# Transition of Local Moments Coupled to Itinerant Electrons in the Quasi One-Dimensional Conductor Copper Phthalocyanine Iodide

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Copper phthalocyanine iodide is a molecular metal whose conducting stacks incorporate a one-dimensional array of local moments strongly coupled to conduction electrons. Below 20 K the EPR $g$ value of the coupled system increases anomalously and at 8 K the EPR signal broadens abruptly and becomes unobservable. Anomalies in the proton NMR spin-lattice relaxation are observed at the transition temperature. Magnetic susceptibility measurements and NMR linewidth data both indicate that there is little if any static magnetic order below 8 K.

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In this Letter, we report that the quasi one-dimensional molecular metal[1] copper phthalocyanine iodide, $[\mathrm{Cu(Pc)}]^{+0.33}[\mathrm{I_3}^-]_{0.33}$, exhibits a novel transition at 8 K involving conduction electrons strongly coupled to a regular array of local electronic moments.

Cu(Pc) is a planar molecule, consisting of an organic phthalocyaninato (Pc) macrocycle with a $\mathrm{Cu}^{+2}$ ion situated at its center. Reaction of Cu(Pc) with $I_2$ produces crystals of Cu(Pc)I that exist as columnar stacks of partially oxidized $[\mathrm{Cu(Pc)}]^{+0.33}$ ions surrounded by parallel chains of triiodide anions.[2] In Cu(Pc)I the Cu-Cu spacing within a conductive stack is 3.2 Å, whereas the closest interstack distance between Cu ions is 13.9 Å. This material is a molecular metal possessing high room-temperature conductivity, $\sigma_{\mathrm{RT}} \approx 10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$. Thermoelectric-power measurements show that the charge carriers are exclusively associated with a $\frac{5}{6}$-filled band comprised of the $\pi$-molecular orbitals of the Pc ring. The Cu sites retain a paramagnetic +2 valency ($d^9$ $\mathrm{Cu}^{+2}$, $S=\frac{1}{2}$), which provides the possibility for an unusual type of coupling between a dense one-dimensional array of local moments and a "Fermi sea" of itinerant electrons within a single conductive stack. EPR, NMR, and magnetic susceptibility data presented here demonstrate that such interactions occur and lead to a transition of the coupled system at 8 K.

EPR measurements were performed on single crystals of Cu(Pc)I at 9.3 GHz and on powdered samples of Cu(Pc) at 35 GHz. Static susceptibility measurements (see Fig. 1) at fields of 1, 5, and 35 kOe were carried out on polycrystalline samples of Cu(Pc)I with a VTS-50 SQUID susceptometer (S.H.E. Co.). Proton NMR measurements on this material are particularly favorable for the study of its electronic and magnetic properties since the sixteen protons at the periphery of a Cu(Pc) molecule are held rigidly to the Pc ring. The proton NMR linewidths, $T_2^{-1}$, and spin-lattice relaxation rates, $T_1^{-1}$, have been measured as functions of frequency in the range 6 to 47 MHz and for temperatures from 1.7 to 300 K. The polycrystalline samples used for NMR contained approximately $10^{20}$ protons. The free-induction decay time for Cu(Pc)I was less than, or of order, 20 $\mu$sec.

At high temperatures the magnetic susceptibility of Cu(Pc)I increases[2] with decreasing temperature and follows a temperature dependence given by

$$\chi(T) = \chi_{\mathrm{Cu}}(T) + \chi_\pi = C/(T-\theta) + \chi_\pi . \qquad (1)$$

The two terms are (i) the temperature-dependent contribution from localized $\mathrm{Cu}^{+2}$ spins, $\chi_{\mathrm{Cu}}(T)$, which is expressed in a Curie-Weiss form to allow for spin-spin interactions, and (ii) the temperature-independent Pauli susceptibility associated with the ligand-based

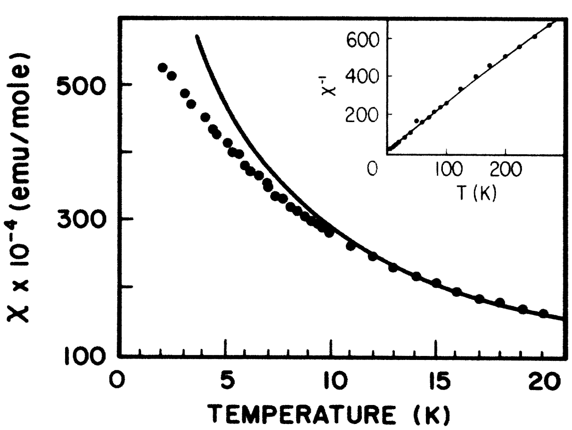


FIG. 1. Magnetic susceptibility of polycrystalline Cu(Pc)I, taken at 5 kOe, as a function of temperature. Inset: The inverse susceptibility (in mole/emu) over a broader temperature range. The solid lines in the figure and inset represent a best fit of the data by Eq. (1) as discussed in the text.

charge carriers, $\chi_\pi$. A nonlinear least-squares fit of the data for 8 K $< T <$ 40 K gives a Curie constant $C = 0.394 \pm 0.004$ emu K mole$^{-1}$; a Curie-Weiss temperature of $\theta = -4.0 \pm 0.1$ K; and a value of $\chi_\pi = 1.9 \times 10^{-4}$ emu mole$^{-1}$, which is nearly identical to that of the isostructural, nonmagnetic conducting homolog, Ni(Pc)I.[3] The Curie constant is within 2% of that calculated from the standard formula, $C = N\mu_B^2 g^2 S(S+1)/3k_B$ where $g^2$ is the average squared EPR $g$ value for Cu(Pc)I discussed below. From these data alone it is not possible to assign the observed Curie-Weiss temperature to direct exchange coupling, $J_{dir}$, occurring between local $Cu^{+2}$ moments, or to the effects of an indirect exchange coupling, $J_{ind}$, between local moments via the itinerant electrons.[4] NMR spin-lattice relaxation measurements presented below suggest that the latter effect may predominate.

Over the temperature range 20 K $< T <$ 400 K, single crystals of this material exhibit a single, axially symmetry EPR line whose temperature-dependent $g$ values occur at the susceptibility-weighted average of the values for free-carrier spins and that of local moments, Fig. 2:

$$g(\phi,T) = f(T) g_{Cu}(\phi) + [1 - f(T)] g_\pi, \qquad (2)$$

where

$$f(T) = \chi_{Cu}(T)/[\chi_{Cu}(T) + \chi_\pi];$$

$$g_{Cu}^2(\phi) = g_{Cu,\parallel}^2 \cos^2\phi + g_{Cu,\perp}^2 \sin^2\phi$$

is the angle-dependent EPR $g$ value of the one-dimensional array of $Cu^{+2}$ spins and $g_\pi$ is the isotropic $g$ value of the $\pi$ carriers. The angle $\phi$ is taken between the stacking, $c$ axis, and the magnetic field. Using the susceptibility results to calculate $f(T)$, we

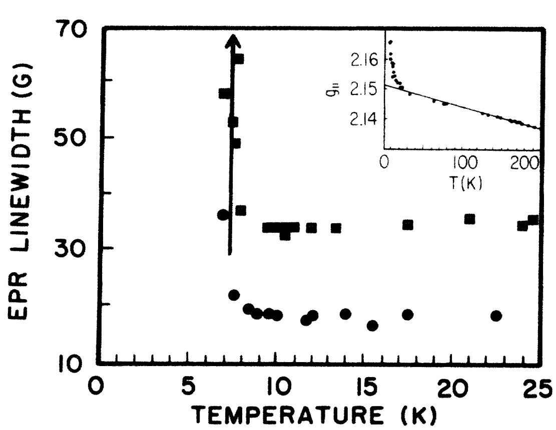


FIG. 2. EPR linewidths ($\Delta H_{p\text{-}p}$) of a single crystal of Cu(Pc)I near the transition temperature: $H_0$ parallel to the $c$-axis, squares; $H_0$ perpendicular, circles. The arrow signifies that the resonance becomes unobservably broad at this temperature. Inset: Single-crystal $g$ values with $H_0$ parallel to the $c$ axis. The solid line represents the best fit of the high-temperature data by Eq. (2) as discussed in the text.

have analyzed the high-temperature data obtaining values for $g_{Cu}$ ($g_{Cu,\parallel} = 2.15$ and $g_{Cu,\perp} = 2.03$) that are very similar to, although somewhat reduced from, those of the unoxidized parent compound, Cu(Pc) ($g_{Cu,\parallel} = 2.167$ and $g_{Cu,\perp} = 2.050$); $g_\pi = 2.00$ as expected[3] for an isolated free carrier. The observation of a single EPR line with a $g$ tensor of the form described by Eq. (2) indicates a coupling between local and itinerant spins,[4] $J_{\pi d}$, that is large compared to the separation between the resonance frequencies of the subsystems,

$$J_{\pi d}/k_B >> \mu_B H_0 (g_{Cu} - g_\pi)/k_B \approx 0.05 \text{ K}.$$

As shown in the inset to Fig. 2, in the range 8 K $< T <$ 20 K the EPR $g$ values increase above that predicted by Eq. (2), an effect that is not understood. Nonetheless, the two spin systems in Cu(Pc)I remain strongly coupled since only one narrow line is observed at all temperatures above 8 K.

The width of the composite EPR line is determined mainly by the $Cu^{+2}$ ions since they have much larger fractional susceptibility. The width has the characteristic anisotropy of a one-dimensional dipolar interaction that is strongly exchange narrowed.[5] The strength of this interaction, $\Gamma_D$, increases upon cooling: $\Gamma_D \approx 7$ G at ambient temperatures; $\Gamma_D \approx 20$ G at 20 K. This is far less than the static dipolar linewidth, $\Gamma_s$, obtained from a second-moment calculation, $\Gamma_s \approx (M_2)^{1/2} = 1.3 \times 10^3$ G, which confirms that there is strong exchange coupling among $Cu^{+2}$ spins. A rough estimate of the exchange energy at 20 K is $\mu_B M_2/\Gamma_D k_B = 5.7$ K, the same order of magnitude as the Curie-Weiss temperature.

The single EPR line of Cu(Pc)I remains exchange narrowed down to 8 K. At this temperature it abruptly broadens and vanishes, Fig. 2, which signals the onset of a transition that involves both the local- and itinerant-spin systems of this material. Preliminary measurements[6] indicate that this magnetic transition is accompanied by an abrupt decrease in the conductivity suggestive of a metal-nonmetal transition. In contrast, the homologous material Ni(Pc)I[3] remains highly conducting down to at least 50 mK and maintains its narrow EPR signal, temperature-independent $g$ value, and integrated EPR intensity down to at least 2 K. In addition, no magnetic transition is observed for the nonconducting crystals of the paramagnetic parent compound, Cu(Pc). Thus, it appears that the observed transition in Cu(Pc)I would not occur in the absence of coupling between local and itinerant spins.

As the temperature is lowered below 8 K, the susceptibility, shown in Fig. 1, continues to rise, although less rapidly than predicted by Eq. (1). Similar results were found at external fields of 5, 10, and 35 kOe. These observations confirm a change in the magnetic behavior of Cu(Pc)I below 8 K; however, they rule out the possibility that the loss of the EPR signal is trivially associated with the loss of paramagnetism. Proton NMR linewidth measurements give further information about the static magnetic behavior. As is evident in the data[7] taken at 6 MHz [Fig. 3(b)], the NMR linewidth does not change on cooling below 8 K. The linewidth is strictly homogeneous and at this frequency is given by the rigid-lattice limit for the nuclear dipolar interaction. These measurements have sufficient sensitivity to preclude the development of a static spin-density wave along the stacking axis of amplitude greater than $2\times10^{-2}\mu_B$, such as is evident in (tetramethyltetraselenafulvalinium)$_2$(PF$_6$).[8]

Proton spin-lattice relaxation measurements provide a direct probe of the spin dynamics of the $Cu^{+2}$ local spin system[9] and thereby give insight into the interactions involved in the 8-K transition. In Cu(Pc)I and its unoxidized parent compound, Cu(Pc), the spin-lattice relaxation rates are comparable and about 3 orders of magnitude larger than in the isostructural Ni(Pc)I homolog that contains no local moments. This indicates that the dipolar interaction between protons and the $Cu^{+2}$ spins is dominant. For Cu(Pc)I the recovery of the magnetization following excitation was markedly nonexponential, in contrast[10] with that of either Cu(Pc) or Ni(Pc)I. We tentatively ascribe this difference to screening by the conduction electrons of the dipolar interaction between local moments and proton spins. The recovery of the magnetization can be accurately represented by a double exponential dependence on time,

$$M(t)=M(0)[1-c_s\exp(-t/T_{1S})-c_L\exp(-t/T_{1L})],$$

with $T_{1L}$ being an order of magnitude larger than $T_{1S}$. The weighting factors, $c_S$ and $c_L$, are temperature independent and $c_S/c_L\approx1$. The shorter relaxation time, $T_{1S}$, has the characteristic[9] Larmor frequency dependence, $\omega^{1/2}$, of one-dimensional diffusive interactions as shown in the inset to Fig. 3(a). Its magnitude is similar to that of the nonconducting material Cu(Pc) shown there for comparison. The longer relaxation time, $T_{1L}$, which we emphasize is only observed for the Cu(Pc)I and not for Cu(Pc) or Ni(Pc)I, increases as the temperature is lowered toward the transition temperature. Further cooling below this is accompanied by a precipitous decrease in $T_{1L}$.

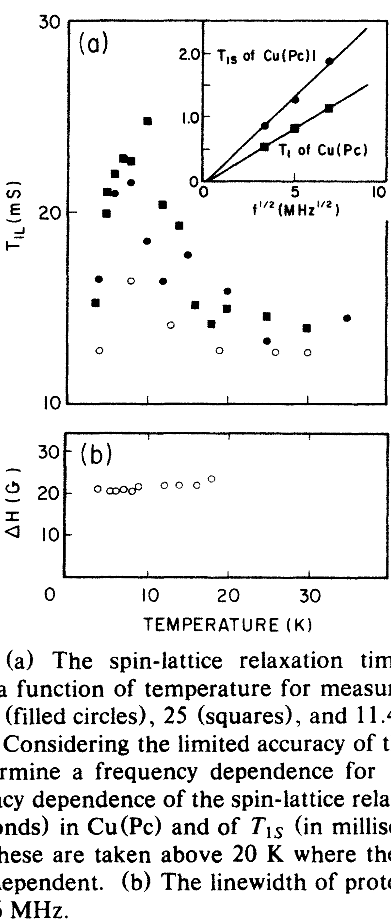


FIG. 3. (a) The spin-lattice relaxation time $T_{1L}$ for Cu(Pc)I as a function of temperature for measurement frequencies 47 (filled circles), 25 (squares), and 11.4 (open circles) MHz. Considering the limited accuracy of the data, we cannot determine a frequency dependence for $T_{1L}$. Inset: The frequency dependence of the spin-lattice relaxation time (in milliseconds) in Cu(Pc) and of $T_{1S}$ (in milliseconds) for Cu(Pc)I. These are taken above 20 K where they are temperature independent. (b) The linewidth of proton NMR in Cu(Pc)I at 6 MHz.

The exchange coupling between localized $Cu^{+2}$ spins can have contributions from direct, near-neighbor interactions ($J_{dir}$), and also from an indirect coupling ($J_{ind}$) mediated by the local-moment–itinerant-spin coupling. The question as to which contribution is the dominant interaction driving the 8-K transition can be explored with a quantitative interpretation of spin-lattice relaxation. Our observation of an $\omega^{1/2}$ dependence of the relaxation time $T_1$ for Cu(Pc) and $T_{1S}$ for Cu(Pc)I is indicative of one-dimensional Heisenberg interactions between the local moments of these materials. Such interactions are expected[9] to have diffusive behavior in the high-temperature limit, corresponding to a proton spin-lattice relaxation rate with a characteristic frequency dependence

$$1/T_1=A(2D_{\parallel}\omega)^{-1/2}+B(2D_{\parallel}\omega\gamma_e/\gamma_n)^{-1/2}, \quad (3)$$

where $D_{\parallel}$ is an intrastack spin-diffusion coefficient, $\omega$ is the nuclear Larmor frequency, $\gamma_e/\gamma_n$ is the ratio of electronic to nuclear gyromagnetic ratios, and $A$ and $B$ are geometric coefficients that depend only on the molecular structure.[9]

We have calculated for Cu(Pc)I that $A=4.46\times10^{12}$ sec$^{-2}$ and $B=10.4\times10^{12}$ sec$^{-2}$, and that for the unoxidized parent compound, Cu(Pc), $A=6.38\times10^{12}$ sec$^{-2}$ and $B=14.9\times10^{12}$ sec$^{-2}$. With the data inset in Fig. 3(a) we find the diffusion coefficients $D_{\parallel}=6.01\times10^{10}$ rad/sec for Cu(Pc)I, and $4.99\times10^{10}$ rad/sec for Cu(Pc). For the Heisenberg one-dimensional magnet,[11] numerical simulations[12] have shown that the spin diffusion coefficient can be written in terms of the intrachain exchange coupling constant $J$,

$$D_{\parallel}\approx2.66S|J/h|, \quad (4)$$

where $S = \frac{1}{2}$ in our case. This gives an intrachain coupling between local moments of $|J/k_B| = 0.34$ K for Cu(Pc)I and 0.29 K for Cu(Pc). Interchain interactions, as well as intrachain dipolar interactions or impurity effects, would introduce a finite limit for the relaxation rate at low frequency. Such a deviation from the behavior given by Eq. (3) is not evident in the data given in the inset to Fig. 3. Application of the theory of Boucher, Ferrieu, and Nechtschein[13] yields an upper bound to $J'$, the Heisenberg interchain exchange coupling: $J'/J << 1\times10^{-4}$. Thus, interactions among the $Cu^{+2}$ spins are highly one dimensional.

We interpret these results as indicating that the direct exchange coupling for both Cu(Pc) and Cu(Pc)I is weak. For Cu(Pc)I this exchange energy is an order of magnitude less than that inferred from the susceptibility measurements, 4 K, or from the EPR linewidth measurements, 6 K, and less than the observed transition temperature of 8 K. Consequently, we infer that the predominant interaction leading to the transition in Cu(Pc)I is most likely the coupling between the local moments that occurs through the conduction electrons.

In summary, EPR linewidth measurements indicate the existence of a new type of transition at 8 K involving a highly one-dimensional array of local moments strongly coupled to conduction electrons in the metallic molecular crystal Cu(Pc)I. Magnetic susceptibility and NMR linewidth data show that the low-temperature state of the combined itinerant-spin–local-moment system is not antiferromagnetic nor can it be that of a static spin-density wave of amplitude greater than $2\times10^{-2}\mu_B$. The EPR and NMR data suggest that the principal magnetic interactions between $Cu^{+2}$ local moments arises from indirect exchange involving the conduction electrons, and that the indirect exchange energy is approximately 6 K, comparable to the transition temperature.

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