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[Pd(dmit)<sub>2</sub>] salts is reported.

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### Superconductivity of [Pd(dmit)<sub>2</sub>] Salts under Pressure Studied by an RF Technique

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An instrument for detection of a shielding effect of RF magnetic fields (2 - 8 MHz) has been developed to investigate the characteristics of the superconductivity (SC) of some [Pd(dmit)<sub>2</sub>] salts. The main part of the system consists of two LC oscillators, which can operate at low temperatures. The shielding signal due to a superconducting transition of the sample in the coil is detected as an increase of the frequency of the RF output. The coils are set within a clamp-type pressure cell. SC in a few [Pd(dmit)<sub>2</sub>] salts was investigated by using this system. An increase in the frequency was observed below 4 K under pressure. This may indicate the existence of the superconducting transition of the [Pd(dmit)<sub>2</sub>] salts. However, the shielding signal was about 10<sup>-2</sup> times as small as that observed in an ordinary organic superconductor such as κ-(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>Br]. This peculiarity of the SC in the

Keywords: [Pd(dmit)<sub>2</sub>] salts; superconductor; RF shielding

#### INTRODUCTION

Molecular conductors based on acceptor molecules, metal-dithiolene complexes  $M(dmit)_2$  (M = Ni, Pd, Pt) (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) are of interest in their various structural and physical properties. In particular, some of  $[Pd(dmit)_2]$  salts are known to show peculiar pressure and temperature dependence of the electric conductivity. For instance,  $(CH_3)_4Sb[Pd(dmit)_2]_2$  and  $(C_2H_5)_2(CH_3)_2P[Pd(dmit)_2]_2$  (abbreviated as  $Me_4Sb[Pd(dmit)_2]_2$  and  $Et_2Me_2P[Pd(dmit)_2]_2$ , respectively) behave as an insulator in the low pressure region. As pressure increases, the systems exhibit metallic behavior and then superconducting transition at low temperature. In addition, a non-metallic phase appears again in higher pressure region<sup>[1,2]</sup>.

In order to probe the characteristics of the SC of these materials, we have developed an instrument which can detect a shielding effect of RF magnetic fields (2 - 8 MHz). We found that the SC in the measured [Pd(dmit)<sub>2</sub>] salts is different from that in an ordinary organic superconductor. In the present paper, the peculiarity of the SC in [Pd(dmit)<sub>2</sub>] salts is reported.

#### **EXPERIMENTAL**

A diagram of the measurement system is shown in Figure 1. The main part of the system consists of two LC oscillators, which can operate at low temperatures. The two coils in the circuits are set within a clamp-type pressure cell. 2 - 3 mg of polycrystalline sample is mounted in the one coil (2.5mm $\phi$ , 30 turns  $\times$  3 layers). The samples put in the coil are put between glass wool containing pressure medium and held

by Teflon stoppers to be kept in the coil. A piece of tin wire  $(1.0\text{mm}\phi)$  was put in the other coil  $(2\text{mm}\phi, 22\text{ turns} \times 3\text{ layers})$  as a manometer.

The RF signal output from the oscillators (2 - 8 MHz, depending upon the L and C values) is led to a frequency counter. The shielding signal due to a superconducting transition of the sample in the coil is detected as an increase of the frequency of the RF output of the oscillator.

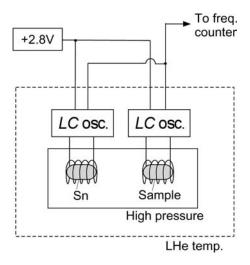


FIGURE 1 Diagram of the measurement system.

In such a system, heating up of the coil is often taken notice. We succeeded to minimize the alternating current in the coil by using CMOS devices which can operate with a low voltage power supply (2.8 V). The oscillator circuit itself is so small that it is easily installed in a LHe dewar together with the clamp cell.

Using this system, the SC in  $Me_4Sb[Pd(dmit)_2]_2$ ,  $Et_2Me_2P[Pd(dmit)_2]_2$  and  $Et_2Me_2N[Pd(dmit)_2]_2$  were studied down to 2 K under pressure. The temperature of the pressure cell was monitored by a thermometer set in a copper block contacted onto the cell.

#### RESULTS AND DISCUSSION

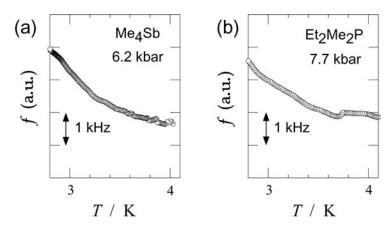


FIGURE 2 Temperature dependence of oscillation frequencies of Me<sub>4</sub>Sb[Pd(dmit)<sub>2</sub>]<sub>2</sub> (a) and Et<sub>2</sub>Me<sub>2</sub>P[Pd(dmit)<sub>2</sub>]<sub>2</sub> (b).

For  $Me_4Sb[Pd(dmit)_2]_2$ , drop of resistivity suggesting a superconducting transition near 10 kbar was previously reported<sup>[3]</sup>. The drop of the resistivity is also reported by A. Eguchi et al. in the pressure region 6 - 8.5 kbar<sup>[1]</sup>. In this pressure region, we observed a gradual increase of the frequency, as shown in Figure 2 (a). Similar behavior observed in the same method was reported by A. Eguchi et al<sup>[1]</sup>. We observed such behavior also for Et<sub>2</sub>Me<sub>2</sub>P[Pd(dmit)<sub>2</sub>]<sub>2</sub> (Figure 2 (b)). SC of this material is suggested to appear at 7 - 10.5 kbar by resistivity measurements<sup>[2]</sup>. An important feature is the small amplitudes of the shielding signal of these two salts; they are about 10<sup>-2</sup> times as small as that observed in another organic superconductor  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>Br] recorded using the same measurement system (Figure 3). It is also noticed that the temperature dependence of the RF shielding signals of the [Pd(dmit)<sub>2</sub>] salts are anomalous, as compared with that of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>Br]. In Et<sub>2</sub>Me<sub>2</sub>N[Pd(dmit)<sub>2</sub>]<sub>2</sub>, we could not recognize any obvious signal in the pressure region 2.4 - 5 kbar, whereas SC was suggested to appear in this region<sup>[4]</sup>.

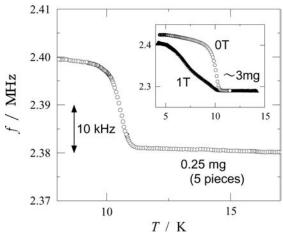


FIGURE 3 Typical RF shielding behavior of  $\kappa\text{-}(BEDT\text{-}TTF)_2Cu[N(CN)_2Br] \ observed \\ by \ present \ method$ 

To explain these results, some reasons are conceivable. If the SC occurs only in a certain conduction path or surface, then the conductivity measurement can observe drop of the resistance. On the other hand, the diamagnetic shielding probes the bulk behavior. Therefore, it is expected that the SC occurs only in a small part of a crystal in the studied  $[Pd(dmit)_2]$  salts. Distribution of  $T_c$  from crystal to crystal may also obscured a clear SC transition. A lower critical field

 $H_{c1}$  may be responsible for the weak shielding. Upper critical field  $H_{c2}$  of  $Et_2Me_2P[Pd(dmit)_2]_2$  is reported to be high when the field is applied parallel to the plane<sup>[5]</sup>, therefore, a low intra-plane  $H_{c1}$  of about 2 - 3 G is expected. Since the RF field in the coil is estimated to be about 2 - 3 G, the shielding effect may be obscured by the RF field during the measurement. However, the shielding signal is still too small, even though an isotropy of the sample mounting is taken into account. It is required to study magnetization process and the transport properties for various field direction, in order to clarify the SC in the [Pd(dmit)\_2] salts, paying attention also to sample dependence.

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