Giant negative magnetoresistance in quasi-one-dimensional conductor TPP$[Fe(Pc)(CN)_2]_2$: Interplay between local moments and one-dimensional conduction electrons

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We have found giant negative magnetoresistance in the one-dimensional conductor TPP$[Fe(Pc)(CN)_2]_2$ below 50 K. The reduction of the resistance is larger in the field perpendicular to the one-dimensional axis than parallel to the axis. The magnetic susceptibility shows anisotropic Curie-Weiss behavior. The experimental results suggest the interaction between the one-dimensional electron system and the local moments. The reduction of the spin scattering of the itinerant electrons by the local moments under the field is proposed as the origin of the giant negative magnetoresistance.

The interplay between conduction electrons and local magnetic moments has provided a variety of interesting phenomena such as Kondo effect, Ruderman-Kittel-Kasuya-Yosida interaction, heavy fermion, giant magnetoresistance, and colossal magnetoresistance.[1–5] The giant negative magnetoresistance was reported in the manganese oxides[5] and λ-$BETS_2FeCl_4$,[6] and is accompanied or caused by the sharp metal-insulator transition.

There have been very few reports on these phenomena in the one-dimensional system, although theoretical studies predict several attractive phenomena such as Kondo effects in a Luttinger liquid.[3,7,8] Quasi-one-dimensional molecular conductors are good candidates for this research. By introducing the local moments (d electron) into these conductors, the interaction (π-d interaction) between the one-dimensional conduction electrons (π electron) and the local moments is expected to give different electronic states. In fact, interesting phenomena such as negative magnetoresistance were reported in the one-dimensional molecular conductor $[Cu_xNi_{1-x}(Pc)](I_3)_{1/3}$,[9,10] where π electron in Pc (=phthalocyanine) forms the conduction band and d electron in Cu^{2+} affords the local moment. However, owing to the experimental difficulty, the systematic studies on the anisotropy of this system have not been reported. The negative magnetoresistance was also reported in the one-dimensional Peierls compounds,[11] and the critical temperature of the negative magnetoresistance decreases on increasing the magnetic-field strength.

The title compound TPP$[Fe(Pc)(CN)_2]_2$ and the isostructural compound TPP$[Co(Pc)(CN)_2]_2$ (TPP=tetraphenylphosphonium) have a one-dimensional conduction band coming from the π orbital of Pc, since the partially oxidized Pc units stack uniformly along the c axis. The Fe compound has $\mathbf{S}=1/2$ local moments of Fe^{3+} in the conduction path,[12] while there are no local moments in the Co compound.[13] TPP molecules and CN ligands hold closed-shell orbitals. The striking difference in the resistance behavior of these compounds was reported.[12,13] This difference suggests the possibility of the interaction between the one-dimensional conduction electrons and the local moments.

The Pc molecule has a structure with fourfold symmetry and one can expect the degeneracy in the molecular orbitals of Pc. It is of great interest how this degeneracy influences the physical properties.

In order to obtain the clear-cut experimental evidence for the interaction between the one-dimensional conduction carriers and the local moments and explore interesting phenomena caused by the π-d interplay, we measured magnetoresistance, magnetic susceptibility, and magnetic torque of the title compound. In this paper we report giant negative magnetoresistance, and discuss the possibility of the spin scattering of the itinerant electrons by the local moments on the basis of the experimental results of the anisotropy for the field direction of the transport and magnetic properties.

We will make a brief reference to the title compound.[12,13] The measured reflectance spectra of the Fe and Co compounds show Drude-Lorenz behavior only along the c axis in agreement with the overlap calculations, and a gap structure is observed in the spectral region near 1000 cm^{-1}.[12] The similar gap is observed in the conventional one-dimensional conductors $(TMTTF)_2X$ (Refs. 14 and 15) and $(DCNQI)_2Li$,[16] owing to the electron-electron correlation. The transport properties are dominated by the itinerant electrons created by the strong fluctuation characteristic of the one-dimensional system and the thermal excitation.

Sample crystals were prepared by a conventional electrochemical method. The crystal system is tetragonal and the space group is $P4_2/n$: $a=b=21.722(2)$, $c=7.448(2)$ Å.[12] The typical shape of the sample is a black needle elongated along the c axis. The typical size of the single crystal is $0.15\times0.15\times1$ mm. We made the gold pads on the ac plane of the sample by the gold vapor deposition and attached the four gold wires to these pads and fixed them by the gold and carbon paint. The typical value of the contact resistance was of the order of 50Ω. The dc four-probe resistance was measured with the current along the c axis under the static magnetic field up to 18 T. In the measurement of the high resistance, we applied the constant voltage to the sample and the standard resistance, and measured the sample current and the

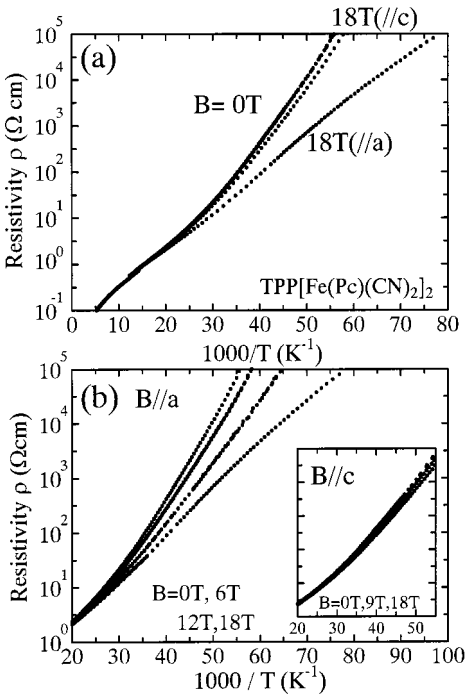

FIG. 1. Temperature dependence of the resistivity of $TPP[Fe(Pc)(CN)_2]_2$. Negative magnetoresistance is observed below 50 K. (a) The resistivity measured in the absence of a field and under the static magnetic field (18 T) along the *a* axis and the *c* axis. Note that the negative magnetoresistance has the high anisotropy for the field direction. (b) The resistivity measured under various strengths of the magnetic field (0, 6, 12, and 18 T, from top to bottom). The field is applied along the *a* axis. Inset: The resistivity measured under various strengths of the magnetic field (0, 9, and 18 T, from top to bottom). The field is applied along the *c* axis.

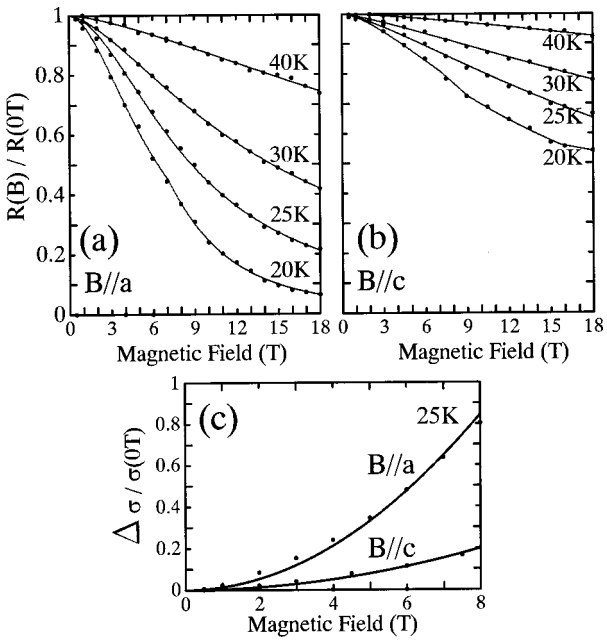

FIG. 2. Field dependence of the resistance of $TPP[Fe(Pc)(CN)_2]_2$. The resistance decreases with increasing magnetic-field strength. The negative magnetoresistance is enhanced on lowering the temperature. The resistance and the conductivity are normalized by the zero-field resistance and the zero-field conductivity, respectively. (a) The resistance measured for the magnetic field along the *a* axis at 20, 25, 30, and 40 K. (b) The resistance measured for the magnetic field along the *c* axis at 20, 25, 30, and 40 K. (c) The magnetoconductivity measured in the low-field region at 25 K. The solid lines represent the best fit of the data by the equation $\Delta\sigma/\sigma(0T)=\alpha\mathbf{B}^2$.

sample voltage. We checked the contact resistance and the Ohmic conduction of the sample under the magnetic field in the low temperature above 20 K. In all the five samples we obtained the results similar to those reported in this paper. Static magnetic susceptibility measurements were performed by use of a Quantum Design MPMS-R2 superconducting quantum interference device (SQUID) susceptometer. The needlelike sample crystals (0.21 mg) were aligned in a thin quartz tube. Magnetic torque measurements were carried out by use of an Oxford split magnet (8 T) and a cantilever magnetometer system. We put the sample (0.02 mg) on the cantilever. The *bc* plane is parallel to the cantilever plane. The *c* axis is perpendicular to the rotation axis. We measured the capacitance of the cantilever during the rotation of the cantilever under the uniform magnetic field and calculated the susceptibility anisotropy of the sample within the *ac* plane.

Figure 1 shows the temperature dependence of the magnetoresistance when the field is applied along the *a* axis and the *c* axis. In the absence of an external magnetic field, the resistance increases with lowering the temperature. There is a kink structure in the resistance around 50 K. The semiconducting behavior is enhanced around 50 K.[12] Above 100 K the resistance may be fitted by an expression of $\ln\rho\sim 1/T^{0.5}$ or $1/T^{0.25}$.[17]

One can see large negative magnetoresistance below 50 K. The negative magnetoresistance has the large dependence on the field direction. The reduction of the resistance by the applied field is greater for the field along the *a* axis than along the *c* axis. As seen in Figs. 2(a) and (b), the resistance decreases with increasing the field strength. It should be noted that the magnetoresistance becomes smaller than one-tenth of magnitude of the zero-field resistance under the applied field of 18 T ($\mathbf{B}\|a$) at 20 K. This large negative magnetoresistance is not caused by a sharp transition such as the metal-insulator transition observed in the manganese oxides and λ-$BETS_2FeCl_4$.[5,6]

The reduction of the resistance in the title compound is much larger than the typical value expected in the Anderson's weak localization in the quasi-one-dimensional conductors.[18] The temperature dependence of the resistance in the title compound is again in contradiction with the temperature dependence of $\rho\sim 1/T^{0.5}$ reported in the Anderson's localization in the one-dimensional system.[19,20] Thus the possibility of the Anderson's localization is ruled out.

The magnetic field suppresses the enhancement of the semiconducting behavior around 50 K as shown in Fig. 1. The temperature of the resistance kink hardly decreases under the magnetic field. These experimental results suggest the existence of additional scattering of the itinerant electrons below 50 K, and the suppression of this additional scattering by the applied field.

The title compound has the local moments in the one-dimensional conduction path. One possible origin of the negative magnetoresistance is the decrease of the spin scat-

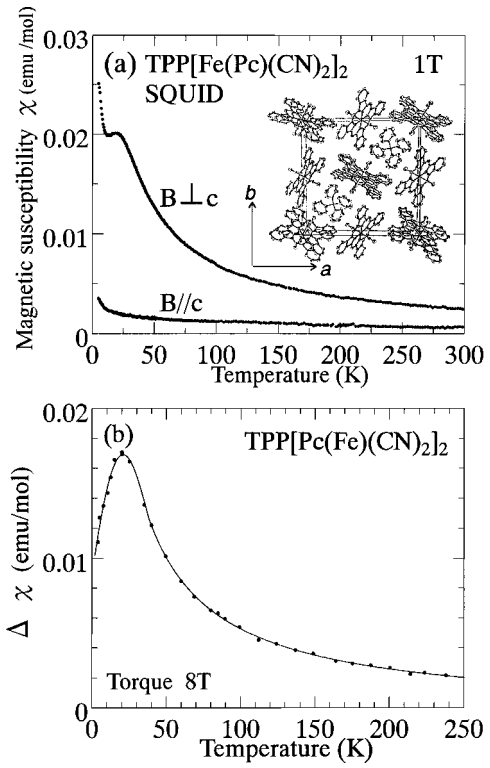

FIG. 3. Anisotropy of the magnetic susceptibility of TPP[Fe(Pc)$(CN)_2]_2$. (a) Temperature dependence of the magnetic susceptibility measured by SQUID in the field of 1 T. The field is applied along the direction parallel and perpendicular to the *c* axis. The anisotropy of the Curie-Weiss behavior is evident above 20 K. The molar unit in the susceptibility is one formula unit of $TTP_{0.5}$[Fe(Pc)$(CN)_2$]. Inset: Crystal structure of TPP[Fe(Pc)$(CN)_2]_2$ as viewed along the *c* axis. (b) Temperature dependence of the anisotropy in the magnetic susceptibility ($\Delta\chi = \chi_a - \chi_c$), which is derived from the magnitude of the torque ΔT by use of the relation $\Delta\chi = 2\Delta T/B^2$.

tering of the conduction electron by the local moments under the magnetic field. In order to examine the relation between the negative magnetoresistance and the local moments, we investigated the anisotropy for the field orientation of the magnetic properties dominated by the local moments.

Figure 3(a) displays the temperature dependence of the magnetic susceptibility measured by SQUID under the applied field (1 T) parallel and perpendicular to the *c* axis. It is evident that the susceptibility has the large dependence on the magnetic-field direction. Under the field perpendicular to the *c* axis, the susceptibility follows the Curie-Weiss law characteristic of the local moments above 20 K. A least-squares fit of the data (**B**$\perp$ **c**) gives the Curie constant $C = 0.81$ emu K mol^{-1} and the Weiss temperature $\theta = -13.7$ K. The susceptibility along the *c* axis has a small deviation from the Curie-Weiss law. Around 20 K, the anomaly is observed only for the field perpendicular to the *c* axis.[12]

The authors (M. Matsuda *et al.*) tried the molecular orbital calculations including the Pc ligand and the Fe atom. The second highest occupied molecular orbital and the third one mainly consist of d_{yz}, d_{zx} orbitals of the Fe atom. In the case of d^5 low-spin configuration, there is $\mathbf{S} = 1/2$ local moment in these orbitals. According to this calculation, the difference between the energy levels of these orbitals is quite small. Thus we think that the spin-orbit coupling leads the large anisotropies of the *g* value and the susceptibility.

The torque measurement gives the straightforward evidence for the anisotropy of the magnetic susceptibility, when the title compound is in a paramagnetic state.[21] Figure 3(b) displays the temperature dependence of the anisotropy of the susceptibility derived from the magnitude of the torque. Since the sample is rotated within the *ac* plane in this experiment, the magnitude of the torque reflects the anisotropy ($\Delta\chi = \chi_a - \chi_c$) of the susceptibility within the *ac* plane. The figure shows the Curie-Weiss behavior above 20 K. It is evident that there is a large anisotropy in the Curie-Weiss paramagnetism. The overall feature of the temperature dependence of $\Delta\chi$ [Fig. 3(b)] is consistent with the SQUID measurement [Fig. 3(a)] above 20 K. As shown in Fig. 3(b), $\Delta\chi$ drops abruptly by one-half below 20 K. The detailed investigation of this anomaly will be left for the further studies.

Let us discuss the relation between the negative magnetoresistance (Figs. 1 and 2) and the magnetic susceptibility (Fig. 3). When the field is applied along the *a* axis, the large magnetic susceptibility and the large negative magnetoresistance are observed. Both of them are small for the field parallel to the *c* axis. The large (small) negative magnetoresistance is observed for the field orientation of the large (small) susceptibility. This suggests that the magnetic moment induced by the field causes the negative magnetoresistance. This gives the evidence for the correlation (π-*d* interaction) between the local moments and the itinerant electrons.

At the present stage, it is unclear whether the nature of the π-*d* interaction is antiferromagnetic or ferromagnetic. The theoretical studies suggest that, in the case of an antiferromagnetic interaction, the probability of the spin scattering of the itinerant electrons by the local moments increases at lower temperatures, while it decreases in a ferromagnetic case.[1] An antiferromagnetic interaction enhances the spin scattering of the conduction electrons and thus increases the resistance at lower temperatures. Figures 2(a) and (b) show that the reduction of the resistance by the applied field increases on lowering the temperature. Since this negative magnetoresistance reflects the magnetic part of the resistance due to the spin scattering, the experimental results suggest the antiferromagnetic interaction.

One possible origin of the π-*d* interaction is an antiferromagnetic one such as the *s*-*d* exchange interaction observed in the Kondo systems. We estimated roughly this exchange interaction *J* by the molecular-orbital calculations. The overlap integral between the highest occupied molecular orbital (HOMO) and the next HOMO in the neighboring molecules gives the mixing between the itinerant electrons and the local moments $V \sim 0.1$ eV. The on-site Coulomb energy was roughly estimated to be $U \sim 1.5$ eV according to the earlier experimental reports.[22,23] If one assumes the symmetric Anderson model for the simplicity, the antiferromagnetic exchange interaction $J \sim \langle V \rangle^2/U$ between the itinerant electrons and the local moments is estimated to be of order of 60 K.[24]

When one applies the field, the population of the local moments parallel to the field increases. The magnetic field disturbs the free motion of the local moments and reduces the probability of the spin-flip scattering. This can give the

negative magnetoresistance. For the field orientation of the larger susceptibility, one expects larger negative magnetoresistance. This feature agrees with the experimental results as shown in Figs. 1(a) and 3(a) and (b).

Figure 2(c) shows an example of the magnetoconductivity normalized by the zero-field conductivity in the low-field region at 25 K. The field dependence along the c axis is similar to that along the a axis. The data may be well fitted by an expression of $\Delta\sigma/\sigma(0\ \mathrm{T}) = \alpha B^2$ as shown by the solid lines in the figure. Here B denotes the field strength and α is a constant. This result is in agreement with the theoretical prediction (B^2 power law) in the low-field limit.[1] Since the magnetization is proportional to the magnetic field below 5 T above 20 K, the negative magnetoresistance (positive magnetoconductivity) is proportional to the square of the magnetization in the low-field region. This result is consistent with the spin scattering mechanism.[25] The least-squares fit for the data at 25 K gives the constant $\alpha_a = 1.3\times10^{-2}$ for the field along the a axis, and $\alpha_c = 3.1\times10^{-3}$ along the c axis. The temperature dependence of α_a follows the power law of $\alpha_a \propto T^{-5}$.

Although the title compound has dense $3d$ local moments in the conduction path (four $S=1/2$ spins per the unit cell), there is the large enhancement of the resistance due to the spin-flip scattering, and the giant negative magnetoresistance appears in the low temperature. The giant negative magnetoresistance reported here is observed in the higher temperature range as compared with the typical temperature region of the negative magnetoresistance observed in the conventional Kondo systems.[25,26] These features might be characteristic of the one dimensionality of the π-d system. The detailed studies in the microscopic measurements will be in need to clarify the nature of the π-d interaction in the one-dimensional system. We hope that this paper will stimulate further work in the low-dimensional Kondo systems.

In conclusion, we have found the giant negative magnetoresistance below 50 K in TPP$[\mathrm{Fe(Pc)(CN)_2}]_2$. This gives the evidence for the existence of the interaction between the $3d$ local moments and the one-dimensional itinerant π electrons. The reduction of the spin scattering of the itinerant electrons by the local moments under the field is proposed as the origin of the giant negative magnetoresistance. The magnetic susceptibility shows anisotropic Curie-Weiss behavior. The large (small) negative magnetoresistance is observed in the field orientation for the large (small) susceptibility. This anisotropy of the susceptibility and the negative magnetoresistance strongly suggests the spin scattering mechanism for the giant negative magnetoresistance.

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