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One-dimensional magnetism in copper phthalocyanine

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Measurements of the proton spin-lattice relaxation rate, T_1^{-1}, reveal that the organic insulator copper phthalocyanine Cu(PC) is a highly one-dimensional Heisenberg system. T_1^{-1} diverges as $\omega^{-1/2}$ down to 11.4 MHz without evidence of cutoff. It was found that $|J/k_B|=0.286$ K with the ratio $|J/J'|\geqq 6\times 10^3$, where J and J' are the intrachain and interchain exchange interactions, indicating that Cu(PC) is an excellent model one-dimensional Heisenberg magnet.

I. INTRODUCTION

The physics of magnetism in less than three dimensions occupies a place of particular significance. In many such cases the theory is tractable, in contrast to the situation for three dimensions. A number of exact statements can be made constraining predicted behavior; e.g., the existence of a phase transition resulting from short-range interactions is forbidden in one dimension. An important example of the effects of dimensionality on physical properties[1] is the singular behavior of the diffusive spin-spin correlation functions of one-dimensional magnetic chains, which diverge in the static limit with the frequency dependence $\omega^{-1/2}$. This unusual behavior can be identified from nuclear magnetic resonance (NMR) spin-lattice relaxation. In this paper, we report that the metal-organic insulator copper phthalocyanine Cu(PC) behaves in this fashion. Cu(PC) is an excellent approximation to a one-dimensional magnetic system and is appropriate for NMR investigations and their theoretical predictions because the positions of the protons of Cu(PC) are known precisely and they are rigidly fixed to the PC ring.

Real materials can be at most quasi-one-dimensional. Consider a system composed of chains of localized moments. If we represent the strength of the intrachain interaction by J and interchain effects by J', the ratio $|J/J'|$ provides a useful measure of the one dimensionality. Our interpretation of the NMR and magnetic susceptibility measurements reported here suggests that for Cu(PC), $|J/J'|\geqq 6\times 10^3$, compared to $|J/J'|\sim 10^4$ for one of the best known quasi-one-dimensional Heisenberg antiferromagnets, tetramethyl ammonium manganese chloride (TMMC).[2,3] Susceptibility measurements at very low temperatures ($T \ll |J/k_B|$) will be useful in clarifying our interpretation.

II. THEORY

The proton nuclear spins of Cu(PC) are coupled directly by the electron-nuclear dipolar interaction to the electronic spins well localized at Cu sites. The dynamic behavior of this magnetic system modulates the local magnetic fields at the sites of the protons and can be probed by measurement of the nuclear spin-lattice relaxation time. The relaxation rate is directly related to the spectral densities of the electronic spin-spin correlation functions which characterize the magnetic behavior of the material. The correlation functions are written as

$$g_j^{\alpha}(t)=\langle S_i^{\alpha}(t)S_{i+j}^{\alpha}(0)\rangle / \langle |S_i^{\alpha}|^2\rangle ,$$

where S_{i+j}^{α} is the α (z or $\pm$) spin component of the jth neighbor of the spin S_i at site i. The nuclear spin-lattice relaxation rate $1/T_1$ of a paramagnetic material can be expressed in terms of the spectral densities $f_j^{\alpha}(\omega)$ of the electronic spin-correlation functions in the high-temperature limit ($|J/k_BT|\ll 1$),

$$1/T_1=\sum_j [A_j(\theta,\phi)f_j^z(\omega_n)+B_j(\theta,\phi)f_j^{\pm}(\omega_e)] , \tag{1}$$

where

$$f_j^{\alpha}(\omega)=\int_{-\infty}^{\infty} g_j^{\alpha}(t)e^{-i\omega t}dt$$

and ω_n,ω_e are the nuclear and electronic Larmor frequencies, respectively. The electron-nucleon coupling constants $A_j(\theta,\phi)$ and $B_j(\theta,\phi)$ are geometrical factors which in the case of a dipolar interaction depend on the angle θ and ϕ between the position vector joining the nucleus with the electrons and the external magnetic field. When a component of the total spin $\sum_i S_i^{\alpha}$ is a conserved quantity ($\alpha=x$, y, or z), the spin-correlation functions of that component can be described by a diffusive process[3] at high temperature in the long wavelength ($k \ll |JS/\hbar D|^{1/2}$) and long-time limit ($t \gg |\hbar/JS|$). Then the spin-correlation function is proportional to $t^{-d/2}$, where d is the dimensionality. In one dimension these functions can be written as[4]

$$g_j^{\alpha}(t)=(4\pi Dt)^{-1/2} \tag{2}$$

and their Fourier transforms

$$f_j^{\alpha}(\omega)=(2D\omega)^{-1/2} , \tag{3}$$

where D, the spin-diffusion coefficient along the chain, is proportional to the intrachain exchange interaction J. The long-time behavior of the pair correlation functions ($j \neq 0$) is the same as that of the autocorrelation function ($j=0$). In two dimensions, the spectral density $f(\omega)$ shows logarithmic behavior and in three dimensions it is independent of frequency; the one-dimensional spectral density, Eq. (3), diverges as $\omega \to 0$.

For the particular case of a one-dimensional array of spins coupled by a Heisenberg Hamiltonian,

$$H=-2J\sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1} \ .$$

Laurie *et al.*[5] have estimated the numerical value of the proportionality constant between the diffusion coefficient and the exchange interaction. They suggest $D=2.66\,|J\,|\,S/\hbar$, where S is the spin. With this result we can relate the spin-lattice relaxation to the strength of the intrachain magnetic interactions between local moments.

In a real magnetic chain various effects can disturb one-dimensional spin diffusion. This introduces a finite value for the spectral density at zero frequency. These perturbation terms can be qualitatively handled in terms of a cutoff frequency ω_c defined as the frequency where the $\omega^{-1/2}$ divergence in the spectral density is truncated. The cutoff mechanisms include effects of the interchain exchange interaction, intrachain dipolar interaction, impurities, and defects.[6] It was shown that the interchain exchange interaction dominates the cutoff when the external field is parallel to the crystal axis, while the intrachain dipolar interaction is most important with the field perpendicular to the crystal axis.[6] As the intrachain dipolar cutoff frequency is itself field dependent, it would be difficult to analyze the spin-lattice relaxation rate of a polycrystalline sample in terms of a single cutoff mechanism if both the interchain exchange interaction and the intrachain dipolar interaction are sufficiently large to be seen and are of comparable magnitude. As will be demonstrated below, neither of these effects appear to be important in Cu(PC).

III. EXPERIMENTAL

Cu(PC) belongs to the space group $P2_1/a$ with $a=19.407$ A, $b=4.790$, $c=14.628$, and $\beta=120.56'$, with two chemical units per unit cell.[7] A Cu(PC) crystal is composed of slipped stacks along the b axis of the Cu(PC) molecules, as shown in Fig. 1. This structure generates an assembly of parallel chains of interactive paramagnetic copper ions (Cu^{+2}, d^9, $S=\frac{1}{2}$) with a large interchain separation. Several features of Cu(PC) make it particularly suitable for using proton NMR as a probe of the electron-spin dynamics. There are 16 protons attached to each phthalocyanine ring, rigidly fixed to the molecular framework at known positions.[7] Theoretical calculation of the geometrical contribution to the spin-spin correlation function can be quite reliable. Furthermore, NMR relaxation in this material is not complicated by heteronuclear dipolar coupling or fluctuations in the proton positions (e.g., rotating methyl groups).

The NMR proton spin lattice relaxation rates (T_1^{-1}) have been measured as a function of frequency (11.4, 25, 47 MHz) and temperature (1.7 to 300 K) (Figs. 2 and 3). Purified polycrystalline samples, typically 40 mg, were cooled in a continuous-flow cryostat (Oxford Instruments Co.). Since the free induction (FID) was on the order of 20 μsec, it was necessary to reduce the receiver dead time to less than 7 μsec. The $\pi/2$ pulse duration was 1 μsec. Signals were averaged using a phase alternating pulse (PAPS) sequence[8] at a digitization rate of 50 nsec/point. The measurement of T_1 was performed by using a conventional π-$\pi/2$ or $\pi/2$-$\pi/2$ pulse sequence. The recovery of the magnetization was purely exponential in all cases over more than a decade. The magnetic susceptibility measurements were performed with a variable temperature susceptometer (VTS-50, S.H.E. Co.) in the range to 300 K.

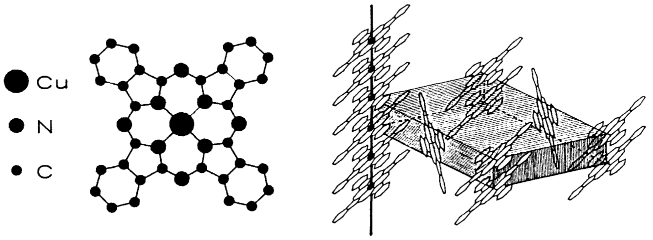

FIG. 1. The structure of a Cu(PC) molecule in a plane (left). The crystal structure of Cu(PC) (right). The hatched box is a unit cell. The vertical line and array of the Cu(PC) molecules show the stacking axis b.

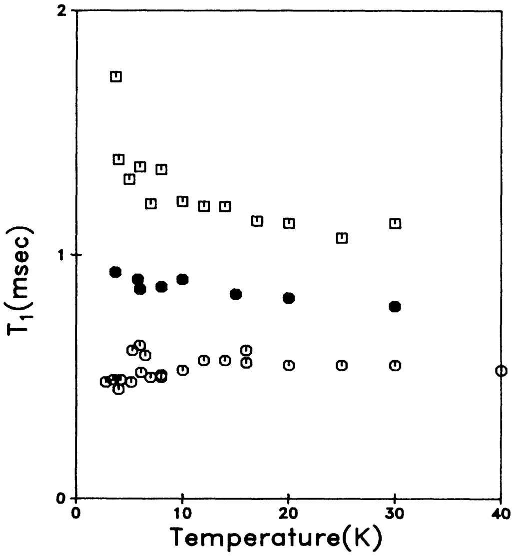

FIG. 2. The spin-lattice relaxation time T_1 for Cu(PC) is shown as a function of temperature for measurement frequencies 47 (□), 25 (●), and 11.4 (○) MHz. These are temperature independent above 10 K.

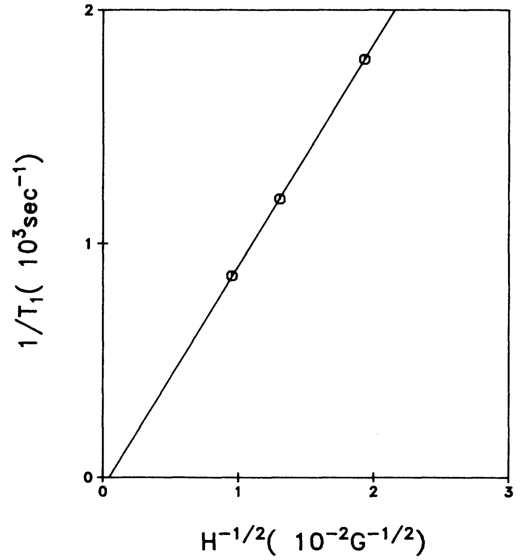

FIG. 3. The spin-lattice relaxation rate T_1^{-1} is shown as a function of the external magnetic field. The point in each field is the average of corresponding data at temperatures above 10 K in Fig. 2. T_1^{-1} is proportional to $H^{-1/2}$ which is expected for one-dimensional spin diffusion.

IV. RESULTS AND DISCUSSION

In Fig. 2, the spin-lattice relaxation time T_1 versus temperature is plotted for three different frequencies. From room temperature down to ~10 K, T_1 is essentially independent of temperature for a given frequency, and increases with frequency. Upon further cooling to 1.7 K, T_1 (47 MHz) increases almost twofold whereas T_1 (25 MHz) and T_1 (11.4 MHz) remain roughly constant. In Fig. 3, $1/T_1$ is plotted versus $H^{-1/2}$. The data points shown here are averaged over all temperatures $T > 10$ K above which the relaxation rates are essentially temperature independent. The results fit an expression of the form

$$1/T_1 = PH^{-1/2} + Q \tag{4}$$

with

$$P = (9.50 \pm 0.06) \times 10^4\ \mathrm{G}^{1/2}\,\mathrm{sec}^{-1}\ ,$$

$$Q = (-47 \pm 10)\ \mathrm{sec}^{-1}\ .$$

It is instructive to compare these results with the spin-lattice relaxation time of Ni(PC), which has essentially the same physical structure but is diamagnetic: for Cu(PC) $T_1 \sim 10^{-3}$ sec, while for Ni(PC) $T_1 \sim 1$ sec. This indicates that the spin-lattice relaxation of Cu(PC) originates from spin coupling between protons and local electronic spins on the Cu sites and that additional contributions from other sources can be neglected. Furthermore, the temperature dependence of the spin-lattice relaxation rate of Cu(PC) is quite weak (Fig. 2). This is as expected when T_1 is dominated by electronic spin fluctuations.[9]

The spin-spin relaxation time for Cu(PC) is 20±2 μsec independent of temperature from room temperature down to 10 K, below which demagnetization effects become important. The spin-spin relaxation time is 20 μsec, independent of temperature, for all *M*(PC) and *M*(PC)I, regardless of whether *M* is paramagnetic (e.g., $M = \mathrm{Cu}$) or not ($M = \mathrm{Ni}$). This result can be explained very well by line broadening due to a proton dipolar coupling in the rigid lattice limit. The second moment calculation for Cu(PC)I,[10] based on this mechanism, predicts a spin-spin relaxation time T_2 of 20.1 μsec, in excellent agreement with the experimental spin-spin relaxation time of 20 μsec for Cu(PC). The second moments of *M*(PC) and *M*(PC)I in principle depend on the central metal *M* and the presence of iodine (I); these factors affect the lattice constants and angles between lattice vectors and the PC planes. However, more than 90% of the contribution to the second moment comes from the protons in the same PC ring, where the minimum distance between protons is 2.14 Å; thus, the experimental result that the second moments of *M*(PC) and *M*(PC)I are the same within 10% and independent of the central atom *M* confirms this conclusion. The hyperfine interaction between localized electronic spins and protons, which controls T_1, can produce an isotropic shift or anisotropic line broadening for polycrystalline samples. These effects are not observed in the frequency range covered in this experiment in part because the NMR frequency is much lower than the exchange frequency as will be shown below.

To apply Eqs. (1) and (3) to interpret the results summarized in Eq. (4), three conditions on the experimental data should be satisfied. (i) *The high-temperature limit.* This limit is defined as $k_BT \gg \omega_{\mathrm{ex}}$, where ω_{ex} is the exchange frequency along the chain,[11]

$$\omega_{\mathrm{ex}} = \left| 16\frac{S(S+1)}{3} \right|^{1/2} \left| \frac{J}{\hbar} \right| . \tag{5}$$

For $S = \frac{1}{2}$, we derive $\hbar\omega_{\mathrm{ex}} = 2\,|J\,|$. As will be discussed below, we find from our analysis of the NMR spin-lattice relaxation experiments that $|J/k_B| \ll 10$ K, consistent with susceptibility and ESR linewidth data. Consequently, the high-temperature limit clearly applies in the temperature range $T > 10$ K. The magnetic susceptibility measurements, Fig. 4, satisfy a Curie-Weiss law $\chi = C/(T-\Theta)$ from 20 down to 2 K, with a Curie-Weiss temperature $\Theta = 0.11 \pm 0.05$ K and a Curie constant $C = 0.401$ K cm^3/mole. This is within 2% of the result expected from the expression $C = N\mu_B^2\,\bar{g}^{\,2}S(S+1)/3k_B$. The average squared *g* shift, $\bar{g}^{\,2}$, was found from ESR measurements at 35 GHz of the parallel and perpendicular *g* shift ($\bar{g}^{\,2} = \frac{1}{3}g_{\parallel}^2 + \frac{2}{3}g_{\perp}^2$; $g_{\parallel} = 2.167$, $g_{\perp} = 2.050$). Since $\Theta \approx J$ in one dimension, these results are qualitatively consistent with the NMR spin-lattice relaxation experiments.

(ii) *The long-wavelength limit.* In one dimension the spin fluctuations at long wavelength dominate the spectral function that determines T_1. It has been shown[3] that a direct consequence of the one-dimensional effect is that the frequency dependence of T_1 is proportional to $\omega^{1/2}$. Our observation of this frequency dependence strongly suggests that this condition is appropriate in the case of Cu(PC).

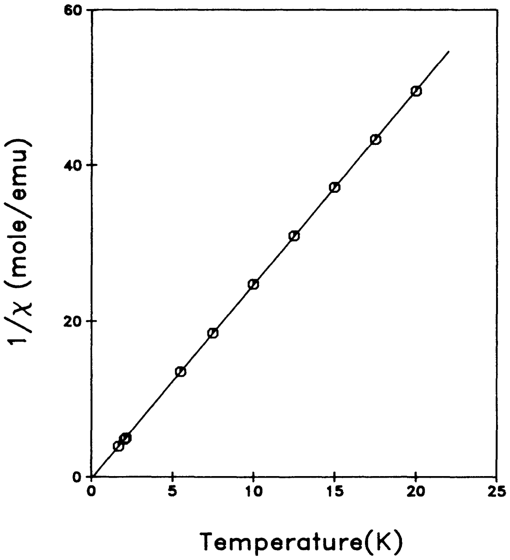

FIG. 4. Magnetic susceptibility of polycrystalline Cu(PC) as a function of temperature. The solid line in the figure represents a best fit of the data to a Curie-Weiss law with $\Theta = 0.11 \pm 0.05$ K and $C = 0.401$ K cm^3/mole. The data follow a Curie-Weiss law down to 1.7 K, the lowest temperature of the experiment.

(iii) *The low-frequency limit.* This restricts the Larmor frequencies to be less than the exchange frequency, i.e., ω_n and $\omega_e \ll \omega_{\mathrm{ex}}$. The low-frequency limit is usually satisfied for one-dimensional magnetic insulators. Nevertheless, we can check this assumption self-consistently after estimating the magnitude of ω_{ex}.

Before interpreting the experimental results using the theoretical expression, Eq. (1) we should take into account the possibility of deviations from one-dimensionality that might be handled in terms of a cutoff frequency ω_c. This is required in the case of TMMC, for instance. If $\omega_n \ll \omega_e < \omega_c$ then the spin-lattice relaxation rate expected from the correlation functions Eq. (3) is roughly frequency independent in contrast to what we have observed for Cu(PC). If $\omega_n < \omega_c < \omega_e$ then one can replace the ω_n frequency dependence of the correlations Eq. (3) by a constant ω_c, giving

$$\frac{1}{T_1} = A(2D\omega_c)^{-1/2} + B(2D\omega_e)^{-1/2} , \tag{6}$$

where $A = \sum_j \langle A_j(\theta,\phi) \rangle$ and $B = \sum_j \langle B_j(\theta,\phi) \rangle$ (the brackets indicate a powder average). We shall show by calculation of A and B that this equation does not hold in the frequency range in which our data was taken; this imposes an upper bound on the cutoff frequency. Dipolar hyperfine couplings with 30 Cu^{+2} ions on each of nine chains, the chain where the proton under consideration resides and eight surrounding chains, were summed with pair correlations added up to $j = 7$. Any additional Cu ion and/or pair correlation contribute less than 1% to the result. After averaging over the four geometrically different proton positions we get $A = 4.46 \times 10^{12}$ sec^{-2} and $B = 10.41 \times 10^{12}$ sec^{-2}. With the first term on the right-hand side of Eq. (6) a constant, the $\omega^{-1/2}$ behavior of $1/T_1$ comes only from the second term. By comparing Eq. (4) with Eq. (6) we obtain $D = 3.38 \times 10^8$ rad/sec and $\omega_c = 1.33 \times 10^{13}$ rad/sec, where the absolute value of Q [Eq. (4)] was used as an experimental bound on the frequency independent term in Eq. (6). Using the relation $D = 2.66 \times |J| S/\hbar$ and Eq. (5) with $S = \frac{1}{2}$, we find that $\omega_{\mathrm{ex}} = 1.50D = 5.07 \times 10^8$ rad/sec. It is clear that $\omega_n < \omega_c < \omega_e$ does not hold; the value inferred for ω_c violates the initial assumption $\omega_c < \omega_e$ and the value of ω_{ex} violates condition (iii), $\omega_e < \omega_{\mathrm{ex}}$, over our whole experimental range of ω_e (from 7.5×10^9 to 3.1×10^{10} rad/sec). We therefore discard this self-contradictory case and consider the last possibility $\omega_c < \omega_n \ll \omega_e$. Under this condition both terms on the right-hand side of Eq. (1) behave as $\omega^{-1/2}$,

$$1/T_1 = [A + B(\gamma_n/\gamma_e)^{1/2}](2D\omega_n)^{-1/2} , \tag{7}$$

where γ_e and γ_n are the electronic and nuclear gyromagnetic ratio, respectively. Comparing (4) with (7) we find $D = 4.99 \times 10^{10}$ rad/sec and $\omega_{\mathrm{ex}} = 7.49 \times 10^{10}$ rad/sec. Although ω_{ex} is slightly larger than ω_e at the highest magnetic field in our experiment, we believe that this is not a serious drawback since the second term is negligible compared to the first term in Eq. (7). These results give an exchange coupling constant $|J/k_B| = 0.286$ K. This rather small exchange interaction is quite consistent with the Curie-like behavior of the magnetic susceptibility and ESR linewidth measurements.

Measurements of the ESR linewidth provide another independent measure of the exchange interaction. The powder averaged, peak-to-peak ESR linewidth Γ for polycrystalline Cu(PC) is 51 G, independent of temperature ($\Gamma_{\parallel} = 196$ G and $\Gamma_{\perp} = 43$ G). This is significantly smaller than the dipolar linewidth Γ_D calculated from the second moment, $\Gamma_D = 5.16 \times 10^2$ G. A rough estimate of the exchange energy can be determined from the exchange-narrowed linewidth,[12] $|J/k_B| = \mu_B \Gamma_D^2 / \Gamma k_B = 0.36$ K. This value of the intrachain interaction is close to the result obtained from the NMR T_1 measurement.

The frequency dependence of T_1 provides clear evidence that Cu(PC) is a Heisenberg system. Heisenberg magnetic interactions are isotropic and all components of the total spin are conserved; therefore the spectral density of the spin correlation function $f^{\alpha}(\omega)$ is diffusive, for all components α. In contrast, for the spin-$\frac{1}{2}$ X-Y system the z component of the total spin is conserved but $f^{z}(\omega)$ is not diffusive.[13] For the Ising system the z component of each spin is conserved and consequently they have no dynamics. The $\alpha = \pm$ components of the total spin are not conserved in the Ising system or the X-Y system. Thus only a Heisenberg magnetic system can be expected to show diffusive behavior of the spin correlations.

We can estimate an upper bound for the interchain exchange interaction $|J'|$ from the spin-lattice relaxation data. The crossover from one to higher dimensions takes place when $\omega_n \sim \omega_c$, the interchain exchange interaction frequency. Since there is no evidence for deviation from the $\omega^{-1/2}$ dependence of T_1^{-1}, we take our lowest measuring frequency as the upper limit of the interchain cutoff, $\omega_c \leqq 2\pi \times 11.4$ MHz. This yields an anisotropy in spin diffusion of $|J/J'| = \omega_{\text{ex}}/\omega_c \geqq 6.4 \times 10^3$. This is the same order of magnitude as that of TMMC, a material with a particularly high magnetic anisotropy.

V. SUMMARY

The use of proton NMR to investigate the magnetic interactions in Cu(PC) suggests that it is a highly one-dimensional Heisenberg system with an exchange interaction between Cu ions on a single chain $|J/k_B| = 0.286$ K, and an anisotropy factor $|J/J'| \geqq 6 \times 10^3$. This can be compared favorably with a calculation of the exchange interaction derived from our ESR linewidth measurements which gives $|J/k_B| \approx 0.36$ K and with our measurements of a Curie-Weiss temperature $\Theta = J/k_B = 0.11 \pm 0.05$ K.

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