmed that the iso-structural but non-magnetic compound PdCoO$_2$ ($Co^{3+}$, $S = 0$) exhibits metallic conductivity [2]. Thus, by comparing the metallic conductivity of these two compounds, we expect to find a character attributable to the interaction between the frustrated spins and the conduction electrons. For this purpose, we performed a comparative study of the metallic conductivity of these oxides. We found a new feature of magnetic correlations persisting up to temperatures much above $T_N$ in the resistivity as well as in the specific heat.
2. Experimental

Single crystals of PdCoO$_2$ and polycrystals of PdCrO$_2$ were prepared using procedures reported in Refs. [2, 3]. The samples were characterized by using powder X-ray diffraction (XRD) with the CuK$_{\alpha 1}$ radiation and energy dispersive X-ray analysis (EDX). XRD patterns revealed no impurity phase, and EDX spectra yielded composition ratios of Pd and $M$ ($M = \text{Cr, Co}$) to be Pd/$M = 1.1 \pm 0.1$, indicating stoichiometry within the experimental resolution.

The electrical resistivity was measured with either an AC or DC four-probe method from 500 K to 23 mK for PdCoO$_2$ and from 300 K to 350 mK for PdCrO$_2$. Specific heat was measured with a thermal relaxation method by using a commercial calorimeter (PPMS, Quantum Design) from 250 K to 350 mK. For magnetic PdCrO$_2$, we carefully collected data points in 0.01 K intervals around $T_N$.

3. Results and Discussion

The temperature dependence of the electrical resistivity of PdCrO$_2$ and PdCoO$_2$ is shown in Fig. 1. Both compounds exhibit metallic conductivity down to the lowest measurement temperatures.

In magnetic PdCrO$_2$, the resistivity exhibits a $T$-linear dependence between 200 K and 300 K; the temperature derivative of the resistivity ($d\rho/dT$) is nearly independent of temperature in this region (inset of Fig. 1). However, as the temperature decreases below 200 K, the resistivity gradually deviates from the linearity, and at $T_N$ a sharp peak is observed in $d\rho/dT$. For a typical magnetic metal with localized moments, the resistivity due to the magnetic scattering is expected to be $T$-independent above its magnetic transition temperature ($T_{\text{mag}}$) and the total resistivity above $T_{\text{mag}}$ is $T$-linear mainly due to the phononic contribution [5, 6]. Therefore, the observed deviation from the $T$-linear dependence at temperatures much above $T_N$ for PdCrO$_2$ is

![Figure 1. Temperature dependence of the electrical resistivity of (a) PdCrO$_2$ and (b) PdCoO$_2$. Inset of the panel (a) is the temperature derivative of the resistivity of PdCrO$_2$. It exhibits a clear peak at about $37.5 \pm 0.5$ K, consistent with the specific heat and other experiments [1, 4].](image-url)
Figure 2. (a) Temperature dependence of the specific heat of PdCrO\textsubscript{2} and PdCoO\textsubscript{2}. The inset shows the low-temperature behavior of $\Delta C/T$. The solid line represents the fitting by eq.(1). (b) The magnetic specific heat estimated by subtracting of the phononic and electronic contribution from the total specific heat of PdCrO\textsubscript{2} (left axis), and the resulting magnetic entropy (right axis); see the text for the details.

unusual. We characterize the temperature dependence by fitting the formula $\rho(T) = A + BT^{\nu}$ to the data below and above $T_N$. The fitting yields $\nu = 2.8 \pm 0.1$ ($T < 38$ K) and $\nu = 0.34 \pm 0.05$ ($38$ K $< T < 150$ K). For non-magnetic PdCoO\textsubscript{2}, whose resistivity consists mainly of the phononic contribution, the resistivity slightly deviates from the $T$-linear behavior at high temperatures: $\rho_{ab} \propto T^{1.4}$ and $\rho_c \propto T^{1.05}$ between $100$ K and $300$ K. This super-linear behavior is attributable to the scattering between high-frequency phonons and the conduction electrons [2]. It is not possible to explain the unusual sub-linear temperature dependence of the resistivity of PdCrO\textsubscript{2} above $T_N$ in terms of the high-frequency phonon scattering. The result indicates that it is the magnetic scattering that causes the sub-linear behavior.

The temperature dependence of the specific heat for PdCrO\textsubscript{2} and PdCoO\textsubscript{2} is presented in Fig. 2 (a). A clear peak associated with the AF transition is observed in PdCrO\textsubscript{2} at 37.5 K, which agrees well with the temperature at which $d\rho/dT$ exhibits the peak. The total specific heat ($C_P$) of PdCoO\textsubscript{2} is noticeably smaller than that of PdCrO\textsubscript{2} even at 250 K; it is often expected that $C_P$ of the iso-structural non-magnetic compound approaches that of magnetic one at high temperatures. This difference may be attributed to the Einstein-phonon modes in the lattice specific heat ($C_L$) of PdMO\textsubscript{2} system [2], and implies that a treatment beyond a simple Debye correction[7] is necessary to estimate $C_L$ of PdCrO\textsubscript{2}. We adopt here another model in which the lattice part for PdCrO\textsubscript{2} ($C_{L, Cr}$) is estimated by multiplying $C_L$ of PdCoO\textsubscript{2} by a constant such that it approaches $C_P$ of PdCrO\textsubscript{2} at high temperatures; we used 1.09 for this constant [8]. It should be noted that the magnetic entropy at $T_N$ as well as the low-temperature analysis below are little affected by the choice of the model. The estimated $\Delta C = C_P - C_{L, Cr}$ after further subtracting the electronic contribution $C_{ele}$ is shown in Fig. 2 (b) with the calculated entropy (the red curve). Here $C_{ele}$ is estimated by fitting the relation

$$\Delta C = C_P - C_{L, Cr} \simeq C_{ele} + C_{mag} = \gamma_{ele} T + A_{mag} T^h,$$

where $\gamma_{ele}$ denotes the electronic specific-heat coefficient, and $C_{mag} = A_{mag} T^h$ is the magnon contribution applicable much below $T_N$. The fitting yields $\gamma_{ele} = 1.4 \pm 0.2$ mJ/mol-K$^2$, ...
\( h = 2.0 \pm 0.1 \) and \( A_{\text{mag}} = 1.2 \text{ mJ/mol-K}^3 \) (the inset of Fig. 2 (a)). The value of \( \gamma_{\text{ele}} \) is similar to that of PdCoO\(_2\) (\( \gamma_{\text{ele}} = 1.28 \text{ mJ/mol K}^2 \)), implying that the mass enhancement between electrons and magnetic moments is not strong. The exponent \( h \) is known to fulfill the relation \( h = d/\varepsilon \), where \( d \) is the dimensionality of magnon excitations and \( \varepsilon \) is a parameter related to the type of magnetic order: \( \varepsilon = 1 \) for AF order and \( \varepsilon = 2 \) for ferromagnetic order. The observed \( T^2 \) dependence is consistent with the expectation that a 2D magnon excitation exists at low temperatures.

It is remarkable that the magnetic entropy is \( 3.9 \pm 0.1 \text{ J/mol-K} \) at \( T_N \), which is only about one third of the expected entropy for a system with \( S = 3/2 \) localized spins, \( R \ln(2S + 1) = 11.53 \text{ J/mol-K} \). This result indicates that the spin randomness is reduced above \( T_N \), reflecting the short-range spin correlations without magnetic ordering due to geometrical frustration.

Let us discuss the origin of the sub-linear temperature dependence of the resistivity of PdCrO\(_2\). As mentioned above, in ordinary magnetic metals, the magnetic scattering above \( T_{\text{mag}} \) yields the \( T \)-independent resistivity, which is attributed to the scattering between random magnetic moments and conduction electrons. Once the spins order, the resistivity of the magnetic origin decreases immediately because of the reduction of the magnetic scattering. Therefore, the \( T \)-sub-linear resistivity of PdCrO\(_2\) is attributed to the gradual development of the short-range spin ordering, which weakens the magnetic scattering of the conduction electrons at temperatures much above \( T_N \).

4. Conclusion
In conclusion, we have investigated the 2D metallic compounds PdCrO\(_2\) and PdCoO\(_2\) with and without frustrated spins on a triangular lattice. Both oxides exhibit metallic conduction down to the lowest measurement temperatures: 350 mK for PdCrO\(_2\) and 23 mK for PdCoO\(_2\). However, the temperature dependence of their resistivity is quite different. In magnetic PdCrO\(_2\), a \( T \)-sub-linear resistivity is observed in a wide temperature range above \( T_N \), which is quite different from the resistivity of ordinary magnetic metals. This behavior cannot be explained by scattering between conduction electrons and high-frequency phonons, which is the origin of the super-linear resistivity for non-magnetic PdCoO\(_2\). The magnetic entropy at \( T_N \) is only one third of the expected entropy of an \( S = 3/2 \) spin system. This small entropy at \( T_N \) indicates that spin correlations substantially develop at temperatures much higher than \( T_N \). Moreover, this short-range correlations characteristic of a geometrically frustrated system should be the origin of the unusual sub-linear temperature dependence of the resistivity observed in PdCrO\(_2\).

Acknowledgment
We would like to thank K. Ishida, S. Yonezawa, M. Kriener, and S. Kittaka for fruitful discussions and for their supports in measurements. This work was supported by a Grant-in-Aid for the Global COE “The Next Generation of Physics, Spun from Universality and Emergence” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. It has also been supported by Grants-in-Aid for Scientific Research from MEXT and from the Japan Society for the Promotion of Science (JSPS).

[1] Takatsu H, Yoshizawa H, Yonezawa S and Maeno Y (unpublished)
[2] Takatsu H, Yonezawa S, Mouri S, Nakatsuji S, Tanaka K and Maeno Y 2007 J. Phys. Soc. Jpn. 76 104701
[3] Shannon R D, Rogers D B and Prewitt C T 1971 Inorg. Chem. 10 713
[4] Mekata M, Sugino T, Oohara A, Oohara Y and Yoshizawa H 1995 Physica B 213 221
[5] Ziman J M 1960 Electrons and Phonons (New York: Oxford University Press)
[6] Kasuya T 1956 Prog. Theor. Phys. 16 58
[7] Nakatsuji S et al. 2007 Science 309 1697
[8] This model empirically corrects for the number of the Debye modes while effectively incorporating the reduction of the Einstein frequencies.