Reentrant Mott transition from a Fermi liquid to a spin-gapped insulator in an organic spin-1/2 triangular-lattice antiferromagnet



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# Reentrant Mott transition from a Fermi liquid to a spin-gapped insulator in an organic spin-1/2 triangular-lattice antiferromagnet

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**Abstract**

The pressure-induced Mott transition is investigated in a quasi-two-dimensional molecular conductor, $EtMe_3P[Pd(dmit)_2]_2$ ($P2_1/m$) with a triangular lattice, which shows a valence bond solid state at ambient pressure. Near the critical pressure of the Mott boundary, an insulator-to-metal transition occurs at 18 K, followed by a first-order reentrant metal-to-insulator transition below 12 K. Finally, a superconducting transition from the insulating state is observed at 5.2 K. The reentrant metal–insulator transition temperature is lowered by application of magnetic field. The result indicates the presence of a spin gap diminished by the Zeeman energy in the reentrant insulating phase neighbouring on the superconducting phase.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The series of two-dimensional (2D) molecular conductors, $X[Pd(dmit)_2]_2$, is a model system of frustrated quantum spin physics and Mott transition on triangular lattice [1, 2], where X are monovalent cations such as Cs, tetramethyl-phosphonium ($Me_4P$), and ethyltrimethyl-phosphonium ($EtMe_3P$), and dmit denotes 1,3-dithiol-2-thione-4,5-dithiolate, displayed in figure 1. One $Pd(dmit)_2$ molecule carries $-0.5$ charges on average, forming a dimer with one electron. Although the conduction band consisting of the highest occupied molecular orbital is half-filled, the strong Coulomb repulsion between electrons on the dimer, $U$, overcoming the bandwidth $W$, makes almost all the salts Mott insulators with a spin $S = 1/2$ on each dimer. The transfer integrals between dimers, $t$ and $t'$, form a triangular lattice, as displayed in figure 1(b). The electronic ground state is essentially mapped on the 2D parameter space

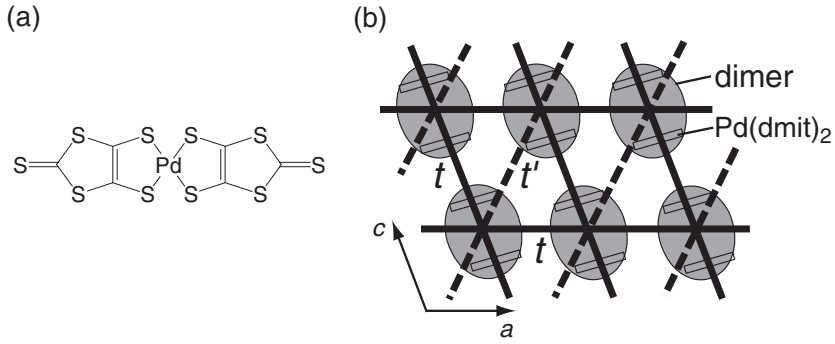


**Figure 1.** (a) Schematic molecular and (b) crystal structure of $Pd(dmit)_2$ salt. The dimers of $Pd(dmit)_2$ form a triangular lattice with respect to the two kinds of transfer integral, $t$ and $t'$.

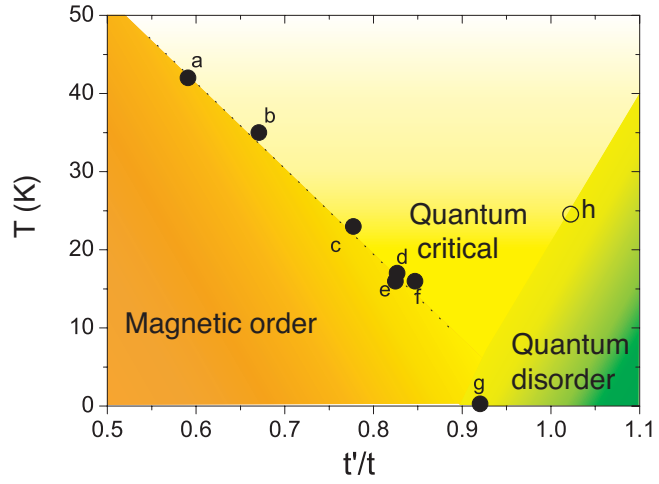


**Figure 2.** Magnetic phase diagram as functions of $t'/t$ and temperature, which is classified into three regions: the magnetic order, quantum critical, and quantum disorder regions. The experimentally obtained Néel temperatures of the $X[Pd(dmit)_2]_2$ salts are plotted as closed circles, where X = (a) $Me_4P$, (b) $Me_4As$, (c) $EtMe_3As$, (d) $Et_2Me_2P$, (e) $Et_2Me_2As$, (f) $Me_4Sb$. No magnetic transition has been observed in the $EtMe_3Sb$ salt (g). The $EtMe_3P$ ($P2_1/m$) salt (h) exhibits the VBS state below 25 K.

of $U/W$, representing the electron correlation, and $t'/t$, determining the strength of spin frustration [1], as known in the typical organic system $\kappa$-$(ET)_2X$ [3, 4].

The $t'/t$ values of $X[Pd(dmit)_2]_2$ ranging from 0.5 to 1.1 would provide a nontrivial magnetic ground state due to the spin frustration. Many of them, however, show antiferromagnetic order at low temperatures [2, 5, 6]. On increasing the spin frustration, namely increasing $t'/t$ from 0.5 to 1, the Néel temperature diminishes on approaching the regular triangular lattice, $t'/t = 1$, around which the magnetic quantum critical point would be present, as displayed in figure 2. In fact, a paramagnetic Mott insulator without any symmetry breaking has been recently found in the nearly regular triangular-lattice material, $EtMe_3Sb[Pd(dmit)_2]_2$, at least down to 2 K [7]. In the region with $t'/t$ close to or even larger than unity, the spin frustration can prohibit long-range magnetic order as suggested theoretically [8–11]. The magnetic phase diagram of the antiferromagnetic triangular lattice

X[Pd(dmit)$_2$]$_2$ as functions of $t'/t$ and $T$, figure 2, resembles that proposed on the square lattice extrapolated to ladders [12]. The recently discovered EtMe$_3$P salt [13], which is expected to have the strongest spin frustration due to the nearly perfect triangular lattice, $t'/t = 1.03$, shows a second-order spin dimerization transition at 25 K, accompanied by a structural change (the molecular dimers [Pd(dmit)$_2$]$_2$ are dimerized along the crystallographic $c$ axis) [14]. A valence bond solid (VBS) state is considered to be realized in this 2D Mott insulator as the ground state arising from the interplay between the lattice and the spin frustration. A remarkable feature is that EtMe$_3$P[Pd(dmit)$_2$]$_2$ is accessible to a Mott–Hubbard transition on increasing the bandwidth by applying hydrostatic pressure. A Mott insulator-to-metal transition and a superconducting transition occur at low temperatures [13]. The Mott transition and superconductivity emerging from the VBS state can have emergent features distinct from the typical Mott insulators with antiferromagnetic order, if the spin degree of freedom plays important roles in the emergence.

In this paper, we report the bandwidth-controlled Mott transition of the EtMe$_3$P salt under pressures applied to near the Mott boundary where the insulating and metallic states compete energetically. We show a novel feature of the Mott transition from a metal to a spin-gap insulator under a magnetic field.

## 2. Experimental details

The single crystals of EtMe$_3$P[Pd(dmit)$_2$]$_2$ were prepared by air-oxidation of [EtMe$_3$P]$_2$ [Pd(dmit)$_2$] in an acetone solution containing acetic acid. The crystal structure belongs to the space group $P2_1/m$, determined from x-ray diffraction measurements [13]. We applied hydrostatic pressure using the pressure media oil (Daphne7373) and clamped pressure in a BeCu cell at room temperature. The applied pressure values mentioned below were monitored at room temperature by the pressure gauge equipped in the piston. At low temperatures, the pressure would be reduced by $\sim$0.2 GPa due to thermal contraction of the pressure media. The in-plane resistance was measured by the four-probe method.

## 3. Experimental results

Figure 3 shows the temperature dependence of the resistance of EtMe$_3$P[Pd(dmit)$_2$]$_2$ under hydrostatic pressure. At 0.32 GPa, semiconducting behaviour is observed in the whole temperature region, as seen at ambient pressure [13]. The resistance begins to decrease around 25 K when we apply 0.36 GPa. The resistance drops three orders of magnitude in the temperature range from 20 to 18 K, where the Mott transition is regarded to occur. The Mott transition should have first-order character as seen in the 2D organic Mott insulator $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl in a pressure range below the critical end point [15–17]. The slight broadening of the transition is attributed to crystal defects or pressure inhomogeneity due to solidification of the pressure media. Once the resistance behaves as a metal below 17 K, it begins to increase again below 13 K. Finally, the superconducting transition is observed at 5.2 K. A clear hysteresis is seen between the cooling and heating processes on the metal-to-insulator (MI) transition, which manifests the first-order nature.

Such a reentrant Mott transition is typically observed in $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl where the antiferromagnetically ordered state emerges at low temperature [17]. This behaviour is understood thermodynamically in terms of the Clausius–Clapeyron relation: the spin entropy of the insulating phase becomes smaller than that of the metallic phase due to the antiferromagnetic ordering at low temperature [15, 18]. The $P$–$T$ phase diagram is in contrast to that of the spin-frustrated Mott insulator $\kappa$-(ET)$_2$Cu$_2$(CN)$_3$ without long-range order, in

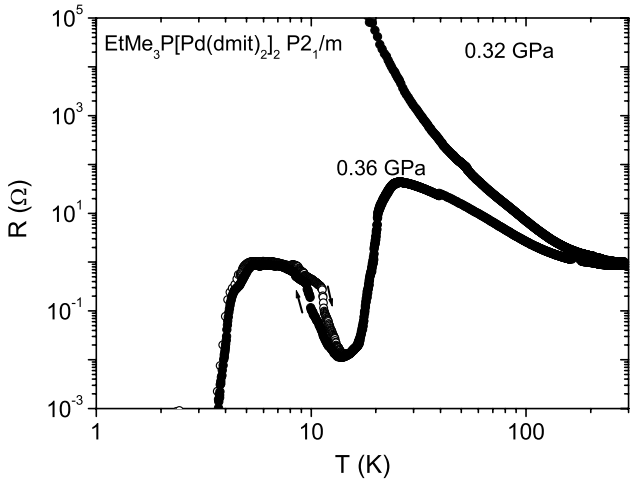


**Figure 3.** Temperature dependence of the resistance of $EtMe_3P[Pd(dmit)_2]_2$ under hydrostatic pressure. The closed and open circles at 0.36 GPa represent the data obtained for the cooling and heating processes.

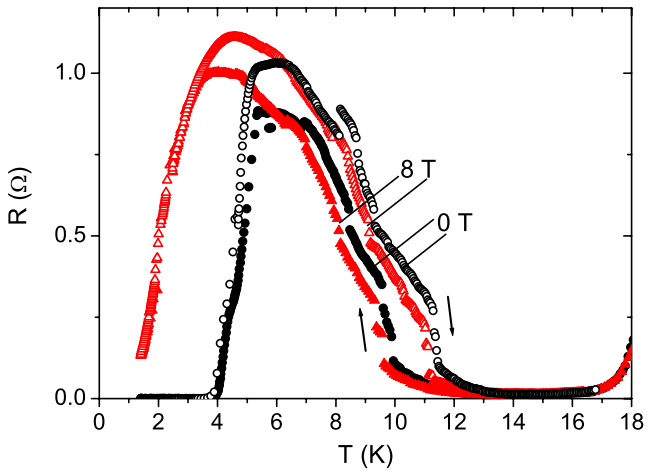


**Figure 4.** Temperature dependence of the resistance of $EtMe_3P[Pd(dmit)_2]_2$ at 0.36 GPa in magnetic fields of 0 and 8 T.

which no reentrant MI transition has been observed in the whole pressure range [19]. In $EtMe_3P[Pd(dmit)_2]_2$, the VBS phase appears below 25 K at ambient pressure, instead of the magnetic ordering [14]. Opening of the spin gap reduces the spin entropy (nearly zero spin susceptibility), which would persist even under pressure and lead to the reentrant MI transition.

To clarify the nature of the reentrant insulating phase, we investigated the magnetic field effect on the MI transition. The magnetic field was applied nearly parallel to the conducting layer. Figure 4 shows the low-temperature part of the resistance at 0.36 GPa in fields of 0 and 8 T. Above 7 K, the temperature dependence of the resistance at 8 T shifts to a lower temperature region with the temperature difference $\Delta T = -0.5 \pm 0.2$ K from that taken at 0 T on the cooling process. The MI transition temperature is also lowered for the heating process. The drop of the resistance again appears at around 3 K, indicating that the superconducting state

still survives in a magnetic field of 8 T. The present result suggests that the reentrant insulating state is unstable against the magnetic field, and hence has a spin gap which is reduced in the magnetic field by the Zeeman energy.

## 4. Conclusion

We observed the reentrant Mott transition on the triangular-lattice VBS Mott insulator $EtMe_3P[Pd(dmit)_2]_2$ under hydrostatic pressure in the vicinity of the Mott critical boundary. The reentrant transition is shifted to lower temperature, which suggests that the low-temperature insulating phase is the VBS state with a finite spin gap, neighbouring on the superconducting phase.

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