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Giant Negative Magnetoresistance in One-Dimensional π-*d* System : $TPP[Fe(Pc)(CN)_2]_2$ (TPP = tetraphenylphosphonium, Pc = phthalocyanine)

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We found the giant negative magnetoresistance in the one-dimensional π-*d* system $TPP[Fe(Pc)(CN)_2]_2$ below 50K. The large negative magnetoresistance was observed for the field along the *a*-axis, while the small one along the *c*-axis. We also observed the anisotropic Curie behavior of the magnetic susceptibility. The large (small) magnetoresistance was observed in the field orientation for the large (small) magnetic susceptibility. The reduction of the spin-flip scattering of the itinerant electrons by the local moments under the magnetic field was proposed as the origin of the negative magnetoresistance. In the isostructural compound $TPP[Co(Pc)(CN)_2]_2$ we observed the large positive magnetoresistance. This positive magnetoresistance cannot be explained in terms of the orbital effects under the field.

Keywords: phthalocyanine; giant negative magnetoresistance; spin scattering; π-*d* interaction

INTRODUCTION

In the title compound $TPP[Fe(Pc)(CN)_2]_2$, the Pc molecules

stack along the *c*-axis, and the π-orbital overlap of these molecules provides the one-dimensional conduction band. There are *3d*-local moments of Fe^{3+} in the conduction path. One expects that the interplay between the local moments and the one-dimensional conduction electrons provides a novel electronic state. The crystal system is tetragonal and the space group is $P4_2/n$: $a = b = 21.722(2)$ Å, $c = 7.448(2)$ Å[1]. The isostructural compound TPP[Co(Pc)$(CN)_2]_2$ has an one-dimensional band similar to that in TPP[Fe(Pc)$(CN)_2]_2$, although Co^{3+} has no local moments.

The reflectance spectra of TPP[Fe(Pc)$(CN)_2]_2$ and TPP[Co(Pc)$(CN)_2]_2$ show a similar Drude-Lorentz behavior in the infrared spectral range for the light polarized along the *c*-axis. For the light polarized along the *a*-axis, we did not observe the Drude behavior in the infrared range. This result suggests the similar one-dimensional electron system in these compounds. The resistance of both compounds increases on lowering the temperature, and the enhancement of the resistance in TPP[Fe(Pc)$(CN)_2]_2$ is several order of magnitude higher than that in TPP[Co(Pc)$(CN)_2]_2$ [1,2]. This striking difference in these compounds suggests the interaction between the conduction electrons (π-electrons) and the local moments (*d*-electrons).

In order to obtain the clear evidence for the interaction between the one-dimensional conduction electrons and the local moments, we measured the magnetoresistance and the magnetic susceptibility of the title compound. The comparison between TPP[Fe(Pc)$(CN)_2]_2$ and TPP[Co(Pc)$(CN)_2]_2$ will also give an valuable information concerning the influence of the local moments to the physical properties.

RESULTS AND DISCUSSIONS

Figure 1 shows the temperature dependence of the resistance under the magnetic field. The resistance increases on lowering the temperature. The DC four-probe resistance was measured with the current along the *c*-axis. One finds the kink structure around 50K. The excitation energy of the conduction is 0.015eV above 50K, and 0.026eV below 40K. When one applies the magnetic field, the resistance decreases below 50K. The negative magnetoresistance is larger for the field along the *a*-axis than along the *c*-axis. It should be

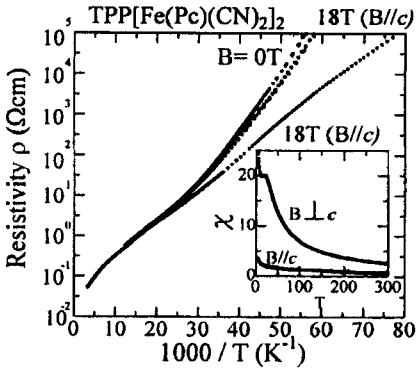

Figure 1 Main panel : Temperature dependence of the resistivity of TPP[Fe(Pc)$(CN)_2]_2$ under the magnetic field (18T) along the *a*-axis and along the *c*-axis. Inset : Temperature dependence of the magnetic susceptibility of TPP[Fe(Pc)$(CN)_2]_2$ for the field parallel and perpendicular to the *c*-axis. The molar unit in the susceptibility is one formula unit of $TPP_{0.5}$[Fe(Pc)$(CN)_2$].

noted that the resistance becomes smaller than one-tenth of magnitude of the zero field resistance at 20K and 18T.

If the negative magnetoresistance in the title compound is given by the Anderson localization, one expects the negative magnetoresistance for the field along the *a*-axis but no negative one for the field along the *c*-axis. It is because the magnetic field parallel to the one-dimensional conducting axis (the *c*-axis) can not change the phase of the electron conduction [3]. As shown in Fig.1, however, we observed the negative magnetoresistance for the field along not only the *a*-axis but also the *c*-axis. Thus we ruled out the possibility of the Anderson localization in the title compound.

The title compound has the local moments in the one-dimensional conduction path. One expects that the local moments cause the spin scattering of the itinerant electrons. In order to investigate the magnetic properties dominated by the local moments, we observed the magnetic susceptibility. The inset of Fig.1 shows the magnetic susceptibility for the field along the direction parallel and perpendicular to the *c*-axis. The susceptibility was measured by use of SQUID under the applied field of 1T. It is evident that the susceptibility shows an anisotropic Curie behavior. We observed the large susceptibility for the field perpendicular to the *c*-axis, while the small one along the *c*-axis. A least-square fit of the data ($B \perp c$) gives the Curie constant C = 0.81 emu K mol^{-1} and the Weiss temperature θ= -13.7 K.

The Pc molecule has a structure with four-fold symmetry. One expects a degeneracy in the molecular orbitals. The authors

(M.Matsuda *et al.*) calculated the molecular orbitals including the central transition atom Fe. The second highest occupied molecular orbital and the third one reflect the d_{yz}, d_{zx} orbitals of the Fe atom. The difference in the energy levels of these orbitals is quite small. Thus the spin-orbit coupling leads the high anisotropy of the *g*-factor and the susceptibility.

When one applies the magnetic field along the direction perpendicular to the *c*-axis, we observed the giant negative magnetoresistance and the large magnetic susceptibility. For the field along the *c*-axis, we observed the small negative magnetoresistance and the small susceptibility. The large (small) negative magnetoresistance was observed for the field orientation of the large (small) susceptibility. This correlation between the resistance and the susceptibility suggests that the magnetic moment induced by the magnetic field causes the negative magnetoresistance. This gives the experimental evidence for the π-*d* interaction between the local moments and the one-dimensional conduction electrons.

The negative magnetoresistance due to the interaction between the conduction electrons and the local moments reminds us of the spin scattering mechanism in the conventional Kondo systems. The negative magnetoresistance is caused by the decrease of the spin scattering of the conduction electrons by the local moments under the field in the Kondo systems. At the present stage, the nature of the interaction between the conduction electrons and the local moments is unclear in the title compound. According to Kondo's theory, in the case of an antiferromagnetic interaction, the spin scattering increases on lowering the temperature, while it decreases in a ferromagnetic one [4]. Figure 1 shows that the negative magnetoresistance increases as the temperature decreases. This temperature dependence suggests that the spin scattering increases on lowering the temperature. We believe that an antiferromagnetic interaction is dominant in the title compound.

The π-*d* interaction gives the spin-flip scattering of the itinerant electrons by the local moments. The magnetic field increases the population of the local moments parallel to the magnetic field, while it decreases the antiparallel ones. As a result, the field disturbs the free motion (spin-flip) of the local moments and reduces the spin-flip scattering of the itinerant electrons by the local moments. This gives the negative magnetoresistance.

We found that the reduction of the resistance under the field is approximately proportional to the square of the magnetic field strength

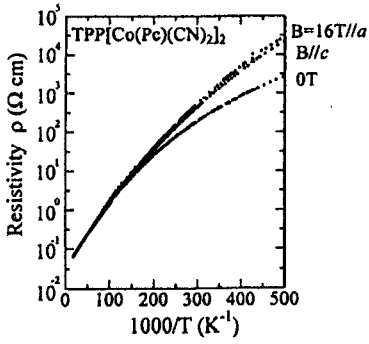

Figure 2 Temperature dependence of the resistivity of $TPP[Co(Pc)(CN)_2]_2$ in an absence of the magnetic field and under the static magnetic field (16T) along the *a*-axis and along the *c*-axis.

in the low field region. We also made sure that the magnetic moment is proportional to the magnetic field strength. Thus the reduction of the resistance is nearly proportional to the square of the magnetic moment. This correlation between the resistance and the susceptibility was also observed in the conventional Kondo systems [5, 6].

In order to compare with the one-dimensional transport properties without the local moments, we measured the magnetoresistance in the isostructural compound $TPP[Co(Pc)(CN)_2]_2$. Figure 2 shows the resistance of $TPP[Co(Pc)(CN)_2]_2$ in an absence of the field and under the magnetic field of 16T along the *a*-axis and the *c*-axis. The resistance increases on lowering the temperature. We found the large positive magnetoresistance below 8K for the field along not only the *a*-axis but also the *c*-axis. The positive magnetoresistance increases on lowering the temperature.

It should be noted that the giant negative magnetoresistance was observed in $TPP[Fe(Pc)(CN)_2]_2$, while the positive magnetoresistance in $TPP[Co(Pc)(CN)_2]_2$. These compounds have the similar one-dimensional conduction band. The former possesses the local moments in the conduction path but the latter has no local moments. Thus this comparison in these compounds strongly suggests that the giant negative magnetoresistance is caused by the local moments.

It is well known that the orbital effects can give the positive magnetoresistance. In such a case, the positive magnetoresistance can be calculated by use of Boltzmann transport equation. When one applies the magnetic field along the *a*-axis, the field is nearly perpendicular to the Fermi velocity and the field strongly confines the

electron motions. Thus the orbital effects under the magnetic field give the large positive magnetoresistance for the field along the ***a***-axis and the small one along the ***c***-axis. As shown in Fig.2, however, we did not observe the high anisotropy of the magnetoresistance. We also made sure that the magnetoresistance in $TPP[Co(Pc)(CN)_2]_2$ did not follow the Kohler's rule characteristic of the orbital effects. Therefore we ruled out the possibility of the positive magnetoresistance due to the orbital effects.

The optical spectra show the gap structure owing to the electron-electron correlation[1]. We think that the electron correlation contributes to the electron localization in the low temperature. The magnetic field confines the motion of the conduction electrons. This field effect enhances the electron localization due to the electron-electron correlation. One can expect a large positive magnetoresistance. However, at the present stage we can not give a definite explanation to the large positive magnetoresistance in $TPP[Co(Pc)(CN)_2]_2$. In order to investigate the nature of the conduction electrons in the correlated one-dimensional system, the measurement of the Hall effect is now under way.

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