NUCLEAR RELAXATION MEASUREMENTS OF ^{35}Cl IN $PrCl_3$

B. W. Mangum and D. D. Thornton*

National Bureau of Standards, Washington, D. C. 20234

(Received 6 March 1969)

We have made spin-spin (T_2) and spin-lattice (T_1) relaxation measurements of ^{35}Cl in $PrCl_3$ from 4.2 to 0.08 K. T_1 and T_2 show unusual temperature dependences in both the paramagnetic and antiferromagnetic states.

The spin-lattice and spin-spin relaxation times of the ^{35}Cl nuclei in $PrCl_3$, T_1 and T_2, respectively, have been measured in the paramagnetic and antiferromagnetic regions by means of pulsed zero-field nuclear-quadrupole-resonance (NQR) techniques. In contrast to previous nuclear relaxation studies[1] of antiferromagnetic insulators which have found T_1 to increase rapidly with decreasing temperature below T_N, we have found the chlorine T_1 in antiferromagnetic $PrCl_3$ to decrease slowly with decreasing temperature. In the paramagnetic region the temperature dependence of the relaxation times is also unusual for an antiferromagnetic salt and most probably reflects the high degree of short-range order which has been observed in this and other hexagonal rare-earth trichlorides.[2] Unlike the more familiar three-dimensional antiferromagnets,[3] $PrCl_3$ orders predominantly in linear antiferromagnetic chains and hence, does exhibit considerable short-range order above T_N.

The cw NQR of ^{35}Cl in $PrCl_3$ has been investigated recently[2,4] in both the paramagnetic and antiferromagnetic states and is observable throughout the range of temperatures above and below the Néel point. Above T_N (0.428 K) the ^{35}Cl NQR frequency is 4.5685 MHz and the linewidth is approximately 7 kHz, while below T_N the line is split into two branches each with a linewidth of about 10 kHz and separated by approximately 90 kHz at the lowest temperature.[2,5]

The relaxation times were measured directly with a pulsed, variable-frequency, spin-echo spectrometer.[6] The spin-echo technique was used to measure T_2, whereas T_1 was measured by two methods: (a) the free-induction decay method (fid), and (b) the three-pulse spin-echo method in which a 180° pulse is followed by a sampling 90°-180° pulse sequence. The length of the 90° pulses was typically 20 μsec, while the cw linewidth measured by Mangum and Utton[5] was of the order of 10 kHz or less over the temperature range covered by these experiments. At low temperatures (<4.2 K), both longitudinal and transverse decays were exponential, the former over times of three to five T_1's, resulting in well defined relaxation times. Between 0.45 and 0.9 K, T_2 was shorter than the receiver recovery time of about 70 μsec and could not be measured directly in this temperature region. Changes of the cw linewidth in this region, however, indicate that T_2 does not get shorter than 50 μsec. The data for T_1 and T_2 are plotted in Figs. 1 and 2, respectively. Below T_N the circles represent the low-frequency branch, while the squares represent the high-frequency branch. The data below 1.5 K, and especially those between 0.4 and 1.5 K, show considerable scatter since the short times of T_2 in this temperature region cause degradation of the signal. The scatter in the T_1 data below 0.4 K arises not only from the shortness of T_2 but also because the NQR line splits into two lines below 0.428 K, the transition temperature, with a concomitant decrease in signal.

The experiments described in this Letter were performed in the same adiabatic demagnetization cryostat as that used in the cw NQR study. In addition, the samples used were the same ones investigated in the heat capacity, magnetic susceptibility, and NQR studies. At temperatures less than the Néel temperature, the temperature variation of the resonant frequency served as a consistency check on the temperature of the sample as measured by the susceptibility thermometer.

The dominant feature of the magnetic properties of $PrCl_3$ above the Néel point is the extensive short-range ordering into antiferromagnetic linear chains as evidenced by the heat capacity and magnetic susceptibility measurements.[2,7] The large anisotropy in the Pr^{+3} g factors would seem to indicate the applicability of the Ising model, but the heat capacity and susceptibility data are better fitted by a Heisenberg model. There is a general paucity of theory for nuclear relaxation in the high-temperature limit, particularly for such systems. One rather general theory developed for high temperatures is that due to Moriya[8] and an attempt was made to fit his high-temperature expansion

$$T_1 = T_{1\infty}\left[1+\frac{J}{4kT}+\frac{1}{2}\left(\frac{J}{kT}\right)^2(\eta_3-2\eta_1^2)\right]^{1/2}\exp\left[\frac{1}{2}\left(\frac{J}{kT}\right)^2\eta_1^2\left(1+\frac{J}{4kT}\right)\right] \quad (1)$$

to the data. Here k is the Boltzman constant. The structural parameters, η_1 and η_3, in the equation were obtained from the crystal structure of the salt, and $T_{1\infty}$ was treated as an adjustable parameter to fit the theory to the data at 4.0 K. Two choices of the exchange parameter J/k were used in the fit in order to show the sensitivity of Eq. (1) to choice of J/k. The value of 0.4 K leads to the dashed curve in Fig. 1, and that corresponding to the Heisenberg model (J/k = 0.9 K) leads to the solid curve. (If the exchange parameter J/k were adjusted for a best fit, it would be somewhat smaller than the Heisenberg value.) In view of the fact that the equation is an expansion in J/kT, it is surprising that so good a fit is obtained near the transition temperature; nevertheless, it does appear to have the proper temperature dependence. It might be well to note at this point that none of the previously studied antiferromagnets exhibit such a slow temperature dependence. In MnF_2, for example, T_1 also increases as the temperature is lowered, but the temperature dependence is much stronger than that observed here. Silbernagel et al.[9] explain this variation qualitatively in terms of pair correlations. Their theory is a first-order high-temperature expansion and, thus, is not valid at temperatures lower than approximately $5T_N$. Since we observe significant temperature variation only below ~2 K ($5T_N$), we have not attempted to use their expansion. We believe that pair correlations are responsible for the observed behavior, although no quantitative theory has been developed at present.

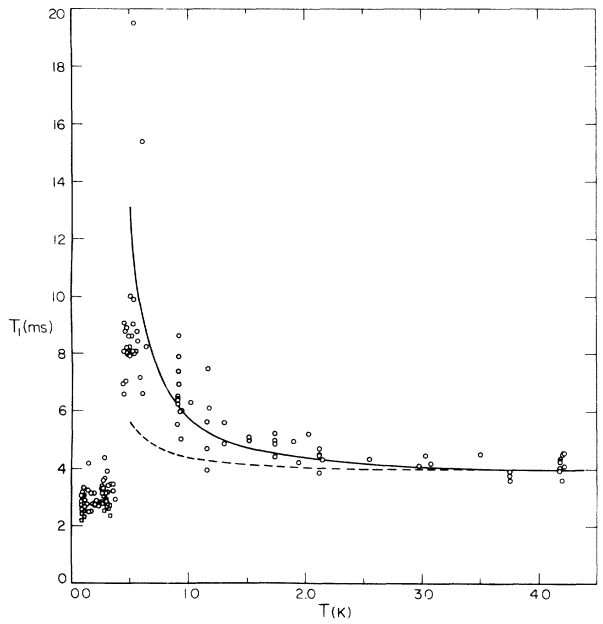

FIG. 1. The spin-lattice relaxation time T_1, in milliseconds, versus temperature. The solid curve was obtained from Eq. (1) with $J/k = 0.9$ K; the dashed curve is that obtained by using a value of $J/k = 0.4$ K.

In the antiferromagnetic regime the unusual temperature dependence of T_1 presents a different kind of difficulty. There are a number of theories[10] relying on various mechanisms for calculating T_1 but none of them predicts a temperature dependence even remotely similar to that observed here. In addition to the temperature dependence observed at both resonant frequencies, T_1 at the higher frequency is somewhat shorter than that at the lower frequency. It is very difficult to understand this behavior in terms of the customary spin-wave processes. With regard to the possibility that impurities may be responsible for the relaxation, we believe this to be unlikely for two reasons: (a) Impurity processes usually lead to a T^{-1} temperature dependence for the spin-lattice relaxation time, and (b) low-temperature magnetic susceptibility measurements, even though very sensitive to magnetic impurities, give no indication of the presence of such impurities.

In the calculation of T_1 by the high-temperature expansion, Moriya has assumed that the spins

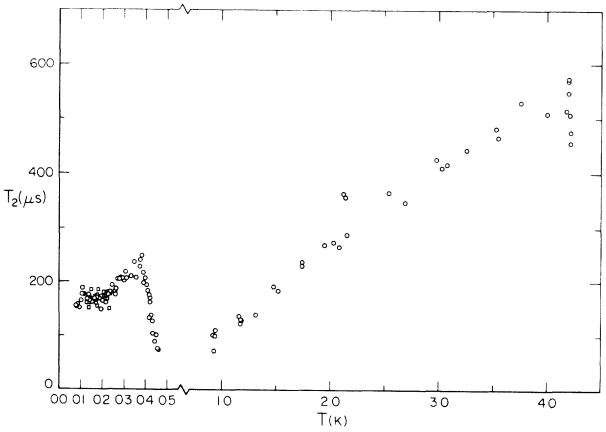

FIG. 2. The spin-spin relaxation time T_2, in microseconds, versus temperature.

are isotropic with the result that $T_1 = T_2$. This is decidedly not the case here. Not only is T_2 a factor of 10 smaller than T_1, but it has quite a different temperature dependence as well. The nearly linear dependence of T_2 on temperature above T_N is most unusual and probably arises from the extensive short-range ordering which occurs in this region. The difference between T_1 and T_2 is probably associated with the anisotropy of the Pr^{3+} ion.

The transverse relaxation times also change drastically with temperature in the transition region, increasing rapidly as the temperature is lowered, passing through a broad maximum below the transition point and finally becoming temperature independent below approximately 0.23 K. As shown in Fig. 2, both frequency branches have the same value of T_2. The behavior of T_2 below 0.23 K is consistent with the Suhl-Nakamura[11] theory which envisions a virtual magnon process and, consequently, gives temperature independence.

In summary we have observed unusual and, as far as we can determine, unique behavior of T_1 and T_2 in both the paramagnetic and antiferromagnetic regions. We have compared the data with the available theories. Above T_N we have obtained a reasonable fit of T_1 to the high-temperature expansion of Moriya. This may be fortuitous, however, since the theory predicts the same temperature dependence of T_1 and T_2 and that certainly is not observed as T_2 decreases linearly with temperature. The behavior of T_2 could undoubtedly be explained by a theory taking into account the extensive short-range order. Below T_N, T_2 is independent of both temperature and frequency. This is consistent with the Suhl-Nakamura theory although quantitative comparison with theory is not possible because of a lack of knowledge of the magnetic structure. Contradictory to all available theories, and they are numerous, T_1 below T_N is decreasing with decreasing temperature. Although this behavior is highly unusual we believe it is due to intrinsic processes.

We would like to acknowledge the invaluable assistance of D. B. Utton in setting up the spectrometer and getting the experiments under way.

---

*National Research Council–National Bureau of Standards Postdoctoral Research Associate 1968-1969.

[1]V. Jaccarino, in Magnetism, edited by G. T. Rado and H. Suhl (Academic Press, Inc., New York, 1964), Vol. II(A); M. Abkowitz and I. J. Lowe, Phys. Rev. 142, 333 (1966); A. Narath and A. T. Fromhold, Phys. Rev. Letters 17, 354 (1966); A. C. Daniel, A. W. Bevan, Jr., and R. J. Mahler, J. Appl. Phys. 39, 496 (1968).

[2]J. H. Colwell, B. W. Mangum, and D. B. Utton, Phys. Rev. (to be published).

[3]T. Nagamiya, K. Yosida, and R. Kubo, Advan. Phys. 4, 1 (1955).

[4]B. W. Mangum and D. B. Utton, Bull. Am. Phys. Soc. 12, 1043 (1967).

[5]B. W. Mangum and D. B. Utton, unpublished results.

[6]The spectrometer was constructed at the National Bureau of Standards under the supervision of Dr. T. Farrar.

[7]J. H. Colwell and B. W. Mangum, J. Appl. Phys. 38, 1468 (1967).

[8]T. Moriya, Progr. Theoret. Phys. (Kyoto) 16, 23 (1956).

[9]B. G. Silbernagel, V. Jaccarino, P. Pincus, and J. H. Wernick, Phys. Rev. Letters 20, 1091 (1968).

[10]A. Narath, in Hyperfine Interactions, edited by A. J. Freeman and R. B. Frankel (Academic Press, Inc., New York, 1967).

[11]H. Suhl, Phys. Rev. 109, 606 (1958); T. Nakamura, Progr. Theoret. Phys. (Kyoto) 20, 542 (1958).