

## Magnetic study of quantum triangular antiferromagnet [Pd(dmit)<sub>2</sub>] salts under pressure

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 145239

(<http://iopscience.iop.org/0953-8984/19/14/145239>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 17:30

Please note that [terms and conditions apply](#).

# Magnetic study of quantum triangular antiferromagnet [Pd(dmit)<sub>2</sub>] salts under pressure

M Tamura, Y Ishii and R Kato

Condensed Molecular Materials Laboratory, RIKEN, Wako, Saitama 351-0198, Japan

E-mail: [tam@riken.jp](mailto:tam@riken.jp)

Received 6 September 2006

Published 23 March 2007

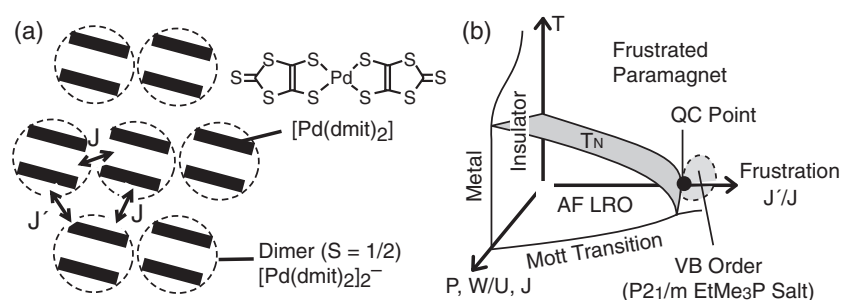
Online at [stacks.iop.org/JPhysCM/19/145239](http://stacks.iop.org/JPhysCM/19/145239)

## Abstract

The magnetic susceptibilities of two [Pd(dmit)<sub>2</sub>] salts, Et<sub>2</sub>Me<sub>2</sub>P[Pd(dmit)<sub>2</sub>]<sub>2</sub> and EtMe<sub>3</sub>P[Pd(dmit)<sub>2</sub>]<sub>2</sub>, were measured under pressure up to about 0.5 GPa. These compounds have different ground states at ambient pressure, but both become metallic under pressure. It is found that the temperature dependence of susceptibility in the metallic states is an unconventional one, magnetically similar to the frustrated paramagnetic states. This indicates that the electrons are strongly correlated even in the metallic state.

## 1. Introduction

Realization of strongly frustrated spin states in some organic Mott insulators [1–3] has received attention from both the experimental and theoretical sides. Such compounds have two-dimensional (2D) nearly close-packed structures, i.e., a spatially anisotropic triangular lattice, formed from dimers of organic molecules (figure 1(a)). At ambient pressure, each unpaired electron is localized on each dimer, as a result of intradimer electron repulsion,  $U$ . Such spin systems can provide substantial physical properties related to the quantum criticality (QC) [4] due to the suppression of magnetic long-range order (LRO) by frustration, because organic molecular systems behave as good spin-1/2 quantum Heisenberg systems. Among them,  $\kappa$ -(ET)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> (ET = bis(ethylenedithio)tetrathiafulvalene) exhibits no LRO down to 32 mK [2], and its possible spin-liquid ground state near QC is a topic of active research. On the other hand, in a series of anion radical salts, Et<sub>*x*</sub>Me<sub>4-*x*</sub>Z[Pd(dmit)<sub>2</sub>]<sub>2</sub> (Et = C<sub>2</sub>H<sub>5</sub>, Me = CH<sub>3</sub>, dmit<sup>2-</sup> = 1,3-dithiol-2-thione-4,5-dithiolate,  $x = 0, 1, 2$  and Z = P, As, Sb), the spatial anisotropy of the exchange couplings  $J$  can be regulated by choosing the counter cations [5]. This gives rise to a variety of ground states, with or without magnetic LRO, showing how the spin system approaches QC with frustration depending on the spatial anisotropy, or on the details of the lattice structure.



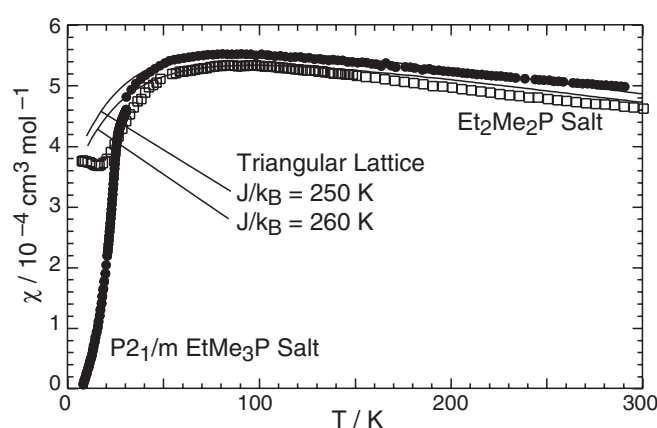
**Figure 1.** (a) Schematic view of the spatially anisotropic triangular packing of molecular dimers in a layer of the  $[\text{Pd}(\text{dmit})_2]$  salt. (b) A sketch of the phase diagram of the  $[\text{Pd}(\text{dmit})_2]$  salt.

Another significant criticality in these systems is the insulator-to-metal (I–M) transition (the Mott transition) observed under pressure. For organic systems, the bandwidth,  $W$ , is readily enhanced by pressure. This reduces the parameter  $U/W$  so that the metallic state attains stability. In fact, most  $[\text{Pd}(\text{dmit})_2]$  salts become metallic due to the increase in  $W$  with pressure [5, 6]. In ordinary unfrustrated half-filled systems, the metallic state competes with the antiferromagnetic (AF) LRO for stability at low temperatures. The stability of the AF LRO, owing to the exchange energy gain and small entropy, is diminished by frustration. This gives rise to relative stability of the metallic state. A sketch of the phase diagram is shown in figure 1(b). The main topic of this work is to observe the magnetic behaviour of this frustration-induced metallic state in the  $[\text{Pd}(\text{dmit})_2]$  salts. This sheds light on the nature of the metallic state near the Mott criticality and the spin QC.

The in-plane structure of the  $[\text{Pd}(\text{dmit})_2]$  salts is schematically shown in figure 1(a). Each dimer  $[\text{Pd}(\text{dmit})_2]_2^-$  has one localized unpaired electron (spin-1/2). The calculations of the interdimer overlap integrals indicate that the spatial anisotropy of the interdimer interactions can be approximated by an isosceles model shown in figure 1(a), and the anisotropy systematically varies with the cation [5]. The correlation between the anisotropy and the AF LRO temperature ( $T_N$ ) has been pointed out [7].

The temperature dependence of magnetic susceptibilities  $\chi$  of the  $[\text{Pd}(\text{dmit})_2]$  salts at ambient pressure is well explained by the high-temperature series expansion theory for the spin-1/2 Heisenberg AF model on the regular triangular lattice [8], particularly above the temperatures of  $\chi$  maxima [1]. Various magnetic properties appear at low temperatures, reflecting the variety of the ground states depending on the cation. Some examples are shown in figure 2. The  $[\text{Pd}(\text{dmit})_2]$  salts can be categorized as follows, in view of the physical properties [1, 5]:

- (i) The  $\text{Me}_4\text{P}$  and  $\text{Me}_4\text{As}$  salts exhibit AF LRO at  $T_N \approx 40$  K. The spatial anisotropy of these salts is the largest in the series. They do not show metallic conductivity at low temperature under hydrostatic pressure, though the resistivity is reduced.
- (ii) The  $\text{Me}_4\text{Sb}$ ,  $\text{Et}_2\text{Me}_2\text{P}$ ,  $\text{Et}_2\text{Me}_2\text{As}$  and  $\text{EtMe}_3\text{As}$  salts exhibit AF LRO in the range  $T_N \approx 15$ –25 K (figure 2). They become metallic under hydrostatic pressure of about 0.5 GPa.
- (iii) The  $\text{EtMe}_3\text{P}$  salt (the  $P2_1/m$  phase) [9, 10] is close to a regular triangular lattice. This salt exhibits a second-order transition to a spin-gapped state at 25 K (figure 2). This transition, as well as the spin–Peierls transition, is accompanied by the breaking of translational symmetry. The ground state is a columnar spin-dimer phase, in which the spin-singlet valence-bonds are ordered (VB order). This salt exhibits metallic conductivity at low



**Figure 2.** Temperature dependence of susceptibilities of the  $\text{Et}_2\text{Me}_2\text{P}$  salt and  $\text{EtMe}_3\text{P}$  salt ( $P2_1/m$ ), together with the calculated values for the regular triangular lattice model.

temperature above about 0.2 GPa, accompanied by superconductivity ( $T_c = 5$  K at 0.2 GPa).

- (iv) The  $\text{Et}_2\text{Me}_2\text{Sb}$  salt undergoes a first-order transition to a non-magnetic state with complete charge separation,  $2\text{dimer}^- \rightarrow \text{dimer}^{2-} + \text{dimer}^0$ , at 70 K. This is the pairing of electrons in a dimer, coupled to the local lattice distortion, which is driven by the two-level structure specific to the dimerized  $[\text{Pd}(\text{dmit})_2]$  system [11–14].
- (v) The  $\text{EtMe}_3\text{Sb}$  salt remains in the frustrated paramagnetic state down to low temperature.

In this paper, we report the pressure dependence of  $\chi$  of the  $\text{Et}_2\text{Me}_2\text{P}$  salt and  $\text{EtMe}_3\text{P}$  salt ( $P2_1/m$ ), which show the AF LRO and VB-ordered ground states, respectively, at ambient pressure. Application of pressure up to about 0.5 GPa suppresses the phase transitions to the ordered phases in both cases, so as to reveal peculiar magnetic behaviour of the frustration-induced metallic state near the Mott criticality.

## 2. Experimental details

Black plate-like crystals of the  $[\text{Pd}(\text{dmit})_2]$  salts were obtained by air-oxidation of the acetone solution of  $(\text{EtMe}_3\text{P})_2[\text{Pd}(\text{dmit})_2]$  or  $(\text{Et}_2\text{Me}_2\text{P})_2[\text{Pd}(\text{dmit})_2]$ , containing acetic acid at 5–10 °C. The polycrystalline samples (8–10 mg) packed in a cylindrical capsule were installed in a slender clamp-type Cu–Be pressure cell (ElectroLAB Co., LPC-15), designed for magnetic measurements, together with spacer rods and Daphne 7373 oil as pressure medium. The capsule and spacer rods were made of fluorocarbon polymer. The magnetization signals of the samples were recorded under 5 T by a Quantum Design MPMS-XL7 SQUID system. The obtained data were corrected for the background from the experimental setup, so as to give the ambient pressure values properly. The pressure applied to the samples at low temperature was estimated at each run by the shift of  $T_c$  of a small Pb piece installed in the capsule.

## 3. Results and discussion

Figure 3 shows the temperature dependence of  $\chi$  of the  $\text{Et}_2\text{Me}_2\text{P}$  salt at various pressures. As well as at ambient pressure, the low-pressure  $\chi$  exhibits a broad maximum near 70 K, which is characteristic of a spin-1/2 Heisenberg triangular antiferromagnet [1, 8]. The appearance

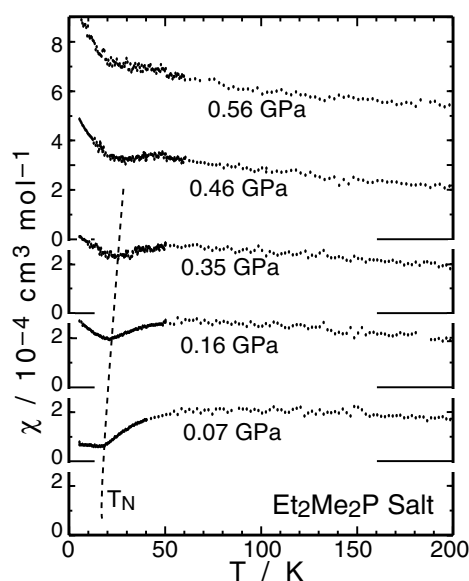
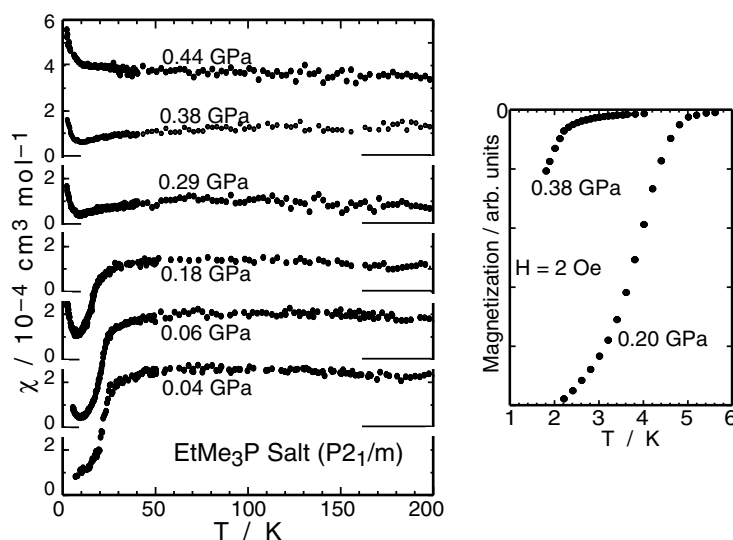


Figure 3. Temperature dependence of  $\chi$  for the  $\text{Et}_2\text{Me}_2\text{P}$  salt at various pressures.

of AF LRO can be recognized as the bend of  $\chi$  curve at  $T_N = 20$  K at 0.07 GPa. It is found that  $T_N$  increases with pressure;  $T_N = 25$  K at 0.35 GPa. The AF LRO anomaly is considerably obscured at 0.46 GPa, and only a shallow minimum is observed around 30 K. This temperature coincides with that of the upturn of resistivity [15]. At a higher pressure, the resistivity behaviour becomes metallic down to low temperature [15]. In this pressure-induced metallic state, the  $\chi$  minimum corresponding to AFLRO disappears, and  $\chi$  gradually increases upon cooling, as indicated by the 0.56 GPa data. The  $\chi$  behaviour above 70 K is substantially unchanged up to 0.56 GPa, while the system changes from a Mott insulator to a metal. The susceptibilities in the metallic state take enhanced values close to those of the paramagnetic insulating state near the boundary. This  $\chi$  behaviour in the metallic state is dissimilar to the temperature-independent Pauli paramagnetic one expected for a simple metal. The enhanced and weakly temperature-dependent  $\chi$  indicates suppression of the double occupancy by the carriers and suggests that the electrons are strongly correlating even in the metallic state near the Mott criticality.

Temperature dependence of  $\chi$  of the  $\text{EtMe}_3\text{P}$  salt (the  $P2_1/m$  phase) at various pressures is shown in figure 4. At low pressures ( $P < 0.1$  GPa), the VB ordering is recognized by the anomaly of  $\chi$ , i.e., the onset of a rapid decrease indicating the transition to the spin-gapped state. Slight lowering of the VB ordering temperature is observed at low pressures; it is 23 K at 0.06 GPa. This is in accord with the x-ray results indicating that the VB ordering is accompanied by volume expansion [9, 10]. The system is entirely insulating in this pressure range.

At 0.18 GPa, the anomaly in  $\chi$  is broadened and shifts to lower temperature, about 18 K, and the drop of  $\chi$  becomes incomplete. These features can be interpreted as a result of suppression of the spin-gap opening by pressure. Another possibility is the disappearance of the VB order even in this pressure range. Since the  $\chi$  behaviour resembles that of the AF LRO case, it is presumable to think that AF LRO occurs near 10 K. The resistivity  $\rho$  exhibits reentrant behaviour [10] in the corresponding pressure range; a metallic state appears between



**Figure 4.** Left: temperature dependence of  $\chi$  for the  $\text{EtMe}_3\text{P}$  salt at various pressures. Right: diamagnetic signal indicating bulk superconductivity below 5 K.

about 10 K and about 20 K. If the incomplete drop of  $\chi$  corresponds to AF LRO, the low-temperature insulating phase is ascribed to the AF LRO phase below 10 K. This tentative idea is open for further research and should be checked by other experimental techniques such as NMR. A large diamagnetic signal indicating superconductivity is observed at low fields below  $T_c = 5$  K. This is the first magnetic evidence of bulk superconductivity among the  $[\text{Pd}(\text{dmit})_2]$  salts.

Above 0.25 GPa,  $\chi$  does not show a remarkable anomaly, whereas  $\rho$  indicates an I–M transition around 30 K as the temperature decreases. Entirely metallic behaviour of  $\rho$  is observed above about 0.4 GPa. However, the  $\chi$  behaviour at 0.44 GPa is similar to that of the insulating state. As well as in the  $\text{Et}_2\text{Me}_2\text{P}$  salt, the  $\chi$  behaviour changes little through the boundary between the frustration-induced metallic state and the paramagnetic insulator phase. This indicates that the electrons are still strongly correlating in the metallic phase. Superconductivity is observed in this pressure range.  $T_c$  gradually decreases with pressure;  $T_c = 3$  K at 0.44 GPa.

#### 4. Conclusion

It has been shown that  $\chi$  varies almost continuously as the system changes from the insulator to the metallic state with pressure. The metallic state shows appreciably temperature-dependent  $\chi$ , indicating the strongly correlated nature of the electrons. Both suppression of the VB order by pressure and pressure-induced superconductivity are found in the  $P2_1/m$  phase of the  $\text{EtMe}_3\text{P}$  salt.

#### Acknowledgments

This work is supported by Grants-in-Aid for Scientific Research (Nos. 15550135, 16GS0219 and 18043024) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

## References

- [1] Tamura M and Kato R 2002 *J. Phys.: Condens. Matter* **14** L729
- [2] Shimizu Y, Miyagawa K, Kanoda K, Maesato M and Saito G 2003 *Phys. Rev. Lett.* **91** 107001
- [3] Zheng W, Singh R R P, McKenzie R H and Coldea R 2005 *Phys. Rev. B* **71** 134422
- [4] Sachdev S 1999 *Phys. Rev. B* **55** 142
- [5] Kato R 2004 *Chem. Rev.* **104** 5319
- [6] Yamaura J-I, Nakao A and Kato R 2004 *J. Phys. Soc. Japan* **73** 976
- [7] Nakamura T, Takahashi T, Aonuma S and Kato R 2001 *J. Mater. Chem.* **11** 2159
- [8] Elstner N, Singh R R P and Young A P 1993 *Phys. Rev. Lett.* **71** 1629
- [9] Tamura M, Nakao A and Kato R 2006 *J. Phys. Soc. Japan* **75** 093701
- [10] Kato R, Tajima A, Nakao A and Tamura M 2006 *J. Am. Chem. Soc.* **128** 10016
- [11] Tamura M and Kato R 2004 *Chem. Phys. Lett.* **387** 448
- [12] Tamura M, Tajima A and Kato R 2005 *Synth. Met.* **152** 397
- [13] Tamura M, Takenaka K, Takagi H, Sugai S, Tajima A and Kato R 2005 *Chem. Phys. Lett.* **411** 133
- [14] Nakao A and Kato R 2005 *J. Phys. Soc. Japan* **74** 2754
- [15] Kato R, Kashimura Y, Aonuma S, Hanasaki N and Tajima H 1998 *Solid State Commun.* **105** 561