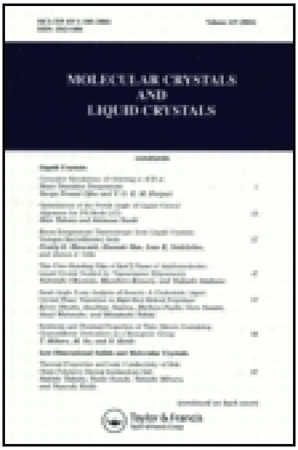

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A Molecular Superconductor Having a Solid-Crossing Column Structure, $Me_4N[Ni(dmit)_2]_2$

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A MOLECULAR SUPERCONDUCTOR HAVING A SOLID-CROSSING COLUMN STRUCTURE, $Me_4N[Ni(dmit)_2]_2$

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Abstract Electrical resistivity, thermoelectric power, and magnetic susceptibility were investigated under ambient pressure for $Me_4N[Ni(dmit)_2]_2$ which exhibits superconductivity under applied pressure. The metal-insulator transition of this salt was reexamined, and then the transition temperature was determined to be about 40 K from the temperature dependence of the thermoelectric power and electrical resistivity. The magnetic susceptibility revealed another phase transition at 11 K from paramagnetic insulator to diamagnetic insulator. This newly-found transition was attributed to the spin-Peierls transition.

INTRODUCTION

$Me_4N[Ni(dmit)_2]_2$ is one of the seven superconductors, known at present stage, in a series of $M(dmit)_2$ salts [M=Ni, Pd, Pt].[1] This salt exhibits superconductivity below 3 K under the pressure of 3.2 kbar, and below 5.0 K under the pressure of 7 kbar.[2] There are two equivalent conduction sheets in this salt.[3] In one conduction sheet, $Ni(dmit)_2$ molecules stack along the [110] direction while in the other conduction sheet they stack along the $[\bar{1}10]$ direction. These two kinds of conduction sheets are separated by the cation Me_4N^+ with the repeating distance of c/2. In the previous reports on this salt,[2a] it was concluded that this salt exhibits two kinds of resistivity anomaly, i.e. the anomaly around 100 K and that below 20 K. However, the origin of these anomaly has not been clarified yet for this salt.

In this report, we will present our experimental results on electrical resistivity, thermoelectric power, and magnetic susceptibility, for single crystals of $Me_4N[Ni(dmit)_2]_2$ under ambient pressure. Based on these results, we will discuss the temperature-pressure (T-P) phase diagram of this salt.

RESULTS AND DISCUSSIONS

Electrical Resistivity

The electrical-resistivity behaviors under the ambient pressure previously reported for this salt can be summarized as follows.[2] a)The resistivity within the ab-plane ($\rho_{//}$) abruptly increases below 20 K. b)The resistivity perpendicular to the ab-plane ($\rho_{\perp}$) behaves like a narrow-gap semiconductor with an activation energy of 0.002 eV over the whole temperature range below 300 K. c)Most of the crystals examined exhibit a jump and a succeeding increase of $\rho_{//}$ below 100 K, although some crystals exceptionally do not exhibit such a behavior.

The behaviors a) and b) were also observed in our measurements. Consequently, we concluded that these are intrinsic behaviors of $Me_4N[Ni(dmit)_2]_2$. As for the behavior c), although an anomalous resistivity increase corresponding to this behavior was observed also in our measurements, the temperature at which the resistivity increase occurred was strongly sample dependent.

We considered that the behavior c) (and the corresponding resistivity increase observed in our experiments) is an experimental artifact resulting from the following two factors, i.e. i)different temperature dependence of $\rho_{//}$ and $\rho_{\perp}$; ii)inhomogeneous current density distribution during the $\rho_{//}$ measurements. The "observed $\rho_{//}$" would be affected by the temperature dependence of $\rho_{\perp}$ as well as that of $\rho_{//}$ through the current distribution within a sample crystal. In addition, a crack formation in a sample crystal would cause a sudden change of the current distribution in the sample, resulting in a change of the temperature dependence of the "observed $\rho_{//}$". All these expectations are consistent with the behavior of c).

In order to examine the above-mentioned hypothesis, we measured the temperature dependence of both $\rho_{//}$ and $\rho_{\perp}$ simultaneously on one sample crystal.

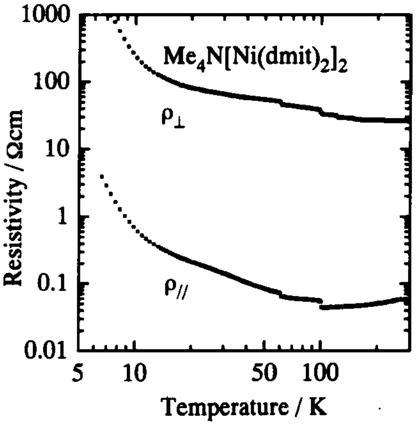

FIGURE 1 Temperature dependence of simultaneously measured resistivities ($\rho_{//}$ and $\rho_{\perp}$) for the current parallel and perpendicular to the crystallographic ab-plane.

Figure 1 shows the result of this measurement. The $\rho_{//}$ data between 100 K and 300 K is an increasing function of temperature, while the $\rho_\perp$ data in the corresponding temperature range is a decreasing function of temperature. Since we obtained these data simultaneously, the observed different behaviors should not originate from any sample-dependent factors. Thus, the temperature dependence of $\rho_{//}$ and $\rho_\perp$ should be inherently different. At 100 K both the curves of $\rho_{//}$ and $\rho_\perp$ exhibit a jump probably due to a crack formation in the sample. The change of sign in $d\rho_{//}/dT$ following the resistivity jump at 100 K can be explained by the above-mentioned interpretation on how the crack formation affects the temperature dependence of the "observed $\rho_{//}$".

In order to examine the effect of the inhomogeneous current distribution, we need geometrical information on a sample, such as the shape and size of a sample crystal, the shape and size of the electrodes attached on a sample, etc. Instead of making a strict analyses, we will roughly consider the geometrical condition that results in a inhomogeneous current density. The effect of inhomogeneous current density will be significant when the distance between the two current electrodes ($\ell_{//}$) is larger than the effective thickness $(\ell_\perp)_{eff}$ (which is defined as the thickness of the equivalent solid whose electrical resistivity is isotropic and whose electrostatic potential has one to one correspondence with the original sample; see Ref. 4). This is too simple, nevertheless, plausible idea, since the electrodes attached on the molecular conductors are generally far from the ideal ones. The value of $(\ell_\perp)_{eff}$ is evaluated to be $(\rho_\perp/\rho_{//})^{1/2}$ times of the actual thickness. Since the ratio of $\rho_\perp/\rho_{//}$ is about 10^3 in the present case, the value of $(\ell_\perp)_{eff}$ amounts to 2.7 mm for a sample having a thickness of 90 μm, (this value is the typical thickness for samples used in our resistivity measurements). On the other hand, the value of $\ell_{//}$ was about 1 mm in our experiments. Although we do not know the actual sample sizes used in the past measurements, [2] the above estimation provides us some grounds to assume that the condition $(\ell_\perp)_{eff} > (\ell_{//})$ was fulfilled in most of experiments. In that case, the current distribution in the sample should be inhomogeneous in the measurements of $\rho_{//}$.

On the basis of discussion given above we conclude that the behavior c) is not an intrinsic behavior but an experimental artifact. This conclusion yields a new question what is the intrinsic temperature dependence of $\rho_{//}$. The resistivity behavior a) seems to give us a clue to the solution for this question. One of the resistivity data previously reported (the curve (c) in Fig. 1 of Ref. 2a) exhibits only the resistivity increase described in the behavior a), i.e. resistivity take a broad minimum around 40 K, and abruptly increases below 20 K. We think that this resistivity behavior is the intrinsic behavior of $\rho_{//}$ in $Me_4N[Ni(dmit)_2]_2$, although we cannot completely exclude the possibility that this temperature dependence is still affected by the temperature dependence of $\rho_{\perp}$.

Thermoelectric Power

As discussed above, the metal-insulator-transition temperature derived from the temperature dependence of $\rho_{//}$ remain still uncertain to some extent. Thus, we have done thermoelectric power measurements in order to determine the transition temperature. Figure 2 shows the results of the measurements obtained for several single crystals of $Me_4N[Ni(dmit)_2]_2$. Although a series of experiments done in a similar condition exhibit sample-dependent behaviors also in this thermoelectric power measurement, the degree of sample dependence was quite low as compared with electrical resistivity. In addition we did not observed any hysteresis behavior in the temperature dependence of thermoelectric power. These facts indicate that thermoelectric power is less affected by the sample quality than the electrical resistivity. We determined the metal-insulator transition temperature of this salt as the temperature corresponding to the inflection point of a curve of thermoelectric power. This temperature is approximately 40 K for all the curves shown in Fig. 2. Thus determined metal-insulator transition temperature is consistent with the conclusion obtained for the electrical resistivity.

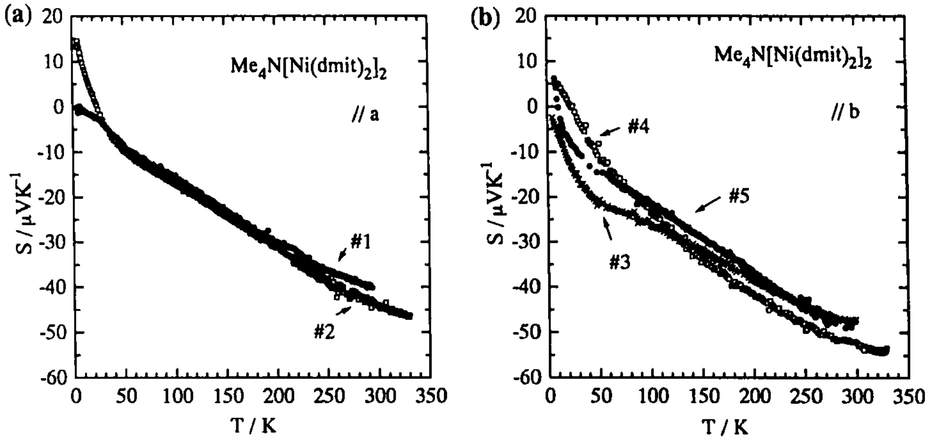

FIGURE 2 Temperature dependence of thermoelectric power parallel to the crystallographic a-axis (a) and to the b-axis (b).

Magnetic Susceptibility

Figure 3 shows the temperature dependence of magnetic susceptibility for $Me_4N[Ni(dmit)_2]_2$. The measurement of magnetic susceptibility was done by use of a single crystal (1.5 mg) under a magnetic field of 1 T. The diamagnetic component of the magnetic susceptibility was estimated by use of Pascal law to be -4.4×10^{-4} emu• mol^{-1}.[5] The magnetic susceptibility gradually increases from room temperature down to 240 K, where it takes a broad maximum. Below this temperature the susceptibility gradually decreases down to 11 K, where the susceptibility suddenly drops. This drop of susceptibility was observed for all the three magnetic field directions applied (*B* // a, *B* // c, *B* // c*). Consequently, we concluded that the transition at 11 K is not a transition into magnetically ordered state but a transition into a diamagnetic state. It should be noted that the magnetic susceptibility does not exhibit any anomaly around 40 K, which is the metal-insulator transition temperature of $Me_4N[Ni(dmit)_2]_2$ determined from the thermoelectric power. In other words, this salt exhibits successive transitions from metal to paramagnetic insulator and from paramagnetic insulator to diamagnetic insulator. Similar behavior has been already known in one-dimensional conductors such as $TMTTF_2AsF_6$.[6] In this salt the upper transition was attributed to $4k_F$ CDW formation and the lower transition to the spin-Peierls transition. By applying this interpretation also to $Me_4N[Ni(dmit)_2]_2$, we attributed the transition at 40 K to the $4k_F$ CDW transition and the transition at 11 K to the spin-Peierls transition.

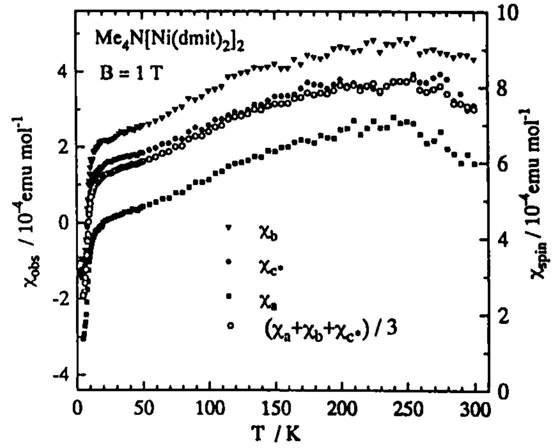

FIGURE 3 Temperature dependence of magnetic susceptibility for the magnetic field applied along crystallographic a-, b-, c*-axis.

T-P phase diagram

Figure 4 shows the universal T-P phase diagram known for one-dimensional conductors[7] and the T-P phase diagram derived for $Me_4N[Ni(dmit)_2]_2$ on the basis of the experimental results obtained in this study and the superconducting-transition temperature determined in Ref. 2. The most striking point in the phase diagram of $Me_4N[Ni(dmit)_2]_2$ is that the spin-Peierls ground state is just in the vicinity of superconducting state. Moreover, there still remain the possibility that these two phases are directly touch each other at some pressure. This possibility should be further examined in future.

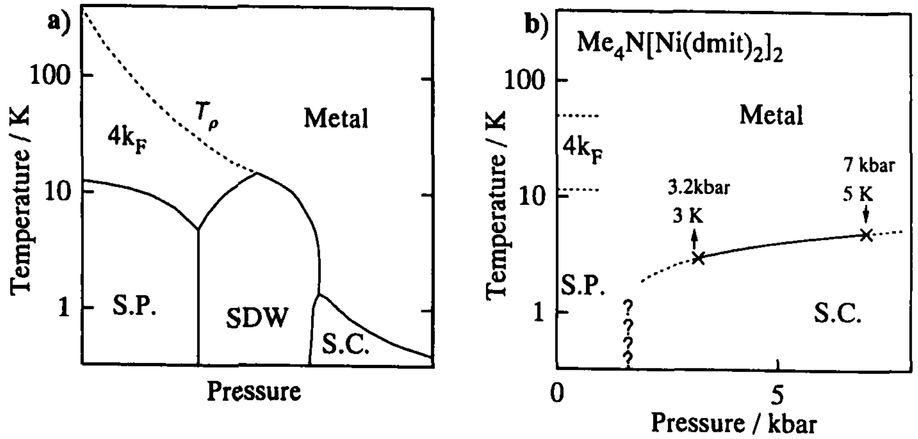

FIGURE 4 (a) The universal T-P phase diagram presented for one-dimensional conductors[7]; (b) Postulated T-P phase diagram of $Me_4N[Ni(dmit)_2]_2$.

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