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First Ambient-pressure Superconductor Based on Ni(dmit)$_2$, α-EDT-TTF[Ni(dmit)$_2$]

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The donor-acceptor type molecular conductor, α-(EDT-TTF)[Ni(dmit)$_2$], was found to be a superconductor under ambient pressure below 1.3 K. This is the first ambient-pressure superconductor in a series of M(dmit)$_2$ salts [M=Ni, Pd, Pt]. The sample dependence and magnetic-field dependence on the superconducting transition are described.

M(dmit)$_2$ [M=Ni, Pd, Pt, Au; dmit=4,5-dimercapto-1,3-dithiole-2-thione] are known to form a number of conducting salts with organic or inorganic cations.1) Among them six salts (i.e. TTF[Ni(dmit)$_2$]$_2$,2) α -TTF[Pd(dmit)$_2$]$_2$,3) α '-TTF[Pd(dmit)$_2$]$_2$,3) Me$_4$N[Ni(dmit)$_2$]$_2$4,) β -Me$_4$N[Pd(dmit)$_2$]$_2$,5) α-Me$_2$Et$_2$N[Pd(dmit)$_2$]$_2$6)) were found to become superconductor at low temperatures by applying high pressure, and five salts (TTF[Ni(dmit)$_2$]$_2$,2) α-Me$_2$Et$_2$N[Ni(dmit)$_2$]$_2$,7) α-C$_7$H$_{16}$N[Ni(dmit)$_2$]$_2$,8) α-EDT-TTF[Ni(dmit)$_2$]9), Na[Ni(dmit)$_2$]$_2$1), EDT-TTF$_2$[Pd(dmit)$_2$]$_2$10)) were reported to remain metallic down to temperatures lower than 4.2 K. However, none of them has been reported so far to be superconductive under ambient pressure.

There are two crystal forms in EDT-TTF[Ni(dmit)$_2$] salt, α- and β-forms. The β–form is a semiconductor with a mixed-stacking structure, while the α-form is a donor-acceptor type of an organic conductor having two types of conduction sheet parallel to the crystallographic ab-plane, one of which is formed by EDT-TTF molecules stacked along [110] and the other by Ni(dmit)$_2$ molecules stacked along [010] direction. This solid-crossing column structure gives quasi-two-dimensional character to the α-form.9) The electrical resistivity of the α-form is metallic down to 20 K. At 20 K, the resistivity begins to increase, has a peak around 10 K-14 K and then decreases down to 1.3 K.9,11) The upturn of the electrical resistivity below 20 K was ascribed to the CDW or SDW formation within a conduction sheet composed of EDT-TTF based on weak-field magnetoresistance measurements for the magnetic field rotated within the ab-plane.11) In this communication we will report the first experiment on superconductivity of this salt under ambient pressure.

The two forms of single crystals were simultaneously obtained by electrochemical crystallization in an acetonitrile solution containing [Bu$_4$N]$_2$[Ni(dmit)$_2$] and EDT-TTF.9) The appearance of these two forms are too close to be discriminated by the observation. In order to select out an α-form crystal from the electrochemically synthesized crystals we have measured reflectivity in the infrared region. In this spectral range α-form has high reflectivity due to its metallic character12), in contrast with the relatively low reflectivity of the β-form. The electrical resistivity was measured by use of a lock-in amplifier with a current of 10 μA at 70 Hz. Four-probe electrical contacts were prepared by carbon paste. The temperature of samples was measured by a platinum film sensor(T>28 K) and a carbon glass sensor attached to the sample chamber. The samples were cooled down by ^{4}He gas above 4.2 K and by pumped liquid ^{4}He below 4.2 K. The lowest temperature achieved by this method was 1.3 K in this experiment.

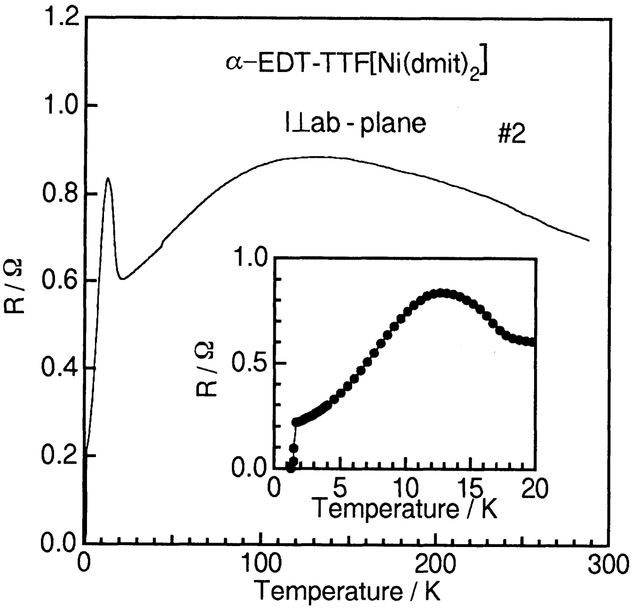

Fig. 1. Electrical resistance of α-(EDT-TTF)[Ni(dmit)$_2$] (sample #2). The inset shows the data below 20 K.

Figure 1 shows the electrical resistance of a crystal (sample #2) for the current perpendicular to the ab-plane. Between 290 K and 20 K the resistance is weekly dependent on temperature, showing broad maximum around 120 K. Below 20 K the resistance abruptly increases on lowering temperature showing a maximum around 12 K, then decreases. Note that resistance drops at 1.5 K and goes to zero at 1.3 K. This indicates that the sample #2 undergoes superconducting transition below 1.5 K.

The behavior seems to be somewhat different depending on the sample crystals, as shown in Fig. 2. However, resistance drops are observed in most of samples around 1.3 K, although resistance does not reach to zero at 1.3 K for the samples other than #2.

In order to confirm the transition to a superconductor at 1.3 K, we have performed the resistance measurements under magnetic field. Figure 3 shows the magnetic-field-strength dependence of the resistance of the sample #8 at 1.3 K and 2.8 K (i.e. below and above the resistance drop) for the magnetic field and current within conductive ab-plane. At 1.3 K the resistance increases by applying the magnetic field and then saturates above 4000 G. On the other hand the resistance at 2.8

K remains almost constant in whole the magnetic-field range shown in Fig. 3. The above results can not be accounted for by the classical mechanism of the magnetoresistance[13] without considering superconductive transition at 1.3 K. First, the saturation of resistance is observed at 4000 G, which is unusually small magnetic field. In order to explain this saturation, we need to assume carriers with extremely small effective mass and long relaxation time. Secondly, the difference of magnetoresistance behavior between 1.3 K and 2.8 K is hard to be understood unless we assume drastic change of relaxation rate between 1.3 K and 2.8 K.

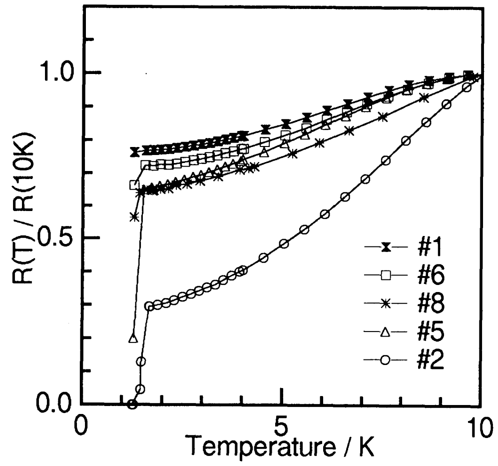

Fig. 2. The electrical resistance versus temperature for several samples.
#1, #6, #5, #2:I⊥ab-plane
#8:I//ab-plane.

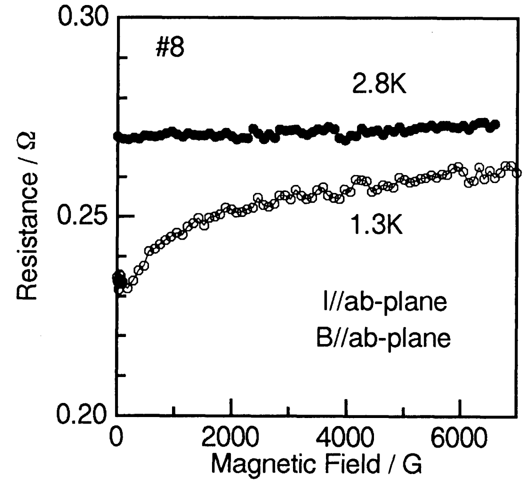

Fig. 3. The magnetic field dependence of the resistance (0 G<H<7000 G) at 1.3 K and 2.8 K.

From these reasons we consider that the saturation phenomena of resistance against magnetic field at 1.3 K depicted in Fig. 3 is attributable to the suppression of the superconductivity due to magnetic field. The magnetic-field strength, 4000 G, can be associated with an upper critical magnetic field of the sample.

In conclusion, we have found the first ambient-pressure superconductor, α-EDT-TTF[Ni(dmit)$_2$], with a transition temperature of 1.3 K. Although most samples do not enter complete zero-resistance state at 1.3 K, their resistance against magnetic field at 1.3 K is that peculiar to a superconductor. Experiments on critical field anisotropy below 1.3 K are now in progress, and will be published elsewhere.

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