NUCLEAR RESONANCE IN FERROMAGNETIC CHROMIUM TRIBROMIDE FROM 4.2°K TO THE CURIE POINT*

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In order to determine the temperature dependence of the magnetization of a localized-spin ferromagnet near its Curie temperature, we have measured the nuclear magnetic resonance frequencies of the Cr^{53}, Br^{79}, and Br^{81} nuclei in the insulating ferromagnet, $CrBr_3$.[1-4] Data were obtained at 4.2°K and in the temperature regions $13° \leq T \leq 29.74$°K for the Cr^{53} nuclei, $13° \leq T \leq 31.35$°K and at 34.5°K for the Br^{81} nuclei, and $13° \leq T \leq 32.35$°K and at 34.5 and 35°K for the Br^{79} nuclei.[5] Davis and Narath[6] have obtained extensive data on the Cr^{53} nuclei in the temperature range 1.5-20°K. The $CrBr_3$ Curie temperature is 32.56°K.

The nmr lines were detected with a frequency-modulated Kushida oscillator[7] using standard lock-in techniques. The sample temperature could be stabilized to within a millidegree or swept slowly. Measurements of the sample temperature with 1-mdeg sensitivity were made with a platinum resistance thermometer calibrated with the Z function.[8] The absolute accuracy of this calibration was checked where possible and found to be ±0.02°K.

We have found that the Cr and Br nmr frequencies themselves are capable of being used as extremely accurate, reproducible thermometers between 4.2 and 29°K.[5] The thermometric sensitivity is 2 mdeg or better over this entire range. Davis and Narath's Cr^{53} data[6] indicate that comparable sensitivities should persist down to about 1.5°K. Details of the thermometric applications of $CrBr_3$, along with a calibration using our frequency versus temperature data, will be published elsewhere.

From the Cr data, we have determined the temperature dependence of the magnetization between 13 and 29.74°K ($0.91T_C$). Data were limited to this upper temperature by the extremely rapid broadening of the nmr line. In this temperature region, $\Delta\nu$ increased by a factor of 25. We have also obtained the temperature dependence of the Cr quadrupole splitting in the same temperature range. From the Br data, we have deduced the magnitudes and temperature dependences of the components of the Br-site electric-field-gradient (efg) tensor both below the Curie temperature and above the Curie temperature (at 34.5°K), and we have determined the temperature dependence of the magnetization between 29.74 and 32.349°K ($0.993T_C$). We find that in the region $0.95 \leq T/T_C \leq 0.993$, the magnetization follows a simple power law, $M(T)/M(0) = (1.32 \pm 0.07)(1-T/T_C)^{0.365 \pm 0.015}$.

The Cr^{53} nmr spectrum from nuclei inside the ferromagnetic domains consists of a closely spaced triplet.[2] The quadrupole splitting of this triplet is 296.6 kc/sec at 4.2°K, decreasing to 280 kc/sec at 29.74°K, a change of about 5%. Most of this change takes place above 20°K. The central line of the triplet occurs at a frequency $\nu^{53}(T)$ which is proportional to the time-average hyperfine field set up by the aligned Cr^{3+} spin. The magnitude of this hyperfine field is proportional to the magnetization, so we obtain

$$M(T)/M(0) = \nu^{53}(T)/\nu^{53}(0). \tag{1}$$

In column (a) of Table I is tabulated the reduced magnetization obtained from our $\nu^{53}(T)$ data using Davis and Narath's[6] extrapolated value of the resonance frequency at 0°K, $\nu^{53}(0) = 58.099$ Mc/sec, as the normalization factor.

A total of four Br nmr lines[3,4] were studied below T_C, two from Br^{79} nuclei and two from Br^{81} nuclei. The frequencies of these lines are determined by the combined effect of magnetic hyperfine and electric quadrupole interactions between the Br nuclear moments and the surrounding electrons and ions. If at a given Br nuclear position we choose the principal axes of the efg tensor as the reference coordinate system, the Hamiltonian representing these interactions is (for $I = \frac{3}{2}$)

$$\mathcal{H} = -\hbar\gamma H_{\mathrm{Br}}\left\{I_z\cos\theta + \tfrac{1}{2}(I_+ + I_-)\sin\theta\right\} + \frac{hqQ}{6}\left\{3I_z^2 - \frac{15}{4} + \frac{\eta}{2}(I_+^2 + I_-^2)\right\}, \tag{2}$$

where γ is the nuclear gyromagnetic ratio; I_z, I_+, and I_- are the nuclear spin operators; and where H_{Br} is the magnitude of the time-aver-

age hyperfine field at the Br nuclear site set up by the aligned spins on the neighboring Cr^{3+} ions. The orientation of this field in the x-z plane of the efg principal axis coordinates is specified by the angle θ. The quantity q is given by $(e/2h)(\partial^2 V/\partial z^2)$ where V is the electrostatic potential at the nucleus. Q is the nuclear quadrupole moment, and η is the asymmetry parameter.

We used the Br nmr data to determine the values of the Hamiltonian parameters q, η, θ, and H_{Br} as a function of temperature. At each of 20 temperatures between 4.2 and 29.74°K, we had data on all four Br nmr lines, and thus values of q, η, θ, and H_{Br} at each temperature could be obtained in a straightforward way with the use of a high-speed digital computer. The computer searched over values of q, η, θ, and H_{Br} until it found that set of parameters which gave eigenvalues of the 4×4 Hamiltonian matrix in agreement with the experimental frequencies. We found, as expected, that $H_{Br}(T)$ and $\nu^{53}(T)$, being both proportional to the magnetization, were very accurately proportional to one another:

$$H_{Br}(T)/\nu^{53}(T) = 0.648\,65 \pm 0.000\,05 \text{ kG/(Mc/sec)}. \quad (3)$$

Furthermore, we found that below 20°K, q, η, and θ could be taken as constant [since q appears in (2) multiplied by the quadrupole moment Q, we give numerical values of the product qQ appropriate to Br^{79}]:

$$\left.\begin{aligned} qQ^{79} &= 101.52 \pm 0.04 \text{ Mc/sec} \\ \eta &= 0.293 \pm 0.001 \\ \theta &= 48.10 \pm 0.05 \text{ deg} \end{aligned}\right\} T \leq 20°\text{K}.$$

Above 20°K, it was necessary to ascribe small temperature dependences to all three of these quantities. Additional information on their temperature dependences was obtained by studying the Br^{79} pure quadrupole resonance[9] at temperatures just above T_c. At 34.5 and 35°K, we measured the Br^{79} pure quadrupole-resonance frequency and obtained 102.75 ± 0.01 Mc/sec at both temperatures. For values of η near 0.3, this frequency corresponds to a value of $qQ^{79} = 101.25$ Mc/sec. This indicates a 0.3% change in qQ^{79} between 20 and 34.5°K. Such a change is too large to be accounted for by the normal thermal-expansion and lattice-vibration temperature dependence of q.[10] This fact, together with the relatively strong temperature dependence of the chromium quadrupole splitting, suggests the existence of an anomalous peak in the $CrBr_3$ thermal expansion near T_c.

Above 29.74°K, two of the four Br lines began to broaden and weaken. The absence of accurate data on all four Br lines made the direct computer calculation of the four Hamiltonian parameters subject to large errors. Furthermore, above 30.76°K, where the weakest Br line faded out altogether, direct calculation of the parameters could not be made at all. Instead, the values of qQ^{79} and η were interpolated between 20 and 34.5°K by assuming smooth curves which (i) fit the data out to 29.74°K and (ii) matched up smoothly with the values obtained from the pure quadrupole-resonance frequency data at 34.5°K. We took the temperature-dependent parts of these curves to be proportional to the magnetization. Since no information on the value of θ above T_c was avail-

Table I. Temperature dependence of the $CrBr_3$ magnetization.

(a) Cr^{53} nuclei		(b) Br^{79} and Br^{81} nuclei	
Temperature (°K)	$M(T)/M(0)$	Temperature (°K)	$M(T)/M(0)$
0	1.000 00	29.740	0.5299
4.21	0.988 70	29.970	0.5152
13.000	0.915 32	30.085	0.5076
16.000	0.878 46	30.360	0.4878
18.000	0.850 22	30.550	0.4733
19.500	0.826 78	30.760	0.4556
21.000	0.800 94	30.915	0.4415
21.640	0.789 03	30.946	0.4387
22.500	0.771 85	31.003	0.4332
23.160	0.757 93	31.039	0.4296
24.360	0.730 23	31.085	0.4253
25.275	0.706 72	31.140	0.4192
26.095	0.683 26	31.188	0.4141
26.680	0.664 80	31.234	0.4090
26.975	0.654 93	31.279	0.4045
27.675	0.629 24	31.323	0.3988
28.125	0.610 85	31.350	0.3957
28.665	0.5873	31.797	0.3359
29.090	0.5663	31.898	0.3191
29.435	0.5476	31.996	0.3011
29.740	0.5299	32.046	0.2926
		32.098	0.2811
		32.147	0.2691
		32.198	0.2567
		32.245	0.2440
		32.294	0.2304
		32.349	0.2130

able, a corresponding curve for θ was determined by fitting the temperature dependence of θ between 20 and 29.74°K with a curve proportional to the magnetization and extrapolating this fit into the region above 29.74°K. The final results obtained for the temperature dependence of $M(T)$ near T_C are not sensitive to the detailed properties of the curves for qQ^{79}, η, and θ.

In Fig. 1 is shown the assumed temperature variation of qQ^{79}, η, and θ. Between 29.74 and 32.349°K, the values of q, η, and θ given in the curves of Fig. 1 were used in the Hamiltonian (2) to calculate $H_{\mathrm{Br}}(T)$ from each Br nmr datum point. Since $H_{\mathrm{Br}}(T)$ is proportional to $M(T)$, we have

$$M(T)/M(0) = H_{\mathrm{Br}}(T)/H_{\mathrm{Br}}(0). \tag{4}$$

In column (b) of Table I is tabulated the reduced magnetization data between $0.91T_C$ and $0.993T_C$ obtained from the Br nmr data in this way. The normalization factor used was $H_{\mathrm{Br}}(0) = 37.687$ kG; it was obtained from the $\nu^{53}(0)$ value of Davis and Narath together with the ratio in (3).

Other choices of interpolation curves were also tried, with little change in the resulting values for $M(T)$. In particular, we tried a set of curves in which half of the total 0.3-Mc/sec change in qQ^{79} occurred below T_C, the remainder occurring between T_C and 34.5°K. Such a curve might correspond to a perfectly symmetric peak in the thermal expansion about T_C. The $M(T)$ values obtained using this assumption were slightly smaller than those given in column (b) of Table I by amounts varying from 0.05% at 29.970°K to 2.4% at 32.349°K. We expect the true behavior to fall somewhere between this symmetric case and the strongly asymmetric case shown in Fig. 1. The form of the temperature dependence of $M(T)$ is quite insensitive to which set of curves is used.

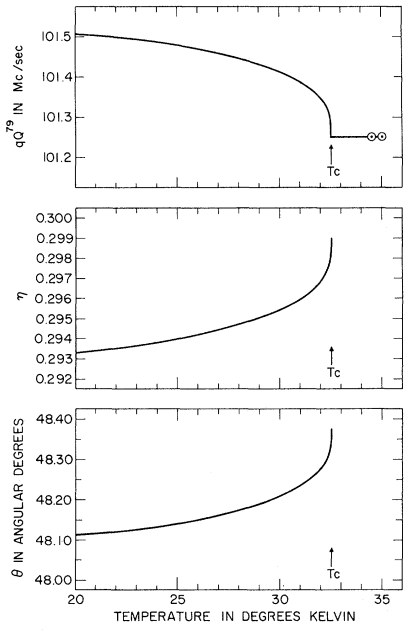

FIG. 1. Assumed temperature variation of qQ^{79}, η, and θ above 20°K. The curves for qQ^{79} and η were chosen so as to fit their known values above the Curie point.

In the limit $T \to T_C$, the magnetization can be represented by a simple power law

$$M(T)/M(0) = D(1-T/T_C)^{\beta}, \tag{5}$$

where β, T_C, and D are adjusted to provide the best asymptotic fit to the data. We plotted, as did Heller and Benedek,[11] the deviations from (5) for different choices of β and found a best fit for β near 0.365. We tested the sensitivity of this result to our choice of interpolation curves for qQ^{79}, η, and θ. The result was that for any smooth interpolation curve which fit the data out to 29.74°K and matched up above T_C with the values obtained at 34.5 and 35°K, the values of $M(T)$ calculated from the Br nmr data followed the same power law within the limits stated below. Our conclusion is that for $0.993 \geq T/T_C \geq 0.95$, the magnetization obeys (5) with

$$\beta = 0.365 \pm 0.015,$$

$$T_C = 32.56 \pm 0.015\,^{\circ}\mathrm{K},$$

$$D = 1.32 \pm 0.07.$$

The value for the exponent β is to be contrasted with 0.333 ± 0.003 in antiferromagnetic MnF_2[12] and with 0.33 ± 0.015 in ferromagnetic EuS.[11] Furthermore, in $CrBr_3$, (5) is valid only above $0.95T_C$ while in the other two materials, the power law is obeyed above $0.90T_C$ and $0.92T_C$, respectively. The value of T_C obtained in this work is in excellent agreement with Jennings and Hansen's[13] value, 32.55°K, obtained from specific-heat data.

We also attempted, without any success, to fit the $CrBr_3$ magnetization with the form $x^2/(1-\ln x)$ suggested by Buckingham[14] for the liquid-vapor coexistence curve.

We note that in $CrBr_3$, there is a large anisotropy in the strength of the Heisenberg exchange coupling between different pairs of neighbors.[4,6] There is also a rather large anisotropy field.[15] Both of these can be expected to influence the behavior of the magnetization near T_C.

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STATISTICAL MODEL OF INTERMEDIATE STRUCTURE

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A model is proposed for the formation and decay of the average compound-nuclear state in which a weak two-body residual interaction causes transitions among the eigenstates of an independent-particle Hamiltonian which lie in the region dE^* near the compound-nuclear excitation energy E^*. The independent-particle model states are classified according to the number of particles and holes (referred to indiscriminately as "excitons")[1] excited from the even-even ground state. The limitation on a two-body interaction, that it can only effect energy-conserving transitions which change the number of excitons by 0 or ±2, is invoked and exploited to eliminate matrix elements which vanish identically. The details of the two-body interaction are suppressed (by replacing all nonvanishing matrix elements by an average value M) in order to exhibit most simply the dependence of decay probability on both the excitation energy of the compound nucleus and the excitation energy of the residual nucleus.

Decay is assumed to occur (in a very short time)[2] to a state with outgoing particle of energy E_0 and residual nucleus of energy U, whenever a nucleus makes a transition to an independent-particle state in which one exciton has energy E_0 in the continuum, and the remaining excitons share the energy $U=E^*-(E_0+B)$, where B is the binding energy of the emitted particle. From a state described initially as a one-exciton independent-particle-model state (appropriate, e.g., for a reaction caused by one nucleon incident on an even-even target), the residual interactions cause successive transitions to 3-, 5-, 7-, $\cdots$-exciton states. At each such stage a small number of decays occur. These "precompound" decays are calculated in the present model.

They are found to describe (e.g., for neutrons) a "high-energy" tail similar to that observed in (p,n) reactions.[3] Finally, an equilibrium dis-