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Bromine Nuclear Magnetic Resonance in Ferromagnetic $CrBr_3$*

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The nuclear magnetic resonance of Br^{79} and Br^{81} has been studied in ferromagnetic $CrBr_3$. Br^{79} resonances were observed at 53.744 ± 0.010 and 130.64 ± 0.10 Mc/sec, and Br^{81} resonances were observed at 55.321 ± 0.010 and 121.61 ± 0.10 Mc/sec in zero applied magnetic field at 1.48°K. This compares with quadrupole frequencies of 101.82 and 85.73 Mc/sec in the paramagnetic state observed for the same two isotopes. The shift in frequencies produced in the ferromagnetic state arises predominantly from the magnetic hyperfine field H_N at the bromine sites. The observed resonant frequencies and their temperature dependence can be explained by assuming $|H_N|\sim 36$kOe at 0°K. Nuclear spin-lattice relaxation rates at 1.3 and 4.2°K are reported. The observed Br^{79} and Br^{81} rates are an order of magnitude faster than the rate calculated for relaxation of the nuclei by the Raman scattering of spin waves.

INTRODUCTION

ONE of the relatively few known *ferromagnetic* materials which are nonmetallic is $CrBr_3$.[1] The absence of exchange interactions through conduction electrons and the fact that the observed magnetization arises solely from spin contributions makes $CrBr_3$ ideal for studies of the thermodynamic properties of a ferromagnet. For this reason, several resonance experiments have previously been performed on this ferromagnetic compound. The Cr^{53} nuclear magnetic resonance (NMR) in the bulk of the ferromagnetic domains was observed[2] and used to determine the temperature dependence of the spontaneous magnetization at temperatures T far below the transition temperature $T_c=37$°K. The results were then compared with the predictions of simple spin-wave theory for the $CrBr_3$ structure. A resonance of the Cr^{53} nuclei lying in the domain walls was subsequently observed[3] and when compared with the resonances from the bulk of the domains yielded a measure of the thermal excitations of the ferromagnetic domain walls, as well as values for the angular dependence of the magnetic hyperfine field at the Cr nuclei. In the present work, we report the observation of Br^{79} and Br^{81} nuclear resonances in ferromagnetic $CrBr_3$. Br^{79} and Br^{81} nuclear quadrupole resonances were previously observed in $CrBr_3$ at temperatures above T_c.[4] The bromine resonances which we have observed lie at different frequencies than the resonances in the paramagnetic state, evidently being shifted by magnetic interactions. Two of the four resonances which we observed have also been seen by another group.[5]

EXPERIMENTAL RESULTS

Samples, consisting of flakes of $CrBr_3$, were prepared in the same manner previously reported.[2] The rf power absorption of the crystals was examined at liquid-helium temperatures using a superregenerative nuclear resonance spectrometer and a modified Robinson oscillating limiter spectrometer.[6] Resonances subsequently identified as Br^{79} and Br^{81} NMR, were observed when relatively strain-free samples of $CrBr_3$ were examined. The intensity of the resonances depended on the state of strain of the samples, the resonances being unobservable in more strained crystals. The maximum absorption intensities were of the same order of magnitude as the domain Cr^{53} absorptions. The frequencies of the lower frequency bromine resonances are displayed against temperature in Fig. 1, along with the frequencies of the Cr^{53} resonances from domains and walls for comparison. The highest frequency triplet was identified as the Cr^{53} resonance from the domains by associating the three relatively narrow ($\Delta\nu=20$ kc/sec) absorption peaks with the quadrupolar split Cr^{53} ($I=\frac{3}{2}$) resonance absorptions which are expected from Cr^{53} nuclei subjected to a magnetic field and an electric field gradient uniformly oriented with respect to each other. The absorption at the next lower frequency was identified as a resonance from nuclei in the domain walls by its greater breadth ($\Delta\nu=250$ kc/sec). This occurs because the magnetic hyperfine fields at different nuclear sites in the wall have different orientation with respect to the crystal axes. The temperature dependencies of these resonances were consistent with these assignments.[1,2]

An extended search in the frequency region 20–170 Mc/sec revealed four additional resonances. We might expect to observe Br^{79} and Br^{81} ($I=\frac{3}{2}$) NMR because of the relatively large nuclear moments and abundances (50.6% and 49.4%) of the two isotopes. Knowing the pure quadrupole resonance frequencies above T_c (101.82

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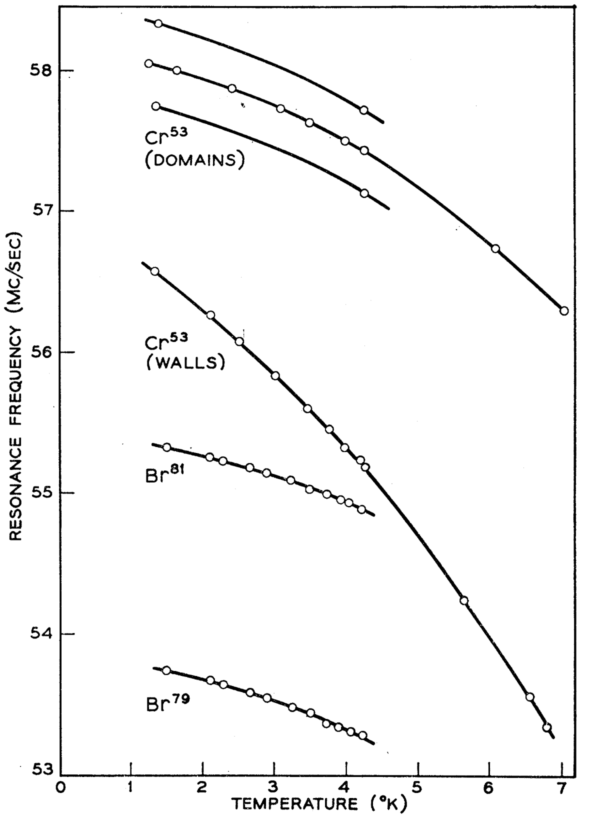

FIG. 1. Observed resonance frequencies versus temperature in $CrBr_3$.

and 85.73 Mc/sec at 77°K) the ratio of the nuclear magnetic moments, $\mu_N{}^{79}/\mu_N{}^{81}=0.9277$, and the ratio of the nuclear electric quadrupole moments, $Q^{79}/Q^{81}=1.1971$, we shall show that the observed resonances are indeed Br resonances and may be uniquely assigned to two given transitions of each of the Br isotopes, and that reasonable values of the magnetic hyperfine field at the Br site may be deduced. The frequencies of the observed resonances, along with the isotope assignments subsequently arrived at in this paper and the resonance frequencies reported in the paramagnetic state are given in Table I.

TABLE I. Observed Br^{79} and Br^{81} resonance frequencies (Mc/sec, 77°K values from Ref. 4).

Isotope	ν(1.48°K)	ν(77°K)	ν(1.48°K)/ν(77°K)
Br^{79}	53.744±0.010	101.82 ± ?	0.528
	130.64 ±0.10		1.283
Br^{81}	55.321±0.010	85.725±0.020	0.645
	121.61 ±0.10		1.418

In analyzing the lines, it is necessary to determine whether the Br nuclei participating in the resonances lie in the ferromagnetic domains or in the domain walls. The shifts in the nuclear energy levels produced by the magnetic hyperfine field depend strongly on the relative orientation of the magnetic hyperfine field and the electric field gradient. A distribution of such orientations is expected within the domain walls, and consequently, a broad resonance spectrum would be expected from nuclei in the walls. However, at 1.4°K, the observed lines at 53 and 55 Mc/sec have linewidths between absorption derivative extrema of only 60 kc/sec. This linewidth is much less than the total shift produced by the magnetic interaction, indicating that the participating nuclei lie on sites within the ferromagnetic domains. The linewidths of the resonances at 121 and 130 Mc/sec were qualitatively similar; no precise measurements of line shapes were possible since the resonances were observed using superregenerative techniques.

ANALYSIS

The crystal structure of $CrBr_3$ is shown in Fig. 2. Hexagonal layers of Cr^{3+} ions, whose moments of $3\mu_B$ per ion are aligned parallel to the c axis in the ferromagnetic state, are separated by two intervening layers of Br^- ions. The two nearest neighbors of a Br^- ion are Cr^{3+} ions, as shown in Fig. 3, while each Cr^{3+} ion is

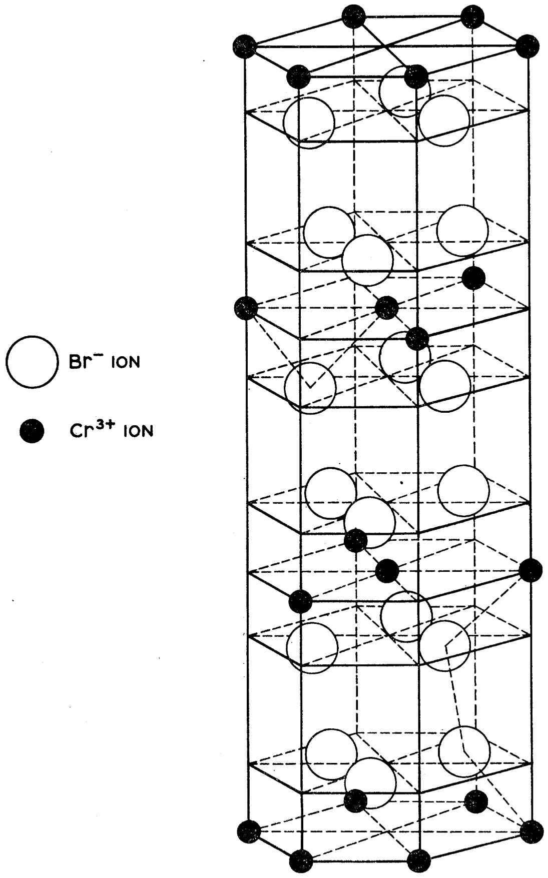

FIG. 2. Crystal structure of $CrBr_3$.

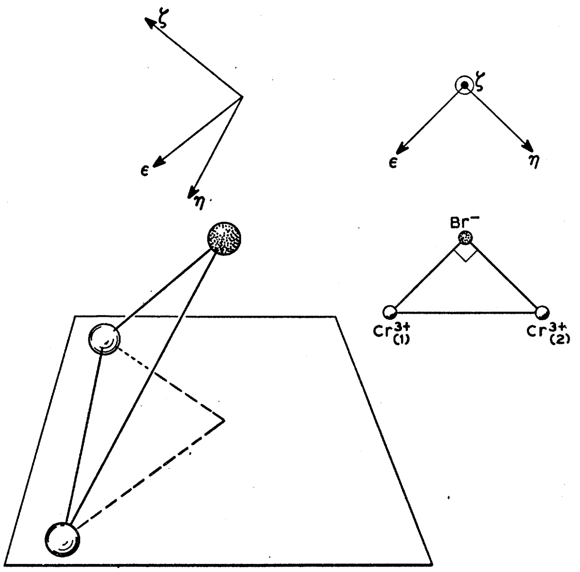

FIG. 3. Nearest-neighbor coordination of Br^- ions.

surrounded by a nearly regular octahedron of Br^- nearest-neighbor ions. The Br^- ions are thus subject to larger electric field gradients than the Cr^{3+} ions. The nearest-neighbor Cr^{3+} ions of a Br^- ion lie at nearly right angles to each other. On a point charge model, they create an axially symmetric electric field gradient at the Br^- site, whose principal axis is perpendicular to the plane of the Br^- and two Cr^{3+} neighbors. The principal axis makes an angle of 54.7° from the hexagonal c axis. (The electric field gradient arising from the covalent contributions of the Br p electrons will also have the same principal axis.)

In the ferromagnetic state, a spontaneous magnetization develops, which produces magnetic fields at both the Cr and Br nuclei. The instantaneous fields at the nuclei will be proportional to the net electronic spin **S**. Since fluctuations in this spin are rapid compared with nuclear frequencies, the field measured in a nuclear resonance experiment will be proportional to the time average electronic spin $\langle \mathbf{S} \rangle$. Magnetic hyperfine interactions are thus added to the Br quadrupole interactions in ferromagnetic $CrBr_3$.

A preliminary analysis of the observed resonance frequencies indicated a magnetic field at the nucleus of more than 2.6×10^4 Oe. The dipolar field from the nearest-neighbor Cr^{3+} ions is only 2.36×10^3 Oe at a Br^- site, at least an order smaller than the total field, and is directed in the basal (ab) plane. Therefore, the dominant contribution to the magnetic field at the Br nuclei evidently arises from other sources, e.g., the hyperfine field of unpaired Br $4p$ electrons. From inspection of the symmetry of the Cr $3d$ wave functions and the ligand wave functions, one can determine the spatial orientation of such a field. Since only Cr $3d\epsilon$ states are occupied, the augmented functions will contain only Br $p\pi$ ligands, i.e., no σ bonding will occur. For an angle of 90° between the nearest neighbor Cr directions, the distribution of ligand electrons is axially symmetric about the line through the Br nucleus perpendicular to the Cr-Br-Cr plane. With $\langle \mathbf{S} \rangle$ directed along the c (easy) axis, the resulting dipolar field of this charge distribution then is directed in the ab (basal) plane, parallel to the dipolar field of the nearest neighbors. Other sources of field at the Br nuclei include core polarization of inner-shell s electrons, the Lorentz field, and the dipolar fields of more distant neighbors. Since these other sources should be smaller than the dipolar field of the $4p$ electrons, the direction of the hyperfine field should be close to that of the dipolar contributions alone.

The energy levels of a spin $\frac{3}{2}$ nucleus in combined external magnetic fields and electric field gradients are readily calculable and have been tabulated by Parker.[7] In Fig. 4 are displayed the nuclear energy levels for the case in which the magnetic hyperfine field and the principal electric field gradient (EFG) axis lie at an angle θ of 33.2° with respect to each other. An investigation of these energy levels and the corresponding energy levels for other relative orientations of hyperfine field and EFG gave nuclear resonance frequencies most consistent with the observed frequencies for this particular value of θ, confirming our original surmise that θ would be close to 35°. In Fig. 4, the spacing

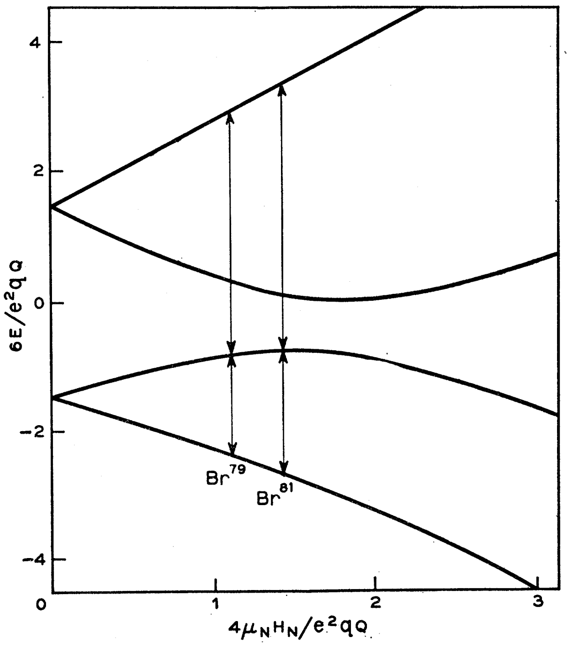

FIG. 4. Energy levels E of spin $\frac{3}{2}$ nucleus with nuclear magnetic moment μN and nuclear electric quadrupole moment Q in magnetic field H_N and axially symmetric electric field gradient q oriented at an angle of 33.2° from H_N to the principal axis of q.

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[7] Paul M. Parker, J. Chem. Phys. **24**, 1096 (1956).

between the energy levels at $H_N=0$ corresponds to $\nu(77°\mathrm{K})$. Since no measurable change in ν occurs between 77 and 295°K, it is assumed that no change in the magnitude of q occurs at still lower temperatures. The transitions marked in Fig. 4 correspond to the observed Br resonance frequencies for $H_N=36.3$ kOe. The two transitions marked for each isotope are only two of six possible transitions between the four nuclear states. The transition probabilities for all six lines were calculated, and for all of the unobserved lines were less than half the probabilities of the observed lines. For the transitions marked the value of $4\mu_NH_N/e^2qQ$ is 1.141 for Br^{79} and 1.472 for Br^{81}. In Table II, the resonance frequencies and their temperature dependences calculated from these energy levels are compared with the experimental results. To calculate the temperature dependence the fractional change in magnetic field at a bromine nucleus is taken to be equal to the fractional change in magnetic field measured at the Cr nuclei in the domains.[2] We believe the discrepancies between the experiment and the calculation to arise from the neglect of asymmetry in the EFG tensor. The uncertainty in the deduced value of θ is approximately 1°, and that in H_N approximately 1 kOe.

TABLE II. Comparison of observed Br^{79} and Br^{81} resonance frequencies (in Mc/sec) and temperature dependences and those calculated for $\theta=33.2°$ and $H_N=36.6$ kOe.

	Experiment	Calculation
ν^{79}	53.744±0.010	53.320
	130.64 ±0.10	131.392
ν^{81}	55.321±0.010	55.836
	121.61 ±0.10	120.422
$\left(\frac{d\nu^{79}}{dH_N}\right)\frac{H_N}{\nu^{79}}$	0.938±0.040	0.88
	0.37 ±0.10	0.29
$\left(\frac{d\nu^{81}}{dH_N}\right)\frac{H_N}{\nu^{81}}$	0.724±0.050	0.77
	...	0.48

Since the dipolar magnetic fields of the neighbors are much smaller than the deduced hyperfine field, the covalant contributions to the hyperfine field are evidently important. It was previously suggested[4] that the electric field gradient arose primarily from unpaired $4p$ electrons on the Br site and that comparison of the observed $\mathrm{CrBr_3}$ EFG with that of a single unpaired $4p$ electron would give a measure of the degree of covalency. The covalency parameter of 0.7 thus indicated was surprising in view of the relatively weak exchange constants determined for $\mathrm{CrBr_3}$.[2] It has subsequently been pointed out that in $\mathrm{CrCl_3}$, which has the same low-temperature crystal structure as $\mathrm{CrBr_3}$, the strongly noncubic character of the Cl site allows substantial contributions to the EFG from the charges of neighboring ions.[8] The nearest neighbor $\mathrm{Cr^{3+}}$ ions in $\mathrm{CrBr_3}$ lead to an EFG of $(6e/r^3)$ $(1-\gamma_\infty)$ at the Br nucleus in the point charge approximation, where r is the Cr to Br interatomic spacing and γ_∞ is the quadrupolar antishielding factor of the $\mathrm{Br^-}$ ion. Using $\gamma_\infty=-123$,[9] and $Q^{81}=0.28$ b for Br^{81}, we obtain $e^2qQ^{81}/h=4\times10^8$ sec^{-1}. The experimentally observed value is 1.70×10^8 sec^{-1}. Thus, the point-charge field gradient of the nearest neighbors is probably the dominant contribution to the observed EFG. That the contribution from covalent effects may be minor cannot be unambiguously established because of uncertainties in calculating the EFG from the neighbors.

The magnitude of the magnetic hyperfine field at the Br nucleus is more sensitively affected by covalency and overlap effects. The augmented wave functions responsible for the Br magnetic hyperfine interaction arising from two nearest neighbor Cr ions (which are assumed to have only $d\epsilon$ states $d_{\xi\eta}$, $d_{\eta\zeta}$, and $d_{\zeta\xi}$ occupied) are[10]:

$$(1-2aS+a^2)^{-1/2}(d_{\xi\eta}{}^{\mathrm{I}}\uparrow-ap_\xi\uparrow)\,,$$
$$(1-2aS+a^2)^{-1/2}(d_{\eta\zeta}{}^{\mathrm{I}}\uparrow-ap_\zeta\uparrow)\,,$$
$$(1-2aS+a^2)^{-1/2}(d_{\xi\eta}{}^{\mathrm{II}}\uparrow-ap_\eta\uparrow)\,,$$
$$(1-2aS+a^2)^{-1/2}(d_{\zeta\xi}{}^{\mathrm{II}}\uparrow-ap_\zeta\uparrow)\,.$$

S is the overlap integral and $a=(\lambda+S)/(1+\lambda S)$, where λ is the covalency parameter. I and II refer to the two neighbors, and ξ, η, and ζ are the directions shown in Fig. 3. The dipolar hyperfine field to second order in a is then $a^2H_{\mathrm{HF}\;p\zeta}{}^{\mathrm{dip}}$, where $H_{\mathrm{HF}\;p\zeta}{}^{\mathrm{dip}}$ is the dipolar hyperfine field of a single spin unpaired Br $p\zeta$ electron. For a spin moment directed along the hexagonal c axis, $H_{\mathrm{HF}\;p\zeta c}{}^{\mathrm{dip}}$ lies in the basal plane and has a magnitude of $(2\sqrt{2}\mu_B/5)\langle1/r^3\rangle$. Taking $\langle1/r^3\rangle=11.9$ a.u.,[11] this is 4.22×10^5 Oe. The observed value of 0.36×10^5 Oe indicates that $a^2=(S+\lambda)^2/(1+S\lambda)^2\approx0.08$. Had we chosen molecular orbitals including p states from all six Br neighbors of each Cr ion, the corresponding value of a^2 would have been four times as large. Factors which have been neglected which could lead to additional contributions to the hyperfine fields are interactions with more distant neighbors, deviations from 90° in the angle between the bonds to the two nearest-neighbor Cr atoms, spin polarization of other than $3p$ shell Br electrons, and spin orbit interaction of the Cr $3d$ states, which would couple $d\epsilon$ and $d\gamma$ states.

RELAXATION MEASUREMENTS

Free induction and spin-echo measurements were also made on ferromagnetic $\mathrm{CrBr_3}$. The three Cr^{53} resonances from nuclei in the domains relaxed with similar relaxation rates, while the lower frequency Br^{79} and Br^{81} resonances showed a different behavior. The results for the nuclear spin-relaxation time T_1 at 1.3 and 4.2°K are given in Table III.

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TABLE III. Nuclear spin-relaxation time.

	T_1(1.3°K)	T_1(4.2°K)
Cr^{53}	13 sec	0.4 sec
Br^{79}, Br^{81}	0.15–0.20 sec	0.005–0.010 sec

Because CrBr$_3$ is an insulator, there are no spin-lattice relaxation processes involving conduction electrons. Instead, relaxation by either nuclear electric quadrupole interactions or via interactions with the ferromagnetic spin system must predominate. The ferromagnetic spin waves via the magnetic hyperfine interaction provide a source of nuclear spin-lattice relaxation. However, because of the gap $g\mu_B H$ in the spin wave spectrum caused by H, the effective anisotropy and applied fields acting on the Cr ions, no spin waves of energy as low as the nuclear Zeeman energy exist, and direct one-magnon processes are ineffective in producing relaxation. This inhibition of direct spin wave relaxation by the gap occurs not only for relaxation by the Cr^{3+} spins, but also for relaxation by other species of magnetic impurities, whose lowest freqencies of excitation are raised by exchange interaction with the Cr^{3+} lattice. However, two-magnon (Raman) processes are allowed,[12] giving, for the CrBr$_3$ structure,

$$\frac{1}{T_1} \simeq -\frac{A^2 \sin^2\theta (kT)^2}{16 J_t^2 J_l S^3 (2\pi)^3 \hbar} \ln(1-e^{-g\mu_B H/kT})$$

for ion core spins S coupled by exchange interaction $-J_t$ to nearest-neighbor spins in the basal plane, by an effective exchange $-J_l$ to neighboring planes, and by hyperfine interaction A to their nuclei. θ is the angle between the axes of quantization of the nuclei and the ion cores. CrBr$_3$ makes an especially attractive material to study such relaxation. The Cr nuclei and ion cores are quantized parallel to each other ($\theta=0$), and from this process, no relaxation is to be expected. The Br quadrupole interactions, on the other hand, create a different effective quantization axis for the Br nuclear levels and for the spin wave excitations in the hyperfine field acting at the Br site. Thus relaxation from the Raman scattering of spin waves *is* allowed at the Br site. The Br nuclear eigenstates corresponding to the observed Br energy levels were found, and the transition probabilities associated with the spin wave processes were calculated. The resulting effective value of $\sin^2\theta$ found was $\sin^2\theta=0.05$. We thus obtain $T_1\simeq 10$ sec at 1.3°K and 0.4 sec at $T=4.2$°K. The rates are approximately one fiftieth of the observed rates at the two temperatures. Relaxation by quadrupolar interaction with the lattice is probably also a contributing mechanism, although no reliable calculation of the rate from this process is available. The Cr^{53} rate is much slower, as expected. The temperature dependences of the Cr and Br relaxation rates are the same within the accuracy of the measurements and indicate that coupling of the Cr^{53} nuclei to the lattice via the Br nuclei may be an important Cr^{53} relaxation process.

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