Experimental Study of Spin Fluctuations in a One-Dimensional Antiferromagnet*

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An experimental study of nuclear relaxation in the low-temperature antiferromagnetic regime of *N*-methyl phenazinium tetracyanoquinodimethan (NMP) (TCNQ) is presented. The data are characterized by a relatively weak temperature dependence; the extrapolated zero-temperature rate is *finite* and of the same magnitude as the rate at $T \gtrsim J/k_B$. These results are in good agreement with predictions based on the fermion representation for the spin-$\frac{1}{2}$ antiferromagnet in one dimension. The conventional Boson assumption, on the other hand, leads to a predicted rate off by four orders of magnitude in comparison with experiment. The experimental measurements of T_1^{-1} thus strongly suggest fermion-like excitations in the spin-$\frac{1}{2}$ one-dimensional antiferromagnet.

Since Bethe's famous solution of the ground state of the one-dimensional (1D) antiferromagnet in 1931,[1] this problem has been of continued interest. Although much progress has been made,[2] especially on the experimental side, our understanding of the spin-fluctuation dynamics in such systems remains unsatisfactory. Antiferromagnetism in 1D is characterized by the absence of long-range order and by large fluctuations in the short-range-ordered state. This results in a smeared "transition" at temperatures of order J/k_B (J is the exchange energy) and in a zero average moment on each site. Spin-$\frac{1}{2}$ antiferromagnetic (AF) systems are especially interesting since they represent the opposite quantum limit to Fisher's solution[3] of the 1D problem with classical spins. This is particularly relevant in light of Richard's recent study[4] of nuclear relaxation in the $S=\frac{5}{2}$ 1D AF $(CH_3)_4NMnCl_3$. In this *large-spin* system the low-temperature relaxation was attributed to the T^{-1} dependence in the staggered susceptibility which arises in the case of classical spins from the approach to a true phase transition at 0 °K. It is the purpose of this paper to present a preliminary account of the low-temperature nuclear-relaxation data from the organic salt (NMP)(TCNQ).[5] The results are qualitatively different from those predicted for the classical spin system and can be accounted for by a simple theory which treats the $S=\frac{1}{2}$ antiferromagnet in one dimension in the fermion representation.

(NMP)(TCNQ) is an organic charge-transfer salt which crystallizes with stacks of planar $(TCNQ)^-$ anion radicals forming well-separated parallel chains.[6] The 1D aspects of the structure are enhanced by the directionality of the π-electron wave functions with the result that interchain coupling is negligible. This electronically 1D system has been thoroughly studied[7,8] and found to undergo a Mott transition from metal to insulator with decreasing temperature. Although not fully in the strong-coupling limit, (NMP)(TCNQ) may be viewed as a spin-$\frac{1}{2}$ antiferromagnet at low temperatures. The evidence for the AF ground state is threefold.[7] First, the spin susceptibility follows the Curie–Weiss law $\chi = C/T + \Theta$, with $\Theta = 60°$ K, rounding off toward a constant value below 40 °K. Second, the low-temperature specific heat shows a term linear in T as expected from AF spin-wave excitations in 1D. Third, the ESR linewidth shows a broad maximum at 60 °K, indicating the onset of the AF state. Evidence of rapid spin fluctuations with correlation time $\tau_c \sim \hbar/J$ was inferred from the narrow unshifted ESR line observed at low temperatures.[7]

The proton-spin–lattice relaxation times were measured in polycrystalline samples by observation of the recovery of the free-induction magnetization after saturating with a comb of rf pulses. At all temperatures the recovery was exponential in time. The resulting relaxation rates are shown in Fig. 1. The relaxation rate extrapolated to zero temperature is, to within experimental accuracy, frequency independent from 4 to 40 MHz, with a value of $T_1^{-1}(0) = 29 \pm 2$ sec^{-1}. The weak temperature dependence shown in Fig. 1 is also insensitive to the measurement frequency in the range above 20 MHz, whereas at low frequencies a somewhat stronger dependence on temperature is observed. This additional low-field contribution arises from the anisotropic ($I^{\pm}S_z$) dipolar terms which couple the nuclei to the longitudinal fluctuations of the uniform mode, and will be discussed in detail elsewhere.[9] The impurity content in the

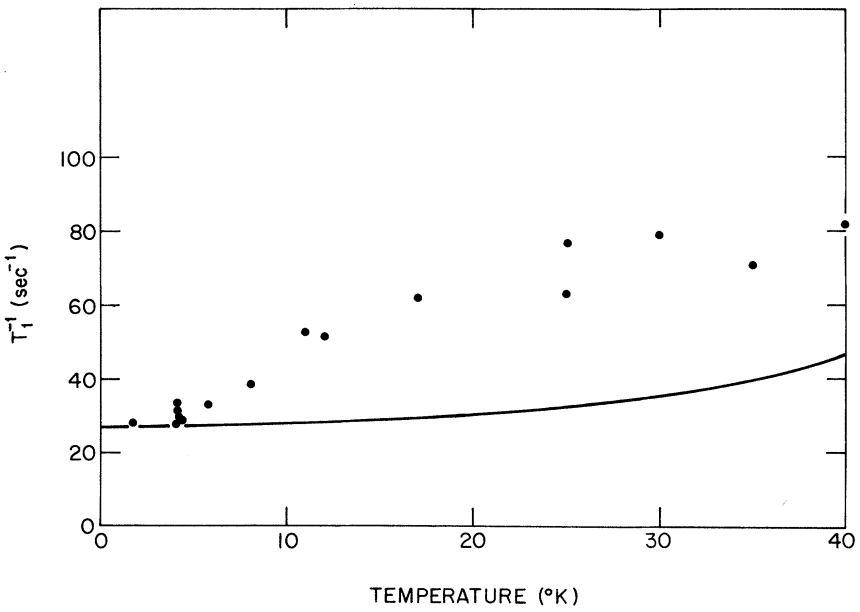

FIG. 1. Proton-spin–lattice relaxation rate in (NMP)(TCNQ) as a function of temperature. The measured rates are frequency independent in the range 20–40 MHz. The solid curve represents the weak temperature dependence predicted by Hartree–Fock theory.

best samples is less than 0.1% as determined from the Curie-law contribution to the low-temperature susceptibility. However, the measured rates were insensitive to an order-of-magnitude increase in impurity concentration, indicating that the results are intrinsic to the system. The data in Fig. 1 are characterized by a relatively weak temperature dependence; the extrapolated zero-temperature rate is *finite* and of the same magnitude as the rate at $T \gtrsim J/k_B$. Thus, qualitatively, the spin-spin correlation time is of order $\hbar/J$ over the entire temperature range.

In order to treat the problem in detail, we approximate the AF state of (NMP)(TCNQ) by a spin-$\frac{1}{2}$ Heisenberg Hamiltonian $H = J\sum \vec{S}_j \cdot \vec{S}_{j+1}$. Using the fermion representation[10] for $S = \frac{1}{2}$, this Hamiltonian can be written in the form

$$H = J\sum_k (\cos k - 1) C_k^\dagger C_k + \frac{J}{N} \sum_{k_1, k_2, q} \cos q \, C_{k_1+q}^\dagger C_{k_2-q}^\dagger C_{k_2} C_{k_1} , \quad (1)$$

where $C_k^\dagger$ and C_k are the creation and annihilation operators for spinless fermions. The total number of fermions is not conserved. The dispersion relation calculated in the random-phase approximation[10] (RPA) takes the form $\epsilon(k) = Jp \cos k$, where p can be approximated by

$$p \simeq 1 + \left(\frac{2}{\pi}\right) 1 - \frac{\pi}{3(1+2/\pi)^3} \left(\frac{kT}{J}\right)^2 + \cdots .$$

The ground state in zero magnetic field consists of $\frac{1}{2}N$ occupied states (shaded region in Fig. 2) and $\frac{1}{2}N$ empty states. Bulaevskii[10] has shown that the ground-state energy in this approximation is within 5% of the exact result.

Since there is no gap in the excitation spectrum, even in an external magnetic field, we consider a direct process in which a nuclear-spin flip is accompanied by emission (or absorption) of a single excitation. T_1^{-1} is given (for spin-$\frac{1}{2}$ nuclei) by[11]

$$T_1^{-1} = W_\uparrow + W_\downarrow , \quad (2)$$

where, for a hyperfine interaction of the form $A\vec{I}\cdot\vec{S}$,[8]

$$W_\downarrow = \frac{2\pi}{\hbar} \sum_k |\langle \uparrow k | A\vec{I}\cdot\vec{S} | \downarrow 0 \rangle|^2 \delta(\hbar\omega + \epsilon(k)) ,$$
$$W_\uparrow = \frac{2\pi}{\hbar} \sum_k |\langle \downarrow 0 | A\vec{I}\cdot\vec{S} | \uparrow k \rangle|^2 \delta(\hbar\omega - \epsilon(k)) . \quad (3)$$

$W_\downarrow$ corresponds to hole emission and is thus proportional to $f(-\hbar\omega) = 1 - f(\hbar\omega)$, where $f(\epsilon)$ is the Fermi distribution function. Similarly, $W_\uparrow$ corresponds to excitation absorption and is proportional to $f(\hbar\omega)$. Since the matrix elements are identical, we have

$$T_1^{-1} = \frac{A^2}{2\hbar^2} \frac{dk}{d\epsilon}\bigg|_{\epsilon=\hbar\omega} [f(\hbar\omega) + 1 - f(\hbar\omega)] = \frac{A^2}{2\hbar Jp} . \quad (4)$$

An alternative approach is to calculate T_1^{-1} directly from the spin-spin time-correlation functions[12]

$$T_1^{-1} = \frac{A^2}{4\hbar^2 N} \sum_j (\langle S_j^+ S_j^- \rangle_\omega + \langle S_j^- S_j^+ \rangle_{-\omega}) , \quad (5)$$

where $\langle S_j^+ S_j^- \rangle_\omega$ is the Fourier transform (at the nuclear Zeeman frequency) of the time-correlation function. Although the RPA results are identical with Eq. (4) for the direct process, the spin-

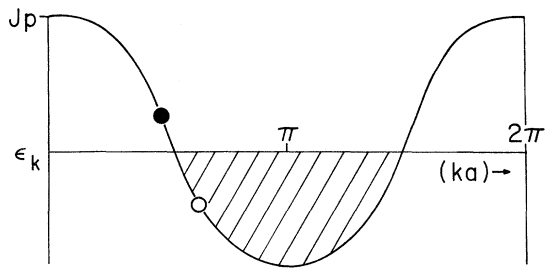

FIG. 2. Dispersion relation in the Bulaevskii fermion representation of the 1D antiferromagnet. The solid dot represents an excitation at $\epsilon_k > 0$ and the open circle an excitation hole at $\epsilon_k < 0$.

correlation functions provide general expressions for T_1^{-1} which can be used in more complete calculations which attempt to include the full response of the system. Expressing the spin operators in the fermion representation, we have

$$T_1^{-1} = \frac{A^2}{4\hbar^2}\frac{1}{N}\sum_k (\langle C_k^\dagger C_k\rangle_\omega + \langle C_k C_k^\dagger\rangle_{-\omega}) \ . \tag{6}$$

The correlation functions are calculated using the Green's-function formalism

$$\langle C_k^\dagger C_k\rangle_\omega = e^{\hbar\omega/k_BT}\langle C_k C_k^\dagger\rangle_\omega = f(\hbar\omega)\rho^+(k,\omega) \ , \tag{7}$$

where $\rho^+(k,\omega)$ is the anticommutator spectral weight function. Equation (6) becomes

$$T_1^{-1} = \frac{A^2}{4\hbar^2} N^{-1}\sum_k \rho^+(k,\omega) \ . \tag{8}$$

The direct process is obtained using the RPA. It is easily shown that $\rho^+(k,\omega) = 2\pi\delta(\omega - \epsilon(k)/\hbar)$, and thus for $\hbar\omega \ll J$, $T_1^{-1} = A^2/2\hbar Jp$ as in Eq. (4). The direct process, in the RPA, thus predicts a finite zero-temperature rate $T_1^{-1} \simeq A^2/3.28\hbar J$ and a weak temperature dependence due to the temperature renormalization of the dispersion relation. In view of the good agreement of the ground-state energy and low-temperature specific heat obtained using the RPA (as compared to the exact results[10,13]), we believe the above zero-temperature value is, aside from a renormalization factor of order 1, the correct value.

The experimental rate shown in Fig. 1 indeed extrapolates to a finite value at $T = 0\ ^\circ$K. Using $A/g\mu_B = 1.57$ G and $J = 5.2\times10^{-3}$ eV, [7,8] we find for the *experimental* rate $T_1^{-1}(0\ ^\circ\text{K}) = A^2/3.37\hbar J$. Thus the RPA result is in excellent agreement with experiment at low temperatures. Examination of the data shows that the temperature dependence is much stronger than predicted by the simple direct process. We attribute this to finite quasiparticle lifetime effects at higher temperature as is the case in three-dimensional (3D) AF[14] and other related problems. A brief examination of higher-order diagrams indicates additional terms proportional to T^2, so that we expect a more complete theory to show a somewhat stronger temperature variation. However, no attempt has been made at this stage to include such effects in detail, especially since single-particle excitations across the Hubbard gap may begin to play a role at higher temperature.

Studies of the nuclear relaxation rate thus provide a direct measure of the spin fluctuations in the 1D antiferromagnet. The weak temperature dependence and finite value at $T \to 0\ ^\circ$K indicate a correlation time of order $\hbar/J$ throughout the AF temperature range. The description of the elementary excitations as fermions is in good agreement with experiment. In this context it is interesting to redo the Golden-rule calculation of the direct process, making the conventional assumption that the spin waves can be treated as bosons at low temperature. Going back to Eq. (4), the statistical factors in the brackets become $1 + 2n(\hbar\omega)$, where $n(\epsilon)$ is the Bose-Einstein distribution function. For the experimental conditions $k_BT \gg \hbar\omega$, one finds

$$T_1^{-1} = \left(\frac{A}{\hbar}\right)^2 \left|\frac{dk}{d\epsilon}\right|_{\hbar\omega} \frac{k_BT}{\hbar\omega} \quad \text{(boson like spin waves)} \ .$$

This differs in magnitude from the experimental rate by a factor of $k_BT/\hbar\omega \sim 10^4$, and the temperature dependence is incorrect. The experimental T_1^{-1} data are thus particularly sensitive to the statistics of the excitations. This is to be contrasted, for example, with the low-temperature heat capacity where either the Bulaevskii fermion theory (see Fig. 2) or the conventional boson spin-wave theory leads to a term linear in T. The magnitudes in the two cases differ by only a factor of 2. [7,10]

Finally, we note that the rate can be calculated using the exact single-spin-wave states of des Cloizeaux and Pearson. [15] *Assuming* these excitations are fermions, one finds, of course, the same result for the direct process as given in Eq. (4), except for a renormalization factor of 1.05. Thus the experimental measurements of T_1^{-1} strongly suggest *fermion*like excitations in this spin-$\frac{1}{2}$ 1D antiferromagnet.

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[9]This mechanism, which is unimportant in 3D systems because of the negligible state density near $q=0$, gives a contribution to T_1^{-1} proportional to $k_B T(1+\omega^2\tau_1^2)^{-1}$, where τ_1 is the *electronic* longitudinal relaxation time, and thus is experimentally unimportant above a few kilogauss and does not affect the rate at $T\to 0$ °K.

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Lead Centers in Cesium Halides

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Lead as an impurity in cesium halides gives the usual *A*, *B*, and *C* bands with some differences, such as the appearance of a doublet structure in the *A* band and the observation of an aggregate lead complex band in the visible region, when compared with the results for the other lead-doped alkali halides. In this paper the peak positions, half-widths, and dipole-strength ratios of these lead centers in CsCl, CsBr, and CsI are reported. In irradiated cesium halides containing divalent lead, a new band is observed in the uv region at about 20 nm to the shorter-wavelength side of the *A* band. This band is interpreted to be due to Pb^+ from various optical absorption studies and is found to be stable up to 110 °C. In crystals irradiated for a longer time, this Pb^+ band goes down along with the Pb^{++} bands and a new band is observed which is attributed to Pb^0. It has been found from conductivity studies that the binding energy for an impurity-vacancy pair in cesium halides is about 0.48 eV and the presence of divalent lead in these crystals decreases the conductivity in the extrinsic region. From the dielectric-loss measurements, the migration energy for a cation vacancy bound to the impurity is found to be ~ 0.62 eV while the preexponential factor is of the order of 3×10^{10} sec^{-1}.

I. INTRODUCTION

A considerable amount of work has been published[1-6] on the nature and properties of defect centers in lead-doped sodium and potassium halides (fcc structure), but no data are available on lead-doped cesium halides (bcc structure). Optical absorption studies[7] of Tl^+ (another ion of the s^2 family) in cesium halides have revealed some new features such as different temperature behavior of the *B* band and six, instead of the usual four, bands in alkali halides containing such impurities. Hence, it was thought desirable to undertake a study of the behavior of lead centers in such bcc structures by optical absorption, radiation damage, electrical conductivity, and dielectric-loss techniques. The electrical conductivity of cesium halides has been investigated previously[8-10] but the association region has not been found. It has also been established[8] that anion vacancies are more mobile than cation vacancies. The dielectric-loss studies in bcc structures containing charge-compensating defects have not been studied so far and the results pertaining to the dielectric-loss measurements of the lead-impurity–vacancy dipole in cesium halides are presented in this paper.

II. EXPERIMENTAL METHODS

Some single crystals of pure cesium halides have been obtained from other research groups, while some pure and lead-doped crystals were grown in our laboratory by the Bridgman technique. Lead was diffused into pure crystals by heating the lead metal and cesium halide crystals together in an