NUCLEAR SPIN-LATTICE RELAXATION OF ^{53}Cr IN THE ORDERED MAGNETIC INSULATOR $CrCl_3$†

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The ^{53}Cr nuclear spin-lattice relaxation rates in $CrCl_3$ have been measured in both antiferromagnetic and ferromagnetic states. The dominant relaxation mechanism is shown to arise from three-magnon scattering processes.

The purpose of this Letter is to report on a study of ^{53}Cr nuclear spin-lattice relaxation rates in the magnetic insulator $CrCl_3$ as a function of temperature and applied magnetic field strength. Our experimental results are in reasonable agreement with theoretical predictions based on a three-magnon relaxation mechanism and, to our knowledge, constitute the first experimental observation of this process.

The hexagonal-layer ($R\bar{3}$) compound $CrCl_3$ has a zero-field magnetic ordering temperature $T_N = 16.8°K$.[1] Below T_N the magnetic moments lie in ferromagnetic (001) layers. The spin directions alternate by 180° along the c axis.[2] The antiferromagnetic interlayer exchange constant, J_L, has a magnitude which is about 300 times smaller than that of the ferromagnetic intralayer constant, J_T, and corresponds to an interlayer exchange field at 0°K of 0.84 kOe.[3] The perpendicular magnetic susceptibility is consequently very large, and the transformation to a ferromagnetic spin configuration requires a magnetic field only 1.6 kOe larger than the demagnetizing field. The magnetic anisotropy field, H_A, is essentially zero in the ferromagnetic state due to a mutual cancellation of dipolar and single-ion contributions.

Measurements of the ^{53}Cr spin-lattice relaxation times, T_1, were carried out on a single-crystal platelet by observing the recovery of the nuclear magnetization following saturation by an rf "comb."[4] The required transient excitation was provided by a variable-frequency pulsed oscillator. The recovery curves were always exponential when care was taken to saturate completely all three transitions of the ^{53}Cr quadrupole triplet ($h^{-1}e^2qQ = 0.88$ MHz). Spin echos were observed in weak fields because of severe inhomogeneous broadening; in fields above a few kOe measurements were usually based on the free-induction decay.

The experimental relaxation times are shown in Fig. 1 for two temperatures and magnetic fields of 0-10 kOe applied perpendicular as well as parallel to the c axis. The field strengths have been corrected for demagnetization[3] and thus correspond to values of the average internal magnetic field, H_i. The general shape of the curves T_1 vs H_i bears a striking resemblance to the field dependence of the sublattice magnetization.[3] This fact suggests that the observed relaxation rates arise from intrinsic processes resulting from hyperfine interactions with thermally excited magnons. The qualitatively similar behavior of $T_1(H_i)$ and $M(H_i)$ provides an immediate explanation for several noteworthy features of the present data. (1) The

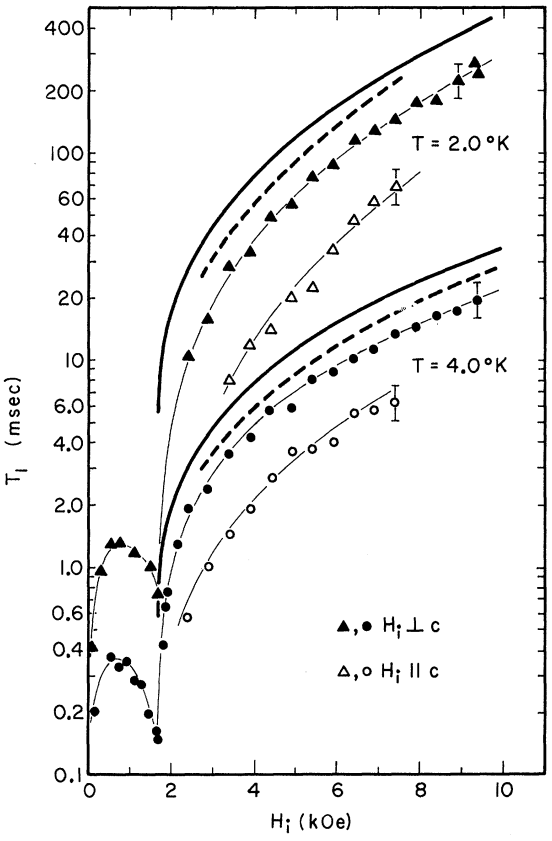

FIG. 1. Summary of ^{53}Cr spin-lattice relaxation times in $CrCl_3$ as a function of magnetic field strength. The heavy lines are calculated rates as described in the text.

T_1's are extremely short considering the relatively small magnetic moment of ^{53}Cr: As in the case of the sublattice magnetization, this effect is related to the high density of low-energy spin-wave states which result from the large anisotropy of the spin-wave spectrum ($J_L \ll J_T$). (2) The T_1's exhibit a very sharp cusplike minimum at the critical field ($H_C = -4J_L z_L S/g\mu_B$) followed by a remarkably rapid increase for $H_i > H_C$: This behavior follows directly from the fact that $H_A = 0$ in the ferromagnetic state. The gap in the magnon spectrum (at $k_T = 0$, $k_L = \pm\pi$),[5] therefore, disappears at H_C and the number of low-energy thermal magnons becomes very large. These excitations are greatly suppressed by the introduction of a gap $g\mu_B(H_i - H_C)$ above the transition, resulting in the observed increase in T_1. (3) The T_1's depend on the orientation of the external magnetic field: This behavior results from spin-wave demagnetizing effects which introduce terms of the form $M \sin^2\theta_k$ into the magnon energies, where M is the macroscopic magnetization and θ_k is the angle between $\vec{M}$ and the propagation direction of magnons with wave vector $\vec{k}$. Thus, when $H_i \perp c$, the energy of the important $k_L \gg k_T$ (i.e., $\theta_k \approx \pi/2$) modes is raised and T_1 consequently increased relative to the case when $H_i \| c$.

We now examine the origin of the observed relaxation rates. The ^{53}Cr hyperfine interaction in $CrCl_3$ is nearly isotropic ($\mathcal{H} = A\vec{I}\cdot\vec{S}$; $A = 2.80 \times 10^{-19}$ erg).[3] Such an interaction can only couple the nuclear spin to an odd number of magnons since the transformation of the electron spin operators, $S^{\pm}$, to magnon variables only yields terms involving products of odd numbers of operators. The creation of annihilation of a single magnon by a nuclear spin flip generally cannot occur because of energy conservation requirements. We therefore consider the three-magnon mechanism. There exist two distinct scattering processes which contribute significantly to the relevant matrix elements, as illustrated diagrammatically in Fig. 2. The first is the direct three-magnon process[6] in which a thermal magnon is scattered via the hyperfine interaction by a nuclear spin flip, resulting in the creation of two new magnons. In the second process the nuclear spin flip results in the creation of a virtual magnon which is then scattered by a thermal magnon via an exchange scattering process.[7] For simplicity we restrict our discussion to the ferromagnetic state of $CrCl_3$ and ignore k-dependent dipolar interactions between chromium spins. The Hamiltonian is given by

$$\mathcal{H} = \sum_i [-J_T \sum_\alpha \vec{S}_i \cdot \vec{S}_{i+\alpha} - J_L \sum_\beta \vec{S}_i \cdot \vec{S}_{i+\beta} - g\mu_B \mathbf{H}\cdot\mathbf{S}_i], \quad (1)$$

where α and β are vectors from the ith spin site to nearest neighbors in the same layer and adjacent layers, respectively. There are two spin-wave branches ($s = 1, 2$) because of the two crystallographically nonequivalent chromium sites in the hexagonal basal planes. At the temperatures of our experiments the upper branch may be neglected and the magnon energies, $\omega_{\vec{k}}$, treated to order k_T^2, so that we obtain

$$\omega_{\vec{k}} = \omega_T k_T^2 - \omega_L(1 - \cos k_L) + \omega_0, \quad (2)$$

where $\omega_T = \frac{1}{2}J_T S$, $\omega_L = 4J_L S$, $\omega_0 = (g\mu_B H + \omega_L)$, and $S = \frac{3}{2}$. To lowest order in $(2S)^{-1}$ the spin-lattice relaxation rate is given by

$$T_1^{-1} = (4\pi A^2 S/\hbar N^3) \sum_{\vec{k},\vec{k}',\vec{k}''} \delta(\omega_{\vec{k}} - \omega_{\vec{k}'} - \omega_{\vec{k}''}) \times n_{\vec{k}}(n_{\vec{k}'} + 1)(n_{\vec{k}''} + 1)[\mathfrak{A} + \mathfrak{B}]^2,$$

$$n_{\vec{k}} = [\exp(\omega_{\vec{k}}/k_B T) - 1]^{-1}, \quad (3)$$

where $\mathfrak{A}$ is the direct three-magnon matrix element, and $\mathfrak{B}$ is the second-order matrix element which arises from the exchange-scattering process. Since $|J_L| \ll J_T$, and $|J_L| \ll k_B T$, we neglect contributions to $\mathfrak{B}$ arising from J_L and find

$$\mathfrak{A} = [8\sqrt{2}S]^{-1}, \quad (4)$$

$$\mathfrak{B} = [8\sqrt{2}S]^{-1}[2\omega_T/\omega_{\vec{k}-\vec{k}'-\vec{k}''}] \times [-\vec{k}\cdot(\vec{k}_T' + \vec{k}_T'' - \vec{k}_T) - \vec{k}_T'\cdot\vec{k}_T'']. \quad (5)$$

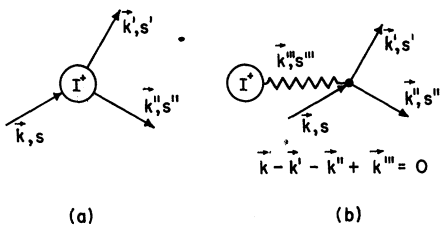

FIG. 2. Diagrammatic representation of three-magnon nuclear relaxation processes: (a) direct three-magnon process, (b) exchange-scattering process. The spin-wave branch index is denoted by s.

If the gap in the spin-wave spectrum is sufficiently large, $\mathcal{A}$ and $\mathcal{B}$ contribute about equally to the relaxation rate. We therefore define a remainder term, $\mathcal{R}$, by the relation $\mathcal{A}=\mathcal{B}(1+\mathcal{R})$. Assuming for the moment that $\mathcal{R}=0$, the relaxation rate is given by

$$T_1^{-1}=\frac{3\sqrt{3}A^2(k_BT)^2}{(64)^2\pi^2\hbar\omega_T{}^3S}\sum_{n=1}^{\infty}\left\{\int_0^{\pi}\frac{dx}{\pi}\sum_{q=0}^{\infty}\frac{\exp\{-(n+q)[\omega_0+\omega_L(1-\cos x)]/k_BT\}}{(n+q)}\right\}^2. \tag{6}$$

The prediction that $T_1^{-1}\propto T^2$ for small ω_0/k_BT is in good agreement with experiment. Equation (6) also accounts for the extremely short T_1's in $CrCl_3$ because of the divergence of the sums in the limit $(|g\mu_BH_i|+|\omega_L|)/k_BT\to 0$. We have calculated absolute rates using $J_T/k_B=5.25°K$ (obtained previously[3] from a fit of spin-wave theory to the temperature dependence of the zero-field sublattice magnetization) and $J_L/k_B=-0.018°K$ (obtained[3] from the low-temperature perpendicular magnetic susceptibility). The results are indicated in Fig. 2 by the heavy solid lines. We have examined the errors in the above calculation which are introduced by neglecting $\mathcal{R}$. This was accomplished by calculating T_1^{-1} in the two-dimensional approximation, which consists of replacing $\omega_L(1-\cos k_L)$ by its average value, ω_L. In this approximation we find that

$$\mathcal{R}=-2\omega_T(\vec{k}_T{}'\cdot\vec{k}_T{}'')/\omega_{\vec{k}-\vec{k}'-\vec{k}''}. \tag{7}$$

Substituting (7) into (3) and carrying out the necessary angular integrations yields an expression for T_1^{-1} which is easily evaluated by a digital computer. The results are indicated in Fig. 1 by the heavy dashed lines. The calculations were not extended into the weak-field region where the two-dimensional approximation becomes inadequate. The smallest values of ω_0 for which the two-dimensional model is adequate were estimated by making the same approximation in (6) and comparing the resulting rates with the exact values. The effect of $\mathcal{R}$ on the relaxation rates becomes negligible for very large ω_0 because of the energy denominator in (7). On the other hand, for very small ω_0 the rates are greatly enhanced. Preliminary calculations show that $\mathcal{R}$ dominates the calculated rates in $CrCl_3$ near the critical field.

The agreement between theory and experiment obtained in the present study, as shown in Fig. 1, is reasonably good, especially since the calculated values did not depend on any adjustable parameters. Although the calculated rates are somewhat slower than the experimental rates, the observed temperature and field variations are predicted correctly by the three-magnon mechanism. The omission of spin-wave demagnetizing effects in the present calculation makes it difficult, of course, to assess with certainty the significance of the small discrepancy between theory and experiment. It is probable, however, that the uncertainty in J_T and the neglect of terms of higher order in $(2S)^{-1}$ can account for the remaining difference. Three-magnon nuclear relaxation processes are probably also important in the ferromagnet $CrBr_3$. Using the published exchange[8] and anisotropy[9] parameters in (6) we calculate for ^{53}Cr $T_1=0.63$ sec at 4.2°K and $T_1=118$ sec at 1.3°K. These values are in order-of-magnitude agreement with experimental estimates by Gossard et al.[10] of 0.4 and 13 sec, respectively. (In view of the relatively long relaxation times in $CrBr_3$, it is possible that the disagreement at the lower temperature is related to impurity-limited relaxation processes.)

In conclusion, we believe that the present work demonstrates the importance of the three-magnon nuclear spin-lattice relaxation mechanism in ferromagnets in cases for which the hyperfine tensor is predominantly isotropic. A more complete report of this work, including an investigation of the effect of very small spin-wave gaps, will be published at a later date.

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NUCLEAR SPIN-LATTICE RELAXATION OF F^{19} IN ANTIFERROMAGNETIC MnF_2

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The temperature and angular variations of $1/T_1$ for the F^{19} nucleus are shown to be in excellent agreement with theoretical predictions for a two-magnon Raman-scattering relaxation mechanism via the transferred hyperfine interaction. The experiments clearly show the effect of the magnon energy gap on the relaxation rates.

This Letter presents an experimental and theoretical study of the F^{19} nuclear longitudinal relaxation time T_1 in the uniaxial antiferromagnet MnF_2. In contrast with previous measurements on antiferromagnets,[1-3] the present results for $1/T_1$ show an exponential falloff at low temperatures and provide clear evidence for the existence of an energy gap in the magnon spectrum.[4] The observed value of $1/T_1$ increases by six orders of magnitude between 3.2 and 26°K. The results are in excellent agreement with calculations of the relaxation of fluorine nuclear spins by a Raman scattering of thermally excited magnons. The theory is an extension of calculations by Moriya[5] to take account of the fact that in MnF_2 the F nuclear spins are coupled to magnons by the "transferred" hyperfine interaction with Mn electronic spins.[4] We believe this to be the first study in an ordered antiferromagnetic insulator for which the nuclear spin-lattice relaxation processes have been clearly identified in terms of intrinsic processes and for which theory and experiment are in quantitative agreement.

The main experiments were carried out on single crystals of MnF_2 prepared by zone-refining nominal 99.999% pure MnF_2. No impurity could be detected in the samples by spectrochemical analysis. Unlike the case for other nominally pure or intentionally doped samples,[6] only the F^{19} free-induction signals could be detected for the present sample in the absence of externally applied inhomogeneity. Standard spin-echo techniques were utilized with a high-power pulsed oscillator producing a rotating field H_1 of about 100 Oe. The recovery of the magnetization was exponential with a characteristic time T_1.

According to the theory,[5,7,8] the longitudinal relaxation rate $1/T_1$ in an antiferromagnet has an angular dependence

$$1/T_1 = (1/T_1^0) + (1/T_1') \sin^2\theta, \qquad (1)$$

where θ is the angle between the axes of quantization of the nuclear and the electronic spins. In antiferromagnetic MnF_2, the Mn electronic spins are aligned parallel to the crystal c axis by the exchange field of about 556 kOe. The resultant hyperfine field H_{hf} (~40 kOe) at each fluorine nucleus, arising from three neighboring Mn ions (see insert in Fig. 1), points along the c axis. Thus $\theta = 0$ in MnF_2 and a zero-field measurement of $1/T_1$ provides a measurement of $1/T_1^0$ in (1). The results of such a measurement are plotted as solid points in Fig. 1. As can be seen, a sharp falloff sets in below the temperature $T_{AE} = 12$°K of the magnon energy gap in MnF_2. The low-