Large Magneto-conductivity Effect in Fe-Phthalocyanine Conductor at Low Temperatures

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Abstract. Magnetoresistance and magnetic torque measurements of one-dimensional $\pi$-$d$ organic conductor TPP[Fe(Pc)(CN)$_2$]$_2$ are performed in the temperature range of 30-1.5 K. The resistance shows semiconducting behavior in the whole temperature range, suggesting a charge ordered state. Quite large negative magnetoresistance is observed at low temperatures, which is associated with the change of the magnetic torque. These results show that the charge gap steeply decreases at about 14.5 T, where some magnetic transition of Fe 3d spins occurs. This is clear evidence that the $\pi$ electron transport is strongly correlated with the local spins via the strong $\pi$-$d$ interaction. Possible theoretical models, double-exchange interaction and $\pi$-$d$ spin-singlet models are discussed.

1. Introduction

Interplay between magnetism and conductivity have brought about various drastic phenomena in magneto-transport properties. Among many kinds of magnetic materials, magnetic-moment introduced organic conductors are good candidates for the studies of novel magneto-transport phenomena because of their great advantages, simple band structure, low dimensionality, high quality single crystals and so on.[2, 4, 5, 6].

TPP[Fe(Pc)(CN)$_2$]$_2$ is a one-dimensional (1D) organic semiconductor, which has conducting chains of stacked dicyano(phthalocyaninato)iron [Fe(Pc)(CN)$_2$] molecules (TPP=tetraphenylphosphonium)[7, 8]. The conducting chain is parallel to the c-axis of the crystal. The a- and b-axes are equivalent because of the tetragonal symmetry of the crystal structure. A [Fe(Pc)(CN)$_2$] molecule has both $\pi$ electrons in the Pc ligand and the local magnetic moment on the central Fe$^{3+}$ ion. Thus, the conduction electrons are strongly coupled with the local moments, i.e., large $\pi$-$d$ interaction is present. Because of the unquenching of the molecular orbital angular momentum, the magnetic moment is quite anisotropic[9]. Although the conduction band is partially occupied (i.e., 3/4 filling) formally, the temperature dependence of electrical resistivity shows semiconducting behavior from room temperature. Since no lattice distortion has been found so far, the ground state is considered as a charge ordered state[8, 10]. The striking feature of this material is the large negative magnetoresistance. The magnetoresistance effect is significantly enhanced when a magnetic field is applied to the a-axis (nearly parallel to the easy axis of the magnetic moment). Although it is very likely that the $\pi$-$d$ interaction plays an essential role in the magnetoresistance effect[11], the mechanism has not
been clarified yet. To further investigate the interplay between the magnetism and conductivity in this system, we have performed systematic measurements of electrical conductivity and magnetic torque at lower temperatures under high magnetic field.

2. Experimental

Single crystals were synthesized by a standard electrochemical method\[8\]. The typical dimensions of the crystals were 100 $\mu$m x 100 $\mu$m x 1 mm for the $a$-, $b$-, and $c$-axis. Transport measurements shown here were performed by two point configuration. We checked that the contact resistance can be negligible, i.e., the result of four point configuration is essentially identical to that by two point method. Magnetic torque measurements were performed using commercial microcantilevers\[12\]. The crystals cut into small pieces with typical dimensions of 40 $\mu$m x 40 $\mu$m x 80 $\mu$m were used for the torque measurements. The temperature is controlled by a $^3$He cryostat, and the magnetic field is applied by a 20 T superconducting magnet.

3. Results and Discussions

The temperature dependences of the low-bias conductance at 0 T and 17.8 T ($B//a$) are shown as open triangles and circles in Fig. 1(a), respectively. The bias voltage is $\pm$10 mV, where the linear current-voltage characteristics are confirmed. At 0T, the conductance follows the Arrhenius law; $\sigma(T) = \sigma_0 \exp(-\Delta_0/2k_B T)$ below 30 K. The data points scattered below 8 K are due to the limitation of the measurement. The activation energy $\Delta_0/k_B$ is estimated as 650 K, where $k_B$ is the Bolzmann constant. This value is slightly larger than the previously reported one, $\Delta_0/k_B \sim$ 600 K. In a magnetic field of 17.8 T, the curvature is significantly shifted upward: large positive magnetoconductance (negative magnetoresistance) behavior is evident below 30 K. We note that the slope in the Arrhenius plot changes at around 12.5 K, i.e., activation energy changes. We obtain $\Delta_0/k_B$=360 K for $\sim$30-13 K and 180 K for $T <$12 K. The origin of the change is not specified at the present. Another important feature is that the activation energy for $T = 30 \sim 13$ K gradually decreases with field and has a tendency to saturate at 15 T (see inset of Fig. 1). It should be noted that the isostructural nonmagnetic salt TPP[Co(Pc)(CN)$_2$]$_2$ does not show such large magnetoconductance and has a low activation energy $\Delta_0/k_B=63$ K below 80 K.

![Figure 1. Temperature dependence of low-bias conductance at 0 T (open triangles) and 17.8 T (open circles). Inset shows the magnetic field dependence of activation energy for $T=13-30$ K.](image)

The magnetic field dependence of conductance defined as $I/V$ is shown in Fig. 2(a). In each field sweep, the bias voltage is kept constant at a small value, so that the current remains at $\sim$10 nA for $B=17.8$ T. As the temperature decreases, the positive magnetoconductance is enhanced, and a steep increase at $\sim$15 T, which amounts to four orders of magnitude or over, is visible below 7 K. Such drastic change suggests the presence of a phase transition. So far, no phase transition has been reported because the measurements were limited in a relatively
Figure 2. (a) Magnetic field dependence of conductance at constant bias voltage for various temperatures. (b) Magnetic torque curves at various temperatures. Inset shows the derivative curve of the torque, indicating the existence of magnetic transition at 14.5 T for 1.5 K.

high temperature range \( (T > 20 \text{ K}) \)[4, 11]. Since the conductance is still semiconducting even at 17.8 T, this transition is an insulator-semiconductor transition, suggesting that the activation energy (charge gap) is reduced rapidly at \( \sim 15 \text{ T} \) by applying a magnetic field. The results are consistent with the magnetic field dependence of the activation energy (see inset of Fig. 1).

We have also measured magnetic torque to investigate the nature of this enormous magnetoresistance. Figure 2(b) shows the torque curves at various temperatures. Magnetic field is applied nearly parallel to the \( a \)-axis. At 1.5 K, the torque changes rapidly at \( \sim 14.5 \text{ T} \), which is evident in the derivative curve as shown in the inset of Fig. 2(b). This torque anomaly suggests the existence of a magnetic phase transition at 14.5 T \( (\equiv B_c) \). As temperature increases, the anomaly becomes less evident and is not appreciable above 13 K. The results in Fig. 2 clearly show that the charge gap in the \( \pi \) electron transport is strongly coupled with the local moments via the strong \( \pi-d \) interaction. The analysis of the magnetic susceptibility measurements suggest that the antiferromagnetic (AF) correlation of the local moments in the 1D chains gradually develops as temperature decreases \( (T < 25 \text{ K}) \)[14]. However, no evidence of the AF long range order is observed in the heat capacity down to 4 K)[14].

Such giant negative magnetoresistance effects have been observed in some perovskite manganites or molecular based magnetic conductors[1, 6]. In these materials, the negative magnetoresistance is interpreted in terms of an increase of the transfer integral between the nearest neighbor sites by applying magnetic field because magnetic field reduces the inhomogeneous magnetic potential formed by AF or paramagnetic arrangement of magnetic moments. This picture is known as double-exchange-interaction scenario[1, 15]. In this case, the magnetoresistance is scaled to the square of the magnetization[15]. Hanasaki et. al. point out that the magnetoresistance effect of this system is not scaled to the square of magnetization, and it is much larger than the expected behavior for usual double-exchange systems[11]. In the present case, since the local moment have very anisotropic g-factor, such scaling behavior might be modified. Hence, further theoretical investigation will be needed.

Recently, Hotta et al. proposed another picture, in which a spin singlet state of the Fe 3d spin and the \( \pi \) electron spin formed by the AF \( \pi-d \) interaction plays a crucial role[16]. In the
spin-singlet state, the π up- and down-spin states have equal probability. This singlet formation effectively reduces the transfer integral \((t)\) to the neighbor site, depending on the Fe 3d spin state at the neighbor site. In sufficiently high fields, the singlet state is broken and the spin-triplet state is induced: all the π and 3d spins are aligned ferromagnetically, which recovers \(t\). The stability of the charge ordered state (charge gap) strongly depends on \(t\), which is well established in the theta phase BEDT-TTF salts\[17\]. Even a small change of the charge gap should cause drastic change of the conductivity at low temperatures when the carrier number is determined by the Boltzman factor as in this case. Therefore, the magnetic-field-induced singlet-triplet transition qualitatively explains the giant negative magnetoresistance in this system. Furthermore, the steep change of the magnetic torque at 14.5 T is interpreted as the spin-singlet-triplet transition.

In summary, we find the quite large magnetoresistance effect of TPP\[Fe(Pc)(CN)\]\(_2\)\(\_2\) at low temperature under high magnetic fields, which is associated with some magnetic transition of the local Fe 3d spins. This feature is explained in terms of the charge gap depending on the magnetic field, where the \(\pi\)-d interaction plays an essential role. For the full understanding, the magnetic ground state should be clarified. Electron spin resonance studies are now in progress.

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