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C$_3$S$_5$): evidence for frustration in spin-1/2 Heisenberg antiferromagnets on a triangular lattice

LETTER TO THE EDITOR

Magnetic susceptibility of β'-[Pd(dmit)$_2$] salts (dmit = 1, 3-dithiol-2-thione-4, 5-dithiolate, C$_3$S$_5$): evidence for frustration in spin-1/2 Heisenberg antiferromagnets on a triangular lattice

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Abstract
The magnetic susceptibilities of a series of compounds, β'-X[Pd(dmit)$_2$]$_2$ (X = Me$_4$As, Me$_4$P, Me$_4$Sb, Et$_2$Me$_2$P, and Et$_2$Me$_2$Sb, where Me = CH$_3$ and Et = C$_2$H$_5$), have been investigated. The temperature dependence of χ has been analysed in terms of the two-dimensional spin-1/2 Heisenberg antiferromagnet on the triangular lattice; it is the first time that this approach has been applied to experimental data. The observed χ can be understood as reflecting the behaviour of the geometrically frustrated spins. The variation among the compounds suggests a role of frustration in relation to the relative stability of the metallic state.

The physical behaviour of a frustrated spin system, the antiferromagnet on the triangular lattice (triangular antiferromagnet, TAFM), has been a focus of extensive research activity [1]. Much theoretical attention has been paid to the nature of the ground state in the quantum regime, the two-dimensional (2D) spin-1/2 Heisenberg TAFM. Whether quantum spin fluctuation destroys the long-range magnetic order has long been a subject of debate [2], originating with Anderson's proposal of the resonating valence bond state [3]. On the other hand, experimental information on such systems is still limited, particularly as regards finite-temperature behaviour. Though the 2D spin-1/2 Heisenberg TAFM is the simplest frustrated quantum spin model, few examples are known.

Effects of spin frustration in 2D organic molecular conductors with approximately triangular lattice structure have been pointed out recently, particularly from theoretical viewpoints [4–10]. It is not surprising that the layered molecular crystals often take on triangular-like structures, because this is the 2D close packing (face-centred lattice) in which each spin-1/2 site has six nearest-neighbour (NN) sites [11]. Since the molecular orbitals are not isotropic, they show some deviation from the regular triangular lattice packing. If the exchange couplings are significantly weak along one or two directions of the triangle,
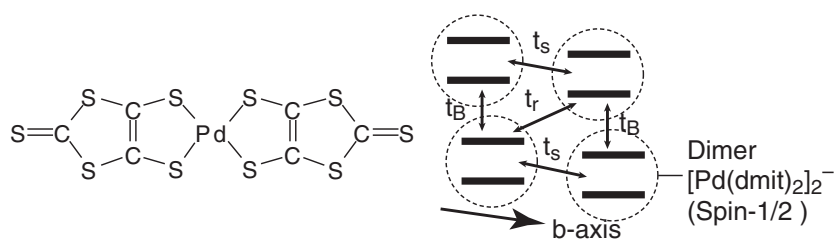
Figure 1. Left: the chemical structure of [Pd(dmit)$_2$]. Right: a schematic diagram of the triangular lattice-like packing in a conduction layer of the [Pd(dmit)$_2$] salt. The interdimer transfer integrals, t_B, t_r, and t_s, are also indicated.

the behaviour of the system can be approximately described using the 2D square lattice or one-dimensional model, respectively, in which the frustration effect is diminished. Since the intermolecular exchange coupling depends sensitively on the molecular packing, it is necessary to examine experimentally in each case how the frustration operates. However, experimental evidence for the frustration has been quite limited. The theoretical calculations of the finite-temperature χ (static uniform susceptibility) for the spin-1/2 Heisenberg TAFM have predicted a characteristic peak profile [12]. Observation of this should be an efficient diagnostic for the spin frustration effect, though it has not been applied yet due to the lack of a good example of a spin-1/2 Heisenberg TAFM. We have applied this, for the first time, to the present compounds, β'-[Pd(dmit)$_2$] salts, so as to show that they have frustration.

In this letter, we describe our analysis of the temperature dependence of χ for the [Pd(dmit)$_2$] salts. Broad peaks of χ around 100 K are commonly found. We have found that this behaviour is well explained by the predicted finite-temperature behaviour of the spin-1/2 Heisenberg TAFM [12]. We point out the role of the frustration lying behind the variation of the electronic properties of the compounds.

Prior to giving the magnetic results, the chemical and physical situations for the present compounds are briefly summarized here. With tetrahedral cations such as Me$_4$P$^+$, metal-complex [Pd(dmit)$_2$] molecules form 2:1 salts, named the β'-salts, which consist of [Pd(dmit)$_2$] layers sandwiched by cation layers, affording a 2D system. The [Pd(dmit)$_2$] molecules are strongly dimerized to form [Pd(dmit)$_2$]$_2{}^-$ units (figure 1). Experiments and calculations indicated that the unpaired electrons occupy the antibonding combination of HOMOs (the highest occupied molecular orbitals) of [Pd(dmit)$_2$] due to the strong dimerization [13–19]. The upper HOMO band thus shows half-filling, favouring the Mott insulating state. Consequently, the system is nearly identical to a close packing (a triangular lattice) of spin-1/2 units, [Pd(dmit)$_2$]$_2{}^-$. Since the HOMO of [Pd(dmit)$_2$] has little amplitude on the Pd atom, the spins are sufficiently isotropic Heisenberg ones, as generally found on organic π-molecules. In fact, principal g-values ranging from 2.01 to 2.08 were observed by means of EPR [20, 21].

All these compounds are insulating under ambient pressure, but show variation in the pressure dependence [22–28]. They can be classified into three groups, in terms of the cation effect. The salts with small cations, Me$_4$P$^+$ and Me$_4$As$^+$ (type A) [22, 23], are insulating under hydrostatic pressures up to 1.7 GPa, though the resistivity gradually decreases with pressure. Recently, we found that uniaxial strains along the b-axis for single crystals of the Me$_4$As$^+$ salt afford metallic behaviour [29]. The metal–insulator transition temperatures of the Et$_2$Me$_2$P and Me$_4$Sb salts (type B) [24–27] decrease with pressure. Above about 0.7 GPa, they are metallic down to 1.5 K. Another non-metallic phase appears at low temperatures above about 1.2 GPa. In their metallic phase, superconductivity was detected by means of resistivity measurements [27], while an rf magnetic study indicates non-bulk superconductivity [30].

The unclear nature of the superconductivity was also pointed out for a closely related material: β-Me$_4$N[Pd(dmit)$_2$]$_2$ [31]. The salt with the largest cation, Et$_2$Me$_2$Sb$^+$ (type C) [25, 27], also becomes metallic under pressure. However, the superconductivity and the high-pressure non-metallic phase are absent in the Et$_2$Me$_2$Sb salt. For this cation effect, a structural study revealed that the ratio of the interdimer transfer integrals is a key factor [32]. The ratio, t_r/t_B, is about 0.6 for type A, 0.7–0.8 for type B, and almost 1 for type C salts, while t_s/t_B remains around 0.9 [32] (see figure 1). From this, it was suggested that the variation from type A to C corresponds to the approach to the regular triangular lattice, and the spin frustration should play a significant role [32–35]. The pressure dependence also correlates with the Néel temperatures determined by EPR measurements at ambient pressure [20]. Type A compounds undergo antiferromagnetic ordering at $T_N = 35$ K, while type B ones show $T_N = 18$ K. The Et$_2$Me$_2$Sb salt indicates no magnetic ordering down to 4.3 K [20]. Thus, the stability of the metallic state should have a close connection with the magnetism [33–35]. However, the temperature dependence of χ, showing a broad maximum around 100 K [26, 27, 31], has not been explained yet.

Polycrystalline samples of the β'-[Pd(dmit)$_2$] salts were prepared as described before [22, 23, 25]. The susceptibility was measured by a Quantum Design MPMS SQUID magnetometer by applying a field of 10 000 Oe, below which the magnetization was a linear function of the field. The raw data for the Me$_4$P and Et$_2$Me$_2$P salts are the same as those given before [26, 27], but the corrections for paramagnetic defects are improved. The spin susceptibility was obtained by subtracting the low-temperature Curie-like ones due to paramagnetic defects and the diamagnetic contributions from the raw data. The diamagnetic contributions were estimated by use of the reported values for [Pd(dmit)$_2$] [36] and Pascal's law. We eliminated small pieces from the Me$_4$As sample before the measurement to minimize the Curie-like component; it was not subtracted for this salt.

Figure 2 (left) shows the temperature dependence of χ for the Et$_2$Me$_2$Sb salt (type C). As temperature decreases from 300 K, χ increases gradually and exhibits a broad peak of $\chi_{max} = 5.8 \times 10^{-4}$ emu mol^{-1} around $T_{max} = 70$ K. The solid curves in figure 2 show the theoretical values of the 2D spin-1/2 Heisenberg TAFM [12] with various exchange couplings, J. Here we define the spin Hamiltonian as the summation of $J\boldsymbol{S}_i \cdot \boldsymbol{S}_j$ ($J > 0$) over all NN pairs of the spin-1/2 units, (i, j). In table 1 of [12], the coefficients a_n of the high-temperature series expansion,

$$\chi = \sum_{n=0}^{14} \frac{a_n}{n!} x^n, \tag{1}$$

for $J = 1$ are given, where $x = J/4k_BT$. Direct estimation of χ using this series gives rise to divergence at low temperature. As in [12], the extrapolation method using the [7/7] Padé approximants is adopted. That is, χ is expressed as

$$\chi = \frac{Ck_B}{J} \frac{4x(1 + b_1x + \cdots + b_6x^6)}{1 + c_1x + \cdots + c_7x^7}, \tag{2}$$

where $C = N_A g^2 \mu_B^2/4k_B$. The coefficients were determined such that equations (1) and (2) agree with each other to the required order. We obtained

$$
\begin{aligned}
&b_1 = 13.138\,2922, &&b_2 = 38.263\,9722, &&b_3 = 214.744\,54, \\
&b_4 = 260.983\,171, &&b_5 = 622.734\,802, &&b_6 = 186.114\,208,
\end{aligned} \tag{3}
$$

and

$$
\begin{aligned}
&c_1 = 19.138\,2922, &&c_2 = 129.093\,725, \\
&c_3 = 597.987\,88, &&c_4 = 1902.064\,91, \\
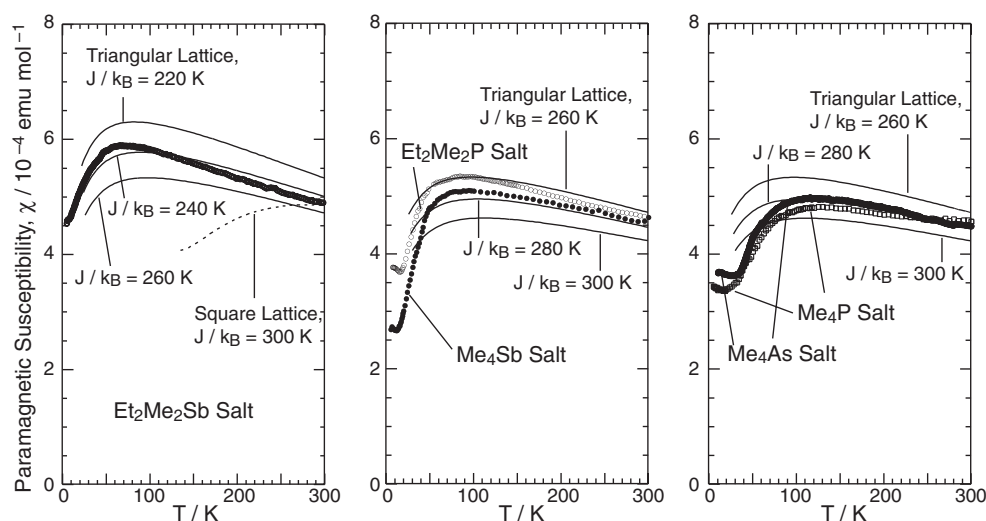&c_5 = 3943.844\,64, &&c_6 = 5164.9974, &&c_7 = 3452.672\,29.
\end{aligned} \tag{4}
$$

Figure 2. The temperature dependence of χ for the β'-[Pd(dmit)$_2$] salts; types C (left), B (middle), and A (right). Solid curves show χ calculated for the 2D spin-12 Heisenberg TAFM with various exchange couplings, J. The broken curve denotes χ for the square lattice.

The solid curves in figure 2 are plotted using equation (2) with these coefficients and the average of the EPR g-values, $g = 2.038$ [20]. The $J/k_B = 240$ K curve reproduces well the observed χ-behaviour. Therefore, we conclude that the Et$_2$Me$_2$Sb salt is in a situation close to the spin-1/2 Heisenberg TAFM with $J/k_B = 240$ K. The exchange coupling J appears to increase slightly with T above 100 K, though the transfer integrals decrease with T due to thermal expansion. The origin of this is not clear at present. Weak interlayer coupling or thermal excitation across the Mott gap may be related to this, but it is possible that there are small experimental errors due to the not very precise diamagnetic correction. The presence of the Curie-like component makes it difficult to judge whether there is a long-range order at low temperature from the present data.

Let us take a look at how the frustration influences the temperature dependence of χ. For this purpose, it is useful to compare the behaviour of the square lattice antiferromagnet with the observed data. The broken curve in figure 2 relates to χ for the spin-1/2 Heisenberg antiferromagnet on the 2D square lattice [37–39] with $J/k_B = 300$ K and $g = 2.038$, which approximates the observed values near room temperature. The square lattice model cannot explain the observed behaviour at all. Since $\chi_{max} T_{max}$ is a constant, independent of J, it is impossible to improve the fit to the observed peak behaviour by adjusting J. The spin-1/2 Heisenberg chain antiferromagnet models also fail to explain the observation. Unlike these models without frustration, suppressed antiferromagnetic correlation and larger entropy due to the frustration in the TAFM model [40] can explain our experiments well.

Figure 2 also shows the temperature dependence of χ for type B and A compounds, which undergo antiferromagnetic transitions at $T_N = 18$ and 35 K, respectively [19], together with the calculated χ for the triangular lattice model with various values of J. As in the type C case, a broad peak appears around 100 K, and the profiles of χ obviously show that these compounds are close to the frustrated spin-1/2 Heisenberg TAFM. Below the peak temperature, χ decreases more steeply with decreasing T than in the type C case; this is followed by a bend at T_N. Below T_N, χ takes a nearly constant value, similarly to polycrystalline samples of other 2D antiferromagnets [38, 39]. The correlation between T_N and the ratio of the transfer

integrals, t_r/t_B [20, 32], suggests that T_N is enhanced mainly by the deviation from the regular triangular lattice, in the presence of weak interlayer couplings. This is in accordance with the calculations of the ground states of anisotropic triangular lattice models [7], which indicate that the Néel order is favoured by the deviation. According to the structural study [32], the deviation is attributed to the relative increase in t_B and t_s for types A and B. If this is the case, the average exchange coupling J, as well as the bandwidth, should be larger in types A and B. Judging from figure 2, the J-values for type A and B compounds, $J/k_B = 260$–280 K, in fact seem to be larger than those of type C, $J/k_B = 240$ K. ^{13}C NMR measurements of types A and B [41, 42] indicate no anomaly of the relaxation rate T_1^{-1} above 100 K. Therefore, the itinerant effect due to the excited carriers is considered to be so minor that the magnetic behaviour of systems should be prescribed by the localized spins. From all the available features, we conclude that frustration is operating in the present systems. On the other hand, $Cs[Pd(dmit)_2]_2$ exhibits almost constant χ for the Pauli paramagnetism in its metallic phase down to 57 K [36].

Similar magnetic behaviour was reported for $CuCl_2$-intercalated graphite, but the effect of the structural inhomogeneity has complicated its interpretation [43–45]. Cs_2CuCl_4 [46] may belong to a category close to that of the present systems, though their χ-peaks were analysed in terms of the Heisenberg chain model previously [47]. A 2D organic superconductor, κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$], also shows similar behaviour [48]. However, the situation is entirely different; it is metallic below about 100 K. An organic antiferromagnet, $(C_1TET-TTF)_2Br$, is reported to have a frustration effect in view of the structure and the absence of magnetic order [49]. This is misleading, because a very low (or zero) critical temperature is a common feature of low-dimensional quantum spin systems. In fact, χ for $(C_1TET-TTF)_2Br$ can be explained simply by the 2D square lattice model [49].

Unlike completely localized systems such as simple Cu^{2+} salts, the present Mott insulator systems are close to the metallic regime, as shown by the pressure experiments. Although the present study was made only at ambient pressure, it provides information about the stability of the metallic state. The ordinary Mott insulators without frustration approach the metallic state as the bandwidth increases. In contrast, in the present systems, the metallic state is more stable in type C, in spite of the narrower bandwidth indicated by the lower T_N, smaller J, and larger χ. On the other hand, type C has the largest degree of frustration. Thus we presume here a crucial role of the frustration, which can diminish the stability of the insulating state by destroying the antiferromagnetic correlation, as several theoretical studies indicate [4, 5, 8, 50]. For the stability of the metallic state below 1 GPa, the degree of frustration seems more important than the release of the one dimensionality of the Fermi surface, because the present results indicate no one-dimensional features.

In conclusion, the temperature dependence of χ for the β'-[Pd(dmit)$_2$] salts is now understood in terms of the spin-1/2 Heisenberg antiferromagnet on the 2D triangular lattice, with J/k_B in the range 240–280 K. The cation effect on χ supports the previous suggestion of the role of the spin frustration in the stability of the metallic state. In an effort to reveal the detailed nature of the magnetic transitions and the spin dynamics of the present systems, magnetic resonance and specific heat measurements are now in progress. Further analysis of the low-temperature part of χ is also under way.

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