Frustration and Valence Bond Formation in a Molecular Mott System

R. Kato

RIKEN
Hirosawa 2-1, Wako-shi, Saitama 351-0198, Japan

The Pd(dmit)$_2$ molecule provides conducting anion radical salts with closed-shell monocations (Et$_x$Me$_4$$_x$Z)$^+$ (Et=C$_2$H$_5$-, Me=CH$_3$-, Z=N, P, As, Sb; $x=0, 1, 2$) [1]. A common feature of these Pd(dmit)$_2$ salts is a conducting anion layer with a quasi (isosceles) triangular lattice of the dimer unit [Pd(dmit)$_2$]$^2^-$. The conduction band is half-filled and two-dimensional. At ambient pressure, all the Pd(dmit)$_2$ salts behave as Mott insulators where one spin is localized on each dimer. Interdimer transfer integrals can be tuned by the choice of the cation, which provides a variety of electronic states.

The EtMe$_3$Sb salt has a nearly regular-triangular lattice. The temperature dependence of the magnetic susceptibility is described by the antiferromagnetic spin-1/2 Heisenberg model on the triangular lattice with an exchange interaction $J=220–250$ K. The $^{13}$C-NMR shows no indication of either spin ordering/freezing down to 20 mK. Below about 1 K, the spin-lattice relaxation rate $T_1^{-1}$ curve starts to bend and is proportional to $T^2$. On the other hand, the temperature dependence of the specific heat was found to include a linearly temperature-dependent term (the $\gamma$ term) with $\gamma \sim 25$ mJ K$^{-2}$ mol$^{-1}$. These results suggest that the spin frustration leads the EtMe$_3$Sb salt into a spin liquid state. In other salts with a nearly regular-triangular lattice, we found instances where the valence bond formation removes the frustration. The Et$_2$Me$_2$Sb salt undergoes a first-order transition toward a charge separation state ($2\text{Dimer}^- \rightarrow \text{Dimer}^0 + \text{Dimer}^2^+$) at 70 K [2]. In the EtMe$_3$P salt, a second-order transition from the frustrated paramagnetic state to the valence bond solid (VBS) state with a spin gap $\Delta/k_B$~40 K occurs at 25 K [3]. The former is an “intra-dimer” valence bond formation, and the latter an “inter-dimer” one. The VBS state in the EtMe$_3$P salt turns to a superconducting state under pressure ($T_c=5$ K at 3.3 kbar) [3,4].