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Longitudinal and transverse spin dynamics of a one-dimensional *XY* system studied by chlorine nuclear relaxation in $PrCl_3$

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T_1 and T_2 measurements of Cl nuclear-quadrupole resonance in $PrCl_3$ are explained with the assumption of one-dimensional *XY* spin dynamics for the Pr spins. The Cl nuclei are relaxed both by fluctuating magnetic fields due to the longitudinal Pr moments, and also by fluctuating electric field gradients due to the transverse Pr moments. Accurate spin-echo measurements of the relative relaxation rates for the two Cl isotopes and of the echo decay functions allow identification of the two mechanisms. T_1 relaxation is primarily magnetic throughout the temperature range of one-dimensional ordering, while T_2 relaxation is quadrupolar at lower temperatures and probably magnetic at higher temperatures. As a result T_1 and T_2 have opposite temperature dependences. The data are consistent with calculations of the relaxation due to longitudinal- and transverse-moment fluctuations for *XY* chains.

I. INTRODUCTION

In the study of one-dimensional spin systems, the *XY* chain is of particular interest because many properties, both static and dynamic, can be calculated exactly.[1] There has been limited opportunity for comparison of these properties with experiment, however, since few physical realizations of the *XY* chain have been identified to date. In some cases one-dimensional spin systems with quasi-Heisenberg interactions have been found to behave as *XY* chains under certain conditions of anisotropy, crystal-field splittings, and temperature.[1-3] In order to study dynamic as well as static behavior over the full range of temperature, however, it is necessary to find a system which approximates the ideal *XY* chain as closely as possible. The most promising candidates for *XY* chain systems are the hexagonal compounds $PrCl_3$ and isomorphs. Culvahouse and co-workers[4,5] showed by careful EPR measurements of Pr pairs in $LaCl_3$ that the dominant Pr-Pr interaction was between nearest neighbors along the hexagonal axis, and had the form

$$H_{i,i+1}=J_{\perp}(S_x^iS_x^{i+1}+S_y^iS_y^{i+1})+J_{\parallel}S_z^iS_z^{i+1} \; . \tag{1}$$

They found that $J_{\parallel}/J_{\perp}$ was only 0.039 in $PrCl_3$ and 0.016 in $PrEtSO_4$, so that the Pr-Pr interaction is very close to the *XY* limit. Interactions with more distant Pr neighbors appear to be small, resulting in a system of chains of coupled Pr spins with weak interactions between chains. The low-temperature ordering properties hence show prominent one-dimensional character, and this has been demonstrated by fits of specific heat and susceptibility data to the predictions of the *XY*-chain model.[6,7] For $PrCl_3$, $J/k_B=2.85$ K ($J=J_{\perp}$ hereafter) and long-range ordering occurs at 0.4 K; for $PrEtSO_4$, $J/k_B=0.76$ K and no phase transition was found down to 0.06 K. More recent investigations of the dynamical properties of these compounds also gave results in agreement with *XY*-chain predictions. Infrared-absorption measurements[8] in $PrCl_3$ showed a peak due to absorption by $k=0$ spin excitations. The magnetic relaxation of impurity Sm spins in $PrEtSO_4$ was studied and found[9,10] to agree satisfactorily with the relaxation induced by Pr spins fluctuating according to *XY*-chain longitudinal correlation functions $\langle S_z^m(t)S_z^n(0)\rangle$.

The dominant *XY* interaction component in these compounds has its origin in the nature of the Pr ground electronic states which are non-Kramers doublets arising from the crystal-field splitting in C_{3h} point symmetry of the $4f^2\,{}^3H_4$ manifold. The magnetic moment is parallel to the hexagonal axis and is small ($g_{\parallel}\sim 1$, $g_{\perp}=0$) giving a small $S_z^iS_z^{i+1}$ magnetic dipolar interaction. However, the Pr

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doublets couple strongly to E-symmetry transverse distortions, giving a large XY interaction between Pr sites in an effective $S=\frac{1}{2}$ representation. Since these distortions transform as x,y they carry an electric dipole moment; the XY interaction can thus be regarded as an antiferroelectric Jahn-Teller coupling. It should be noted that although we use S_x,S_y to describe the transverse Pr moments, they are symmetric operators with respect to time reversal, whereas S_z, which describes the magnetic moment, is antisymmetric. This use of an $S=\frac{1}{2}$ representation for the states of a non-Kramers doublet has been discussed by Abragam and Bleaney[11] and others.

Nuclear magnetic and quadrupole resonance have been important techniques for studying spin dynamics in one-dimensional systems. Most previous applications have been to Heisenberg chains[12] where the low-frequency dynamical behavior is dominated by spin diffusion. Characteristic and contrasting results are expected in XY chains, since diffusive spin propagation should not be present.[13] The longitudinal spin correlations $\langle S_z^m(t)S_z^n(0)\rangle$ are known at all temperatures and are characteristic of the excitations of noninteracting fermions. On the other hand, the transverse correlations $\langle S_x^m(t)S_x^n(0)\rangle$ change dramatically between the limits of high and low temperatures, but the intermediate behavior is not known; experimental information on this point would therefore be of considerable interest.

The recent study of Sm spin relaxation[9,10] in PrEtSO$_4$ was successfully interpreted on the basis of XY-chain spin dynamics, but because J is small in this compound only the limiting high-temperature behavior could be observed. Also since Sm is a Kramers ion, only the fluctuating magnetic, or S_z, Pr moments are effective in relaxation. These experiments, therefore, probed only the longitudinal correlations of the chain and gave no information on the transverse-moment dynamics.

The investigation of the relaxation of Cl nuclei in PrCl$_3$ reported in this paper significantly extends the study of XY-chain dynamics. Since J is reasonably large, the temperature dependence is much more accessible. Also, nuclear-quadrupole transitions can be induced by electric-field-gradient (EFG) fluctuations as well as magnetic fluctuations so that both transverse- and longitudinal-moment dynamics can be studied. These two mechanisms can be identified, moreover, by comparing relaxation rates for the ^{35}Cl and ^{37}Cl isotopes.

Our measurements, for the most part, confirm earlier measurements in this compound by Mangum and Thornton[14] and also provide accurate and important new data on the relaxation decay functions and on the isotope dependence. The earlier results[14] had not been understood because the Pr-Pr interactions were not known at that time.

The principal conclusions, based on our present results and on the previous data of Mangum and Thornton, are briefly as follows. The T_1 decays are exponential and T_1 increases as the temperature is lowered. The temperature dependence and the isotope ratio both agree with a magnetic relaxation mechanism due to neighboring Pr S_z moments. The T_2 decays are more rapid than exponential and the temperature dependence is opposite to that for T_1. These facts are qualitatively consistent with electric quadrupolar relaxation due to the fluctuating transverse Pr moments; this mechanism is also confirmed by the isotope ratio. At higher temperatures electric quadrupolar relaxation apparently becomes ineffective and magnetic dipole relaxation then dominates. Owing to our limited knowledge of the Cl hyperfine-interaction parameters and of the temperature dependence of the $\langle S_x^m(t)S_x^n(0)\rangle$ correlations, rigorous fits of the data cannot be made, but the results are consistent with XY-chain spin dynamics.

II. EXPERIMENTAL

A conventional fast Fourier-transform NMR spectrometer was used for the measurements. The pulses were formed by gating the output of a Fluke 6039A synthesizer and by using an Amplifier Research 200L power amplifier as transmitter. Received nuclear-quadrupole resonance (NQR) signals were detected in phase quadrature and digitized for signal enhancement and analysis. The pulse programming and data analysis were controlled by a Nicolet 1180 Data Acquisition System. For measurements at 4.2 K the sample was immersed in liquid helium. Higher temperatures were obtained by means of a flow of vaporized helium regulated with a Lakeshore Cryotronics temperature controller.

PrCl$_3$ has a hexagonal dipyramidal structure[15] with space group C_{6h}^2. The Pr ions have point symmetry C_{3h} while the Cl ions have only C_s symmetry: the identity and the reflection σ_h. The structure is shown schematically in Fig. 1. Nearest-neighbor Pr ions form chains along the hexagonal axis. Each Pr ion has nine close Cl neighbors which form three equilateral triangles; one triangle lies in the plane perpendicular to the hexagonal axis passing through the Pr ion while the other two triangles are located above and below the plane on mirror-image sites. For the analysis of Cl NQR it is important to note that each Cl ion has three close Pr neighbors. The Pr ions labeled 1,2 in Fig. 1 are on one chain, equidistant from the Cl plane, while Pr ion 3 is in the same plane as the Cl but on a different chain.

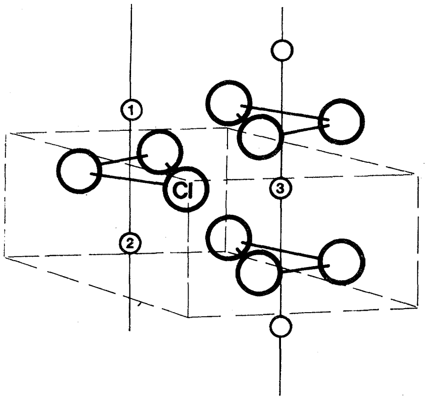

FIG. 1. Crystal structure of $PrCl_3$. The small circles are Pr ions and the large circles are Cl ions. Pr ions 1, 2, and 3 are nearest neighbors of the labeled Cl ion. The dashed lines indicate a unit cell.

In the high-temperature phase the six Cl sites in the unit cell are equivalent and a single NQR line is expected. Below the phase-transition temperature $T_D = 0.4$ K the NQR splits into two equal components. Hessler and Carlson[16] have shown that this splitting is a result of a structural (Jahn-Teller) phase transition, not a magnetic transition. Our measurements and analysis deal only with the high-temperature phase where one-dimensional ordering effects can be studied.

The sample consisted of an assortment of single crystals of $PrCl_3$. They were coated with oil to minimize hydration; nonetheless, the NQR line showed a slight asymmetry (Fig. 2) which is believed to be due to surface deterioration. At 4.2 K the NQR frequencies were 4.566 MHz for the ^{35}Cl isotope and 3.599 MHz for the ^{37}Cl isotope. Spin-lattice relaxation times were obtained using a modified Freeman-Hill inversion recovery pulse sequence[17] $(\pi-\tau-\pi/2-t-\pi/2-t)$ which yields $M(\infty)-M(\tau)$ for each value of τ. The spin-spin relaxation times were measured using a Hahn spin-echo sequence[18] $(\pi/2-\tau-\pi-\tau)$. Normally, each data point was derived by averaging 1024 scans.

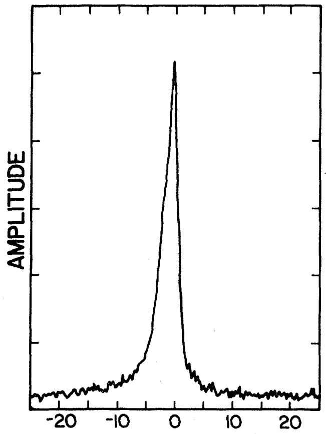

FIG. 2. NQR line shape of ^{35}Cl at 4.2 K for a sample consisting of many small randomly packed crystals.

III. RESULTS

Measurements of the Cl spin-lattice relaxation were performed at 4.2 K only. Mangum and Thornton[14] reported T_1 data for the ^{35}Cl isotope at 4.2 K and below. Their data showed that T_1 was essentially independent of temperature near 4.2 K but increased slowly below this temperature. The temperature dependence of the relaxation rate T_1^{-1} is shown in Fig. 3. Our objective was to measure the spin-lattice relaxation for both isotopes at a single temperature sufficiently accurately to identify unambiguously the relaxation mechanism. Our data points are shown in Fig. 4 with least-squares fits to a simple exponential decay function. It is apparent that the recovery to equilibrium is accurately exponential. For ^{35}Cl we found $T_1 = 4.11 \pm 0.04$ msec at 4.2 K, a value consistent with that of Mangum and Thornton. For ^{37}Cl, T_1 was found to be 5.68 ± 0.06 msec. The value 1.38 ± 0.03 is therefore obtained for the isotope ratio $T_1(^{37}\text{Cl})/T_1(^{35}\text{Cl})$.

The spin-spin relaxation was found to be more rapid than exponential when measured carefully up to τ values of $2T_2$. Typical results for the two isotopes are shown in Fig. 5.

Our data were analyzed in two ways. As indicated in Fig. 5, the initial part of the decay can be fitted to a simple exponential to give an effective decay time $\hat{T}_2$. At 4.2 K, $\hat{T}_2$ was found to be 546 ± 8 μsec for ^{35}Cl and 870 ± 10 μsec for ^{37}Cl. The former value is in satisfactory agreement with the results of

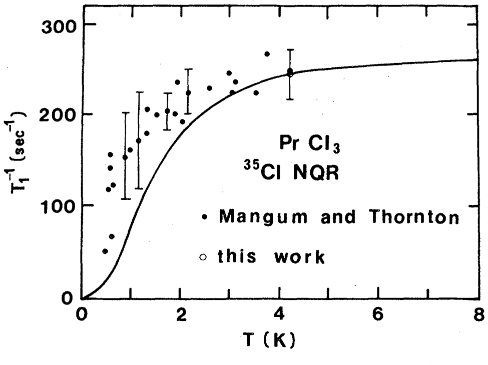

FIG. 3. Temperature dependence of T_1^{-1} for ^{35}Cl NQR. The error bars indicate the scatter in Mangum and Thornton's data. Our measurement at 4.2 K (○) has an uncertainty of ±1.0%. The solid curve is calculated from Eq. (2) with A chosen to fit the data at 4.2 K.

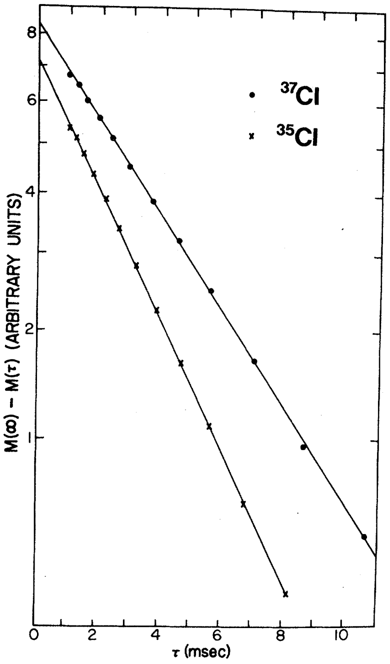

FIG. 4. Typical T_1 data at 4.2 K showing exponential decays.

Mangum and Thornton.[14] The ratio of the $\hat{T}_2$ values for the two isotopes is 1.59±0.04.

Guided by the theoretical analysis to be described later, the data were also fitted to the function $\exp(-bt^{3/2})$. This function provides an excellent fit to the data, as illustrated in Fig. 6. The b coefficients in the $\exp(-bt^{3/2})$ decay function were obtained for both isotopes and their ratio was found to be 1.67±0.05.

A thorough investigation of the nonexponential decay was carried out to confirm that it was intrinsic to the relaxation mechanism. In particular, it should be noted that the nonexponential character was unaffected when the relaxation from different and separate parts of the echo decay was analyzed rather than the decay from the entire echo-decay signal. In addition, the free-induction decay signal was also found to decay more rapidly than exponentially, and this is reasonable since the full linewidth T_2^{*-1} is only a few times broader than the homogeneous linewidth T_2^{-1}.

Measurements of the spin-spin relaxation were also carried out above 4.2 K to extend Mangum and Thornton's data to learn whether a limiting value of $\hat{T}_2$ was reached at temperatures much greater than J/k_B. Our data for ^{35}Cl in the range 4.2–17.4 K are shown in Fig. 7; data of Mangum and Thornton at lower temperatures are also indicated. Above 6 K it is seen that a plateau is reached quite abruptly. At the higher temperatures, due to temperature instability, the isotope ratio could not be determined reliably. Comparison of Fig. 7 to Fig. 3 shows the remarkable result that T_1 and T_2 depend oppositely on temperature in the temperature range where one-dimensional ordering develops.

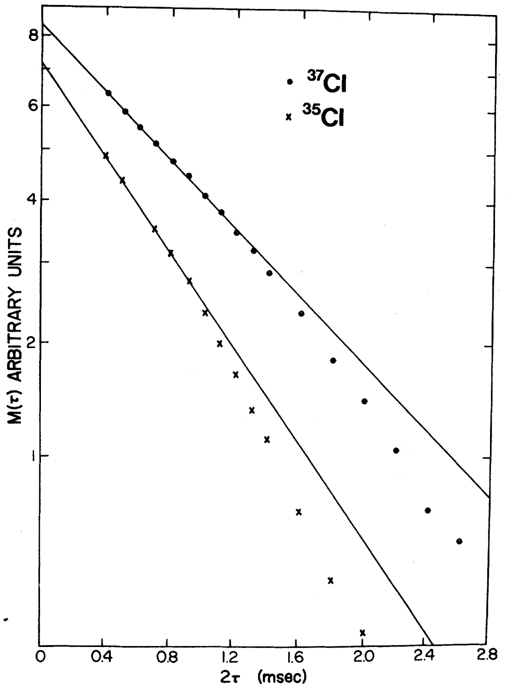

FIG. 5. Typical spin-spin relaxation data at 4.2 K showing decays more rapid than exponential.

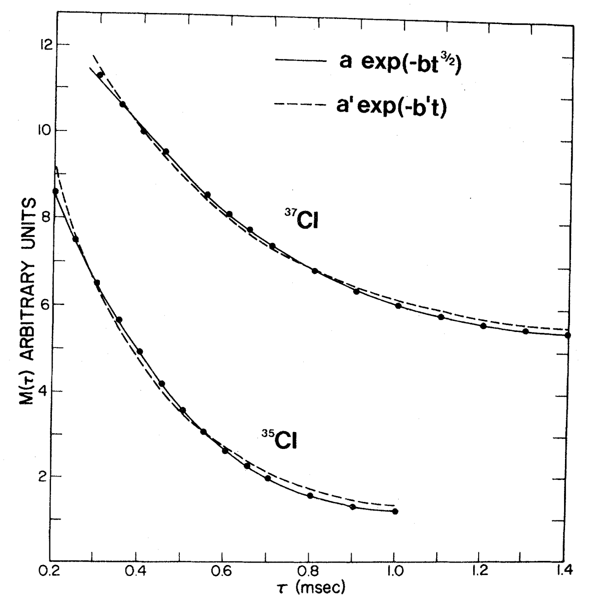

FIG. 6. Spin-spin relaxation data showing excellent fits to the decay function $\exp(-bt^{3/2})$.

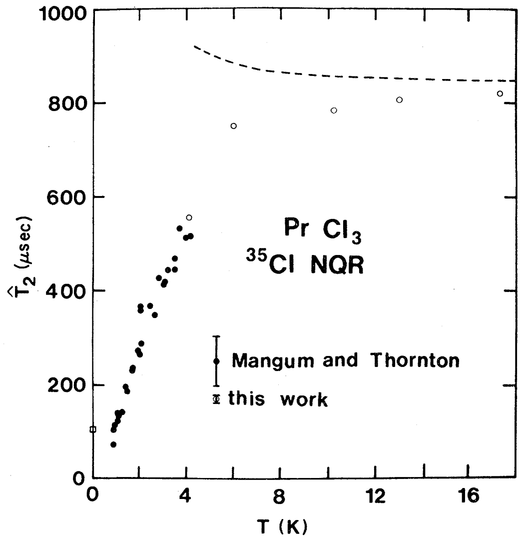

FIG. 7. Temperature dependence of $\hat{T}_2$ for ^{35}Cl NQR. The dashed line is the estimated magnetic contribution to $\hat{T}_2$. The square at $T=0$ represents the estimated quadrupolar contribution.

IV. ANALYSIS

Since T_1 and T_2 for the Cl NQR change significantly in the temperature range near $J/k_B=2.85$ K it follows that the Cl nuclei are relaxed by the fluctuating fields of the Pr spins. For relaxation by fluctuating magnetic fields the rate is expected rather generally to be proportional to the square of the nuclear magnetic moment. For the two isotopes ^{35}Cl and ^{37}Cl the ratio of the relaxation rates should thus be 1.44. Similarly, when relaxation results from fluctuating electric field gradients the relaxation rates should be in the ratio of the squares of the nuclear-quadrupole moments, which is 1.61 for the Cl isotopes. Our data therefore imply that in PrCl$_3$ the T_1 relaxation is magnetic whereas the T_2 relaxation is quadrupolar, at least at 4.2 K. It is unusual that T_1 and T_2 should depend on different fields, and indeed that a quadrupolar mechanism should be significant in a "magnetic" compound at low temperatures. Analysis shows that these features are consequences of the small magnetic moment and large electric dipole moment of the Pr ground doublet, and of the properties of XY-chain spin dynamics.

The T_1 relaxation will be analyzed first since it is the more tractable of the two. In a standard approach[19,20] the nuclear spins respond independently to the fluctuating fields due to neighboring electronic moments. The nuclear relaxation rate T_1^{-1} depends on the hyperfine-interaction parameters and on the time-dependent correlation functions for the electronic spins. In this case, where only magnetic fields are relevant and the Pr magnetic moment is given by S_z, we need only consider the longitudinal correlation functions

$$\Phi_{zz}^{mn}(t)=\langle S_z^m(t)S_z^n(0)\rangle \ .$$

Only the nearest-neighbor Pr moments need to be considered because magnetic contributions to T_1^{-1} fall off at least as rapidly as r^{-6}. The Pr ions labeled 1 and 2 in Fig. 1 are 3.0 Å from the Cl site and make angles ±45° with the mirror symmetry plane through the Cl site. Their magnetic moments generate magnetic fields at the Cl site with components both parallel and perpendicular to the hexagonal axis. Since the Pr-Cl hyperfine interactions have not been measured, we minimize the number of unknown parameters by assuming an interaction with each ion of the form $A(S_z^iI_z+S_z^iI_x)$, where S and I refer to the electronic and nuclear angular momenta, respectively. The contribution of ions 1 and 2 to T_1^{-1} is then readily shown to be[19,20]

$$T_1^{-1}=(A^2/\hbar)[\Phi_{zz}^{11}(\omega)+\Phi_{zz}^{12}(\omega)] \ , \tag{2}$$

where ω is the NQR angular frequency and $\Phi_{zz}^{mn}(\omega)$ is the Fourier transform

$$\Phi_{zz}^{mn}(\omega)=\int_{-\infty}^{+\infty} dt\, e^{i\omega t}\Phi_{zz}^{mn}(t) \ . \tag{3}$$

Pr ion 3 is at a similar distance from the Cl nucleus but because of symmetry produces only a parallel magnetic field at the Cl site. This will not affect the T_1^{-1} relaxation since only the perpendicular component induces nuclear-spin flips, and we accordingly neglect its contribution. Although our model drastically oversimplifies the magnetic hyperfine interactions, it provides a basis for explaining the temperature dependence and for checking if the magnitude of the hyperfine interaction deduced is reasonable.

To calculate T_1^{-1} the quantities $\Phi_{zz}^{mn}(\omega)$ are required as a function of temperature. For $T=\infty$ an exact expression for $\Phi_{zz}^{mn}(\omega)$ has been given by Katsura *et al.*,[21] but at arbitrary temperatures numerical integration is required. It is of some interest to derive an expression for $\Phi_{zz}^{mn}(\omega)$ valid at low temperatures; the XY chain corresponds to a noninteracting fermion system and should show characteristic temperature dependence in this limit. This dependence may not be realized experimentally, however, since interchain couplings will normally induce three-dimensional ordering and a phase transition in this temperature range.

A general expression for $\Phi_{zz}^{mn}(t)$ has been given by Katsura *et al.*[21] and equivalently by Niemeijer[22]:

$$\Phi_{zz}^{mn}(t)=(4\pi)^{-2}\int_0^{2\pi}dq\int_0^{2\pi}dp\,\exp[i(m-n)(p-q)]\exp[iJt(\cos p-\cos q)/\hbar]\times[1+\tanh(\tfrac{1}{2}\beta\cos p)][1-\tanh(\tfrac{1}{2}\beta\cos q)]\,, \tag{4}$$

where $\beta=(J/k_BT)$ and our J is twice that of Refs. 21 and 22. For $m-n=0$ (autocorrelation) the Fourier transform is straightforward and can be put in the form

$$\Phi_{zz}^{11}(\tilde{\omega})=\left[\frac{\hbar}{\pi J}\right]\int_0^{1-(1/2)\tilde{\omega}}dx\frac{\{1-\tanh[\frac{1}{2}\beta(x-\frac{1}{2}\tilde{\omega})]\}\{1+\tanh[\frac{1}{2}\beta(x+\frac{1}{2}\tilde{\omega})]\}}{[(1+\frac{1}{2}\tilde{\omega})^2-x^2]^{1/2}[(1-\frac{1}{2}\tilde{\omega})^2-x^2]^{1/2}}\,, \tag{5}$$

where $\tilde{\omega}=\hbar\omega/J$. It is assumed that $\tilde{\omega}<2$; for $\tilde{\omega}\geq 2$, $\Phi_{zz}^{11}(\tilde{\omega})=0$. An expression equivalent to Eq. (5) has been given by Groen *et al.*[23]

The high-temperature limit is readily found by setting $\beta=0$ and yields, in agreement with Katsura *et al.*,[21]

$$\Phi_{zz}^{11}(\tilde{\omega})_{T=\infty}=(\hbar/2\pi J)K(1-\tfrac{1}{4}\tilde{\omega}^2)\,, \tag{6}$$

where $K(x)$ is the complete elliptic integral of the first kind.[24] Although this expression has a logarithmic divergence for $\tilde{\omega}\rightarrow 0$, in our case $\tilde{\omega}$ is small but finite and no divergence occurs. However, this sensitivity for small $\tilde{\omega}$, which is characteristic of one-dimensional systems generally, does have an experimental implication in that the isotopic dependence of T_1^{-1} [Eq. (2)] arises not only from the change in A through the nuclear magnetic moment, but also from the frequency dependence of $\Phi_{zz}^{mn}(\omega)$. Since pair correlations are negligible at high temperatures, Eq. (2) predicts

$$\frac{T_1^{-1}(^{35}\text{Cl})}{T_1^{-1}(^{37}\text{Cl})}=\left[\frac{\gamma_n(^{35}\text{Cl})}{\gamma_n(^{37}\text{Cl})}\right]^2\frac{\Phi_{zz}^{11}(\tilde{\omega}(^{35}\text{Cl}))}{\Phi_{zz}^{11}(\tilde{\omega}(^{37}\text{Cl}))}\,. \tag{7}$$

The predicted ratio therefore becomes 1.41 rather than 1.44, in noticeably better agreement with our measured value 1.38 ± 0.03 at 4.2 K.

To investigate the low-temperature behavior ($k_BT\ll J$) further we first make use of the addition formula for $\tanh(A+B)$ to express Eq. (5) as

$$\Phi_{zz}^{11}(\tilde{\omega})=\left[\frac{\hbar}{\pi J}\right]\int_0^{1-(1/2)\tilde{\omega}}dx\frac{(1+\tanh\frac{1}{4}\beta\tilde{\omega})^2(1+\text{sech}^2\frac{1}{4}\beta\tilde{\omega}\,\sinh^2\frac{1}{2}\beta x)^{-1}}{[(1+\frac{1}{2}\tilde{\omega})^2-x^2]^{1/2}[(1-\frac{1}{2}\tilde{\omega})^2-x^2]^{1/2}}\,. \tag{8}$$

For large β the $\sinh^2\frac{1}{2}\beta x$ term makes the integrand negligible except for small x. Hence the terms in the denominator will be essentially constant provided $\beta(1-\frac{1}{2}\tilde{\omega})\gg 1$, and Eq. (8) reduces in this limit to

$$\begin{aligned}\Phi_{zz}^{11}(\tilde{\omega})_{T\rightarrow 0}&\simeq\left[\frac{\hbar}{\pi J}\right]\frac{(1+\tanh\frac{1}{4}\beta\tilde{\omega})^2}{1-\frac{1}{4}\tilde{\omega}^2}\left[\frac{2}{\beta}\right]\\&\quad\times\int_0^{\infty}\frac{dv}{1+\text{sech}^2\frac{1}{4}\beta\tilde{\omega}\,\sinh^2 v}\\&=\left[\frac{\hbar\omega}{\pi J}\right]\frac{1+\coth\frac{1}{2}\beta\tilde{\omega}}{1-\frac{1}{4}\tilde{\omega}^2}\,.\end{aligned} \tag{9}$$

At $T=0$ this has the limiting value $2\hbar\tilde{\omega}/\pi J(1-\frac{1}{4}\tilde{\omega}^2)$, but over the range of temperatures for which $h\omega\ll k_BT\ll J$ and which is accessible experimentally, Eq. (9) is approximately $2\hbar k_BT/\pi J^2$. Hence $\Phi_{zz}^{11}(\tilde{\omega})$ does show a linear temperature dependence characteristic of fermion excitations.

The pair correlation function required in Eq. (2) can be analyzed in a similar way. $\Phi_{zz}^{12}(\tilde{\omega})$ is given by Eq. (5) with an additional factor $(x^2-\frac{1}{4}\tilde{\omega}^2)$ in the numerator and has a T^3 temperature dependence at low temperatures.

From these results the calculation of T_1^{-1} from Eq. (2) at all temperatures is straightforward. The parameter A is chosen to fit our data at 4.2 K and has the value $A=5.5\times 10^6$ sec^{-1}. The comparison between theory and the low-temperature data of Mangum and Thornton is shown in Fig. 3. There is reasonable agreement considering the rather large scatter in the data. The value of A may be compared with the estimated magnetic dipolar interaction between a Cl nucleus and a Pr neighbor, $g_{\|}g_N\mu_B\mu_N/\hbar r^3\sim 1.5\times 10^6$ sec^{-1}. Since there are three close Pr neighbors and also additional hyperfine interactions whose magnitude is expected to be comparable to the dipolar interaction we conclude that our value for A is quite reasonable. Better agreement with the data would be obtained if J was taken to be smaller than 2.85 K, but this value was determined from other experiments and is believed reliable. A recent study[25] of Raman scattering in $PrCl_3$, however, gives a somewhat lower value of 2.4 K.

The decrease in the relaxation rate T_1^{-1} as the temperature falls can be attributed to the suppression of spin fluctuations as the fermions condense into the Fermi sea. Alternatively, it corresponds in the time domain to $\Phi_{zz}^{11}(t)$ changing[21] from $\frac{1}{4}J_0^2(Jt/\hbar)$ to

$$\tfrac{1}{4}J_0^2(Jt/\hbar)-\tfrac{1}{4}H_0^2(Jt/\hbar)\ ,$$

where $J_0(x)$ and $H_0(x)$ are Bessel and Struve functions, hence reducing the spectral density at low frequencies.

Next we undertake a similar analysis of the spin-spin or T_2 relaxation, and for convenience discuss first the expected contribution to T_2^{-1} due to the magnetic field fluctuations just studied. Corresponding to Eq. (2) there is a simple expression[19,20] for the relaxation rate T_2^{-1} of Cl nuclear spins:

$$T_2^{-1}=\tfrac{1}{2}T_1^{-1}+(A^2/\hbar)[\Phi_{zz}^{11}(0)+\Phi_{zz}^{12}(0)]\ , \quad (10)$$

where the first term is the loss of phase memory due to nuclear-spin flips and the $\omega=0$ terms represent dephasing due to changes in the local precession frequencies. However, as remarked earlier the quantities $\Phi_{zz}^{mn}(\omega)$ diverge as $\omega\to 0$. Although this divergence prevents the calculation of T_2^{-1} in this way, in practice the $\omega=0$ limit will not be relevant in the case of spin-echo decays on the time scale ~ 100 μsec. The implication is that the spin-spin relaxation is not exponential and we must therefore adopt a more general approach to its analysis. The two-pulse echo-decay function can instead be calculated using a density-matrix method,[10] and becomes identical to the Kubo-Tomita relaxation function[12] if correlations of the phase changes between the two time intervals of the spin-echo sequence are neglected. If this approximation is made and interactions of the form $A(S_z^iI_z+S_z^iI_x)$ are assumed as before, the echo-decay function is given by

$$\phi(t)=\exp\left[-2A^2\int_0^t d\tau(t-\tau)[\Phi_{zz}^{11}(\tau)+\Phi_{zz}^{12}(\tau)]-A^2\int_0^t d\tau(t-\tau)[\Phi_{zz}^{11}(\tau)+\Phi_{zz}^{12}(\tau)]\exp(i\omega\tau)\right]\ . \quad (11)$$

At long times $(t\gg\hbar/J)$, $\phi(t)$ takes the approximate form

$$\phi(t)=\exp\left[-2A^2t\int_0^t d\tau[\Phi_{zz}^{11}(\tau)+\Phi_{zz}^{12}(\tau)]\right]\times\exp(-t/2T_1)\ . \quad (12)$$

At high temperatures $(T\gg J/k_B)$ where[20]

$$\Phi_{zz}^{mn}(\tau)=\tfrac{1}{4}[J_v(J\tau/\hbar)]^2\quad(v=|m-n|)\ ,$$

the integral in Eq. (12) can be evaluated as described in Ref. 9 to give a contribution to $\phi(t)$ in the form $\exp(-pt\ln qt)$, where $p\sim A^2/J\hbar$, $q\sim J/\hbar$. Although $\phi(t)$ thus decays more rapidly than a simple exponential, the difference is very slight over the range of times of interest experimentally and cannot account for the observed echo-decay functions which are markedly nonexponential. To examine the time scale of the echo decay without concern for its shape, an effective time constant $\hat{T}_2$ was obtained using Eq. (12) from the time required for an e^{-1} decay of $\phi(t)$. No additional parameter is involved since A was determined by fitting our T_1 data. This contribution to the echo-decay time is shown as the dashed line in Fig. 7. Comparison with the data implies that magnetic field fluctuations are responsible for the high-temperature plateau but below ~ 6 K the magnetic mechanism becomes ineffective and some other mechanism is dominant. This is consistent, of course, with the result from the isotopic ratio measurements that EFG fluctuations determine $\hat{T}_2$ at 4.2 K, and this contribution will now be examined.

As will become apparent, the electric quadrupolar mechanism can be analyzed only to a limited extent because of the uncertain magnitudes of the quadrupolar interactions and because the required spin-correlation functions are only partially known. The transverse Pr moments S_x,S_y transform as electric dipole moments and physically represent transverse distortions at Pr sites. Hence they create EFG's at Cl sites proportional to S_x,S_y and lead to hyperfine interactions of the form $S_xT_m^2,S_yT_m^2$, where T_m^2 is a second-rank nuclear-spin operator. Even though the Pr electric dipole moment has been measured by electric susceptibility[6] and other experiments these quadrupolar interactions depend on the actual atomic displacements and on shielding factors which cannot realistically be estimated. We therefore simplify the situation as much as possible by considering only a single Pr neighbor and the single interaction component $BS_xI_x^2$. In analogy with Eq. (2) and Eq. (10) the quadrupolar contribution to T_1^{-1} will be $\sim(B^2/\hbar)\Phi_{xx}^{11}(\omega)$, and to T_2^{-1} it will be $\sim(B^2/\hbar)\Phi_{xx}^{11}(0)$ where only the autocorrelation function

$$\Phi_{xx}^{11}(\omega)=\int_{-\infty}^{+\infty} dt\, e^{i\omega t}\langle S_x^1(t)S_x^1(0)\rangle$$

is taken into account. The transverse spin-correlation functions are not known at all temperatures, but some results are available at high and low temperatures. At $T=\infty$, $\langle S_x^1(t)S_x^1(0)\rangle$ has been shown[26] to be a Gaussian, $\frac{1}{4}\exp(-\frac{1}{4}J^2t^2/\hbar^2)$. To evaluate T_1^{-1} and T_2^{-1} we can roughly estimate B from the observed Cl quadrupole splitting when long-range electric dipole ordering develops below the phase transition at 0.4 K. If B (in frequency units) is set equal to the low-temperature splitting[27] of 0.09 MHz, we obtain $T_1^{-1}\simeq T_2^{-1}\simeq\sqrt{\pi}B^2/2J\hbar\simeq 1\ \mathrm{sec}^{-1}$. This shows that the electric quadrupolar contribution is over 2 orders of magnitude smaller than the magnetic dipolar contribution in the high-temperature limit. Quadrupolar relaxation is ineffective in this case partly because B is smaller than the magnetic interaction parameter A, and in addition because the transverse spin-correlation function decays rapidly in time compared to the t^{-1} dependence of the longitudinal correlation function. As the temperature is lowered, however, the longitudinal or magnetic correlations become less effective, as has been shown above, whereas the transverse correlation function no longer decays as a Gaussian function of time, but develops a long tail.[28] At $T=0$ it has been shown[29] that

$$\langle S_x^1(t)S_x^1(0)\rangle\simeq(\hbar/Jt)^{1/2}\ ,$$

apart from a factor of order unity. Accordingly, relaxation by EFG fluctuations will be strongly enhanced at low temperatures.

T_2^{-1} cannot be calculated directly in the $T=0$ limit since $\Phi_{xx}^{11}(\omega)$ diverges for $\omega\rightarrow 0$. As before, we calculate instead the Kubo-Tomita relaxation function

$$\phi(t)=\exp\left[-B^2\int_0^t d\tau(t-\tau)(\hbar/J\tau)^{1/2}\right]\ , \tag{13}$$

which reduces to

$$\phi(t)\simeq\exp[-2B^2(\hbar/J)^{1/2}t^{3/2}]\ .$$

Thus the echo-decay function is predicted to be of the form $\exp(-bt^{3/2})$, in agreement with the observed decay functions. Moreover, the ratio of the b coefficients for the two Cl isotopes should be in the ratio of the squares of the nuclear-quadrupole moments, or 1.61, in satisfactory agreement with the observed ratio of 1.67±0.05. To compare the magnitudes, we can calculate an approximate $\hat{T}_2=b^{-2/3}=(J/4\hbar B^4)^{1/3}\simeq 100\,\mu\mathrm{sec}$. This represents an increase in the relaxation rate of 4 orders of magnitude from $T=\infty$ to $T=0$ and is consistent with $\hat{T}_2$ values observed by Mangum and Thornton at low temperatures. Unfortunately, it is not possible at present to calculate the full temperature dependence of the transverse correlation functions; the $\hat{T}_2$ data of Mangum and Thornton (Fig. 7) show a nearly linear temperature dependence for $T\lesssim J/k_B$.

The question can be raised as to whether the T_1 relaxation should show a similar crossover from the magnetic dipolar to the electric quadrupolar mechanism as the temperature is lowered. Such a crossover need not occur at the same temperature ($\sim$6 K) as in the case of T_2 relaxation since the two mechanisms depend on different frequency components of the spin fluctuations, but it should nevertheless take place at some low temperature unless some other effect intervenes. The data of Mangum and Thornton[14] indicate that T_1^{-1} reaches a minimum at about 0.55 K, then increases before becoming unobservable near the phase transition at 0.4 K. This could be the onset of quadrupolar relaxation, but the scatter of the data and the proximity of the phase transition prevent a positive identification.

V. CONCLUSIONS

Observations of chlorine T_1 and T_2 relaxation in $\mathrm{PrCl_3}$ can be satisfactorily explained in terms of the fields of Pr spins which fluctuate according to one-dimensional *XY* dynamics. The longitudinal (S_z) Pr moments generate magnetic fields while the transverse moments (S_x,S_y) generate EFG's, both of which contribute to the Cl nuclear relaxation. The magnetic dipolar interactions are inherently stronger than the electric quadrupolar interactions, but the two mechanisms have opposite temperature dependences, the magnetic contribution increasing and the electric mechanism decreasing with temperature; hence the electric quadrupolar interaction becomes significant at lower temperatures. As a result, at temperatures high compared with the Pr interaction parameter J, T_1 and T_2 are independent of temperature, are controlled by magnetic field fluctuations, and are similar in magnitude. On cooling, the magnetic relaxation becomes less effective, decreasing linearly with temperature in a manner characteristic of excitations in a fermion system. The observed relaxation rate T_1^{-1} decreases in agreement with the expected magnetic contribution, while the quadrupolar mechanism contributes only below 0.5 K, if at all. For T_2^{-1} relaxation the crossover to the quadrupolar mechanism occurs at 6 K, and hence T_2^{-1} increases as the temperature is lowered.

The identification of the magnetic and quadrupolar relaxation mechanisms is based not only on these temperature dependences, but also on echo-decay functions and on the ratio of relaxation rates for the two Cl isotopes. The observed isotopic ratios clearly show that the T_1 mechanism is magnetic while the T_2 mechanism is quadrupolar at 4.2 K. It would have been valuable to use this test to confirm magnetic relaxation in both cases at higher temperatures, but experimental difficulties prevented accurate determinations of the isotope ratios at elevated temperatures.

One significant discrepancy between our results and the interpretation remains to be understood. The echo-decay function for the T_2 measurements is predicted to change from a simple exponential at high temperatures to the form $\exp(-bt^{3/2})$ at low temperatures, while the experimental data are nonexponential and fit the $\exp(-bt^{3/2})$ function equally well at all temperatures. It is possible that this behavior results from the contribution of the residual non-XY interaction between Pr spins, in particular the $S_z^i S_z^{i+1}$ component which is about 4% of the XY interaction. We have not attempted to estimate the contribution of this interaction, but it is clear that spin fluctuations due to diffusive behavior, which are prohibited for an ideal XY chain, will be present to some extent. In Heisenberg chains this spin-diffusion mechanism is dominant at high temperatures[12], and is known to induce a magnetization decay with an $\exp(-bt^{3/2})$ time dependence. Hence the interpretation of the high-temperature T_2 data in terms of magnetic relaxation alone should not be considered as final. At lower temperatures, the isotope ratio measurements for the T_2 data clearly show quadrupolar relaxation and provide strong evidence for relaxation by the transverse-moment fluctuations of the Pr chains.

For a more quantitative analysis of Cl relaxation in $PrCl_3$ it would clearly be desirable if the relevant hyperfine-interaction parameters could be measured directly. There would then be no adjustable parameters in the analysis we have presented and a much more rigorous comparison with the data would be possible. Some means of calculating or estimating the temperature dependence of the transverse spin correlations for the XY chain will also be necessary. Developments in both of these areas appear difficult but should not be impossible.

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