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Impurity-Controlled Nuclear Relaxation

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This work reports proton spin-lattice relaxation-time measurements performed as a function of temperature and magnetic field on a single crystal of paradibromobenzene, at liquid-helium temperatures and at room temperature. Strong evidence is displayed that at low temperature the proton spin-lattice relaxation is controlled by one kind of paramagnetic impurity. Both domains of diffusion-limited relaxation and domains of free diffusion relaxation are clearly exhibited, and the transition between these domains is consistent with a steep decrease of the spin diffusion coefficient D at a distance b_0 from the impurity, the diffusion barrier. Order-of-magnitude calculations of D and b_0 seem reasonable. The following information is derived as to the paramagnetic impurities: They probably have a Kramers degeneracy, in which case their spin-lattice relaxation in the neighborhood of 4°K is due to a Raman process. Their spin-lattice relaxation time τ at 4.2°K is comparable to 1.5×10^{-5} sec and their concentration N is of the order of 10^{-7} impurities per molecule. At room temperature, a different relaxation mechanism is effective, which is likely to originate from the dipole-dipole coupling of the protons with the bromine nuclei.

I. INTRODUCTION

THE importance, for the spin-lattice relaxation of nuclear spins in solids, of their coupling with paramagnetic impurities was first recognized by Bloembergen,[1] who stressed the role of spin diffusion in making it an effective relaxation mechanism, and wrote the differential equation governing the evolution of the nuclear polarization in time and space.

Subsequent approximate solutions of this equation by Khutsishvili[2,3] and DeGennes[4] put this model on a more quantitative basis, of which Blumberg[5] gave a physical analysis. A few features of this theory have been checked by experiment.[5–8]

The present work is a study of the spin-lattice relaxation time of protons in paradibromobenzene as a function of temperature and magnetic field, at liquid-helium temperatures and at room temperature.

The experimental results exhibit a close fit to the theoretically predicted behavior, which at the same time verifies the correctness of the theory and proves that the proton relaxation at low temperature is indeed due to paramagnetic impurities, about which some information can be drawn.

The low-temperature measurements are performed in magnetic fields ranging from 0 to 140 G. For measuring relaxation times at such low fields, the proton signals are enhanced through the use of the dynamic-polarization method by thermal mixing with the bromine nuclei described in the preceding article. It is the possibility of achieving such enhancements which determined the choice of this compound.

The high-temperature measurements, performed between 100 and 12 000 G display a different relaxation mechanism for the protons, attributed to their coupling with the bromine nuclei.

We give a brief review of the theory of relaxation by paramagnetic impurities before describing the experiments.

II. THEORY OF RELAXATION

The spin operator $\mathbf{S}$ of a fixed paramagnetic impurity closely coupled to the lattice can be considered as a stochastic variable which modulates randomly the dipole-dipole interaction between this impurity and the nearby nuclei.

The component I_z of a nuclear spin $\mathbf{I}$ at a distance r from the impurity is subjected to relaxation transitions, due to this interaction, with a probability

$$W=Cr^{-6}. \tag{1}$$

If the correlation time of the randomly varying Hamiltonian is long compared with the Larmor period of the electronic spin, only the operators I_+S_z and I_-S_z of the dipole-dipole interaction need be retained.

The angular average of C is then

$$C=\tfrac{2}{5}\hbar^2\gamma_S{}^2\gamma_I{}^2S(S+1)\tau/(1+\omega_I{}^2\tau^2). \tag{2}$$

$\omega_I=H\gamma_I$ is the nuclear Larmor frequency in field H. The correlation time τ is equal to the electronic spin-lattice relaxation time T_{1e}.[9]

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[9] It has been argued that when the electronic spin-spin relaxation time T_{2e} is shorter than T_{1e}, then the correlation time τ must be taken equal to T_{2e}. However, in the case of low-impurity concentrations, which the theory is dealing with, the heat capacity of the electronic spin-spin interactions is far smaller than the heat capacity of the nuclear Zeeman interactions. The electronic spin-spin interactions then must act as a heat reservoir intermediate between the nuclear reservoir and the lattice, and the nuclear relaxation time must be influenced by the spin-lattice relaxation time of the electronic spin-spin interactions. We are indebted to Professor A. Abragam for pointing this fact to our attention.

Direct relaxation transitions tend to produce different polarizations at different distances from the impurity. This trend is counterbalanced by spin diffusion which tends to equalize the polarizations throughout the sample.

The evolution of the nuclear polarization in a given small domain of the crystal is governed by the equation

$$\partial p/\partial t = D\nabla^2 p - (p - p_0)\textstyle\sum_i C_i r_i^{-6}. \tag{3}$$

The sum is taken over all paramagnetic impurities.

p_0 is the thermal equilibrium polarization. An order-of-magnitude value of the diffusion coefficient is

$$D \simeq a^2/30T_2, \tag{4}$$

where a is the internuclear spacing and T_2 is the nuclear spin-spin relaxation time.

Approximate solutions of Eq. (3) show[2,4] that after a short perturbed time and outside of small perturbed regions around the impurities, the nuclear polarization varies exponentially in time, with a relaxation time T_1 given by the equation

$$T_1^{-1} = 4\pi NbD. \tag{5}$$

The length b is equal to

$$b = 0.68(C/D)^{1/4} \tag{6}$$

when there is only one kind of impurity, the concentration N of which is supposed to be low, so that the contributions of all individual impurities are additive.

We have also, from (5) and (6)

$$T_1^{-1} = 4\pi NC/4.67b^3. \tag{7}$$

Following Blumberg's picture,[5] for the nuclei inside spheres of radius b' approximately equal to b around each impurity, direct relaxation is faster than spin diffusion, and their signal varies as $(Ct)^{1/2}$. For the nuclei outside these spheres, which are the majority when the impurity concentration is low, spin diffusion is faster than direct relaxation and ensures a uniform polarization which then varies exponentially with time. The inverse relaxation time is an average of the direct transition probabilities.

$$T_1^{-1} = (N/n)C \sum_{r_i = b'}^{\infty} r_i^{-6},$$

where n is the nuclear concentration. The equation of motion (3) treats the nuclear lattice as a continuum and is valid only if $b \gg a$. In that case, the sum can be replaced by an integration which gives the result

$$T_1^{-1} = 4\pi NC/3b'^3$$

which, by comparison with Eq. (7) shows that $b' = 1.16b$.

When τ is field-independent, and $\omega_I\tau \gg 1$, we find from formulas (2) and (4) that $b \propto H^{-1/2}$ and $T_1 \propto H^{1/2}$.

It has been pointed out by Bloembergen[1] and emphasized by Blumberg[5] that the diffusion coefficient falls to zero at short distances from the impurity: Different nuclei, experiencing different dipole-dipole interactions with the electronic spin, have different resonance frequencies and a flip-flop process is energetically possible only if the energy balance can be absorbed by the nuclear dipole-dipole interactions.

A rough separation can be made between the region where spin diffusion is slow and the region where it is normal; the former corresponds to spheres of radius b_0, the distance from the impurity at which the electronic field seen by a nucleus is equal to the nuclear linewidth[10]

$$\tfrac{1}{2}\hbar\gamma_S\gamma_I b_0^{-3} = T_2^{-1}$$

whence

$$b_0 = (\tfrac{1}{2}\hbar\gamma_S\gamma_I T_2)^{1/3}. \tag{8}$$

This is valid only if the electronic relaxation time is longer than the nuclear T_2. If this is not the case, i.e., if $T_{1e} \ll T_2$, the nuclei see only a time average of the electronic field, which is $(\mu_e H/kT)$ times the instantaneous field. The diffusion barrier b_0 then varies as $(\mu_e H/kT)^{1/3}$ until it reaches a minimum at high temperature of the order of the distance between the impurity and its nearest nuclear neighbor.

The formula (5), established without taking into account the diffusion barrier, is valid only when $b \gg b_0$. In the opposite limit, when $b \ll b_0$, the relaxation rate is obtained by averaging the direct transition probabilities of the nuclei outside the spheres of radius b_0, since for all of them and only for them is spin diffusion faster than direct relaxation.

The relaxation time is then given by

$$T_1^{-1} = (N/n)C \sum_{b_0}^{\infty} r_i^{-6} = 4\pi NC/3b_0^3. \tag{9}$$

If τ is field-independent and larger than T_2, so that b_0 is field-independent and $\omega_I\tau \gg 1$, we have

$$T_1 \propto H^2.$$

When the field H is increased, since b decreases, we must go from a region where $T_1 \propto H^{1/2}$ to a region where $T_1 \propto H^2$. The transition between these two domains depends on the variation of the diffusion coefficient D as a function of distance from the impurity. Owing to the difficulty of solving Eq. (3) when the diffusion coefficient is a function of r, Khutsishvili[3] has calculated T_1 in the simplified following case: D is zero when r, the distance from the impurity, is smaller than b_0, and constant when $r > b_0$. His result is expressed as

$$T_1^{-1} = 4\pi NFD. \tag{10}$$

The ratio F/b is given as a function of b/b_0 by the

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[10] A slightly different definition of b_0 is given by Khutsishvili in Ref. (3): b_0 is the distance from the impurity where the difference in electronic fields seen by neighboring nuclei is equal to the nuclear line width. Owing to the crudeness of the theory of spin diffusion, the actual value of b_0 is probably somewhere between these limits.

equation

$$\frac{F}{b}=\frac{2xI_{3/4}(x)}{2xI_{5/4}(x)+I_{1/4}(x)}, \tag{11}$$

where

$$x=C^{1/2}(2D^{1/2}b_0^2)^{-1}=1.08b^2/b_0^2$$

and the $I_p(x)$ are modified Bessel functions

$$I_p(x)=i^{-p}J_p(ix).$$

The asymptotic values of F are

$$b\gg b_0;\quad F=b;$$

yielding for T_1 a value in accordance with Eq. (5)

$$b\ll b_0;\quad F=C/(3Db_0^3);$$

yielding for T_1 a value in accordance with Eq. (9). The midpoint of the transition when $b\simeq b_0$ is reached at a field H_0 which can be estimated from the order-of-magnitude values of D and b_0. It is the field at which C is given by

$$C=Db_0^4(0.68)^{-4}.$$

When $\tau>T_2$ so that b_0 has the field-independent value given by Eq. (8), this corresponds to

$$\omega_I^2T_2\tau\sim 6S(S+1)(\gamma_S/\gamma_I)^{2/3}.$$

The transition field H_0 predicted in this case is very low; between 1 order and 2 orders of magnitude larger than the nuclear linewidth.

III. EXPERIMENTAL METHODS

The present work describes measurements of spin-lattice relaxation times of protons in a single crystal of paradibromobenzene referred to as sample C in the preceding article. The crystal was grown from the three times sublimized commercial product by solidification of the melt in a temperature gradient oven. Most measurements are concerned with temperatures ranging from 2.7 to 4.2°K and magnetic fields ranging from 0 to 140 G.

The spin-lattice relaxation time is determined by observing the decay of the proton polarization as a function of time, starting with a polarization far higher than the thermal equilibrium value. The initial polarization enhancement is achieved by the method of zero-field thermal mixing with the bromine nuclei described in the preceding article. The experimental sequence is the following:

(1) The system is prepared in such a way that the dipole-dipole interactions are saturated and the bromine quadrupole alignment is a well defined fraction of its thermal equilibrium value.

(2) The crystal is irradiated 15 sec in zero dc field with a rf field of frequency 18 kc/sec above the bromine quadrupole resonance frequency. This mixing results in the cooling of the dipole-dipole interactions to a well defined spin temperature.

(3) An adiabatic magnetization is performed up to the field H, which increases the proton spin temperature to a value still well below the lattice temperature.

(4) The crystal stays a time t in field H, during which the proton spin temperature increases under the effect of spin-lattice relaxation.

(5) The magnetic field is increased to 300 G and the proton signal is observed by fast passage at 1100 kc/sec. This signal decreases exponentially as a function of the time t. Each relaxation time is determined from about five points covering a time interval of the order of $1.5T_1$. The accuracy of these measurements is 10 to 15%.

Measurements at room temperature, in the field range of 100 to 12 000 G are performed by observing the increase of the proton fast passage signals toward their equilibrium value as a function of time, starting from saturation. The accuracy of these measurements is about 15%.

IV. EXPERIMENTAL RESULTS

A. Low-Temperature Measurements

The proton spin-lattice relaxation times T_1, in the particular single crystal of paradibromobenzene under study, have been measured at 4.2°K from 0 to 140 G for an unknown orientation of the crystalline axis with respect of the magnetic field. The experimental values between 1 and 140 G correspond to the open circles in Fig. 1. On this figure is also noted the spin-lattice relaxation time in zero field, namely, 25 sec.

At low field, the system is described by a single spin temperature, and what is measured is the relaxation time of the spin temperature, which is a weighted average of the relaxation time of the Zeeman interaction T_{1z} and the relaxation time of the dipole-dipole interactions T_D.

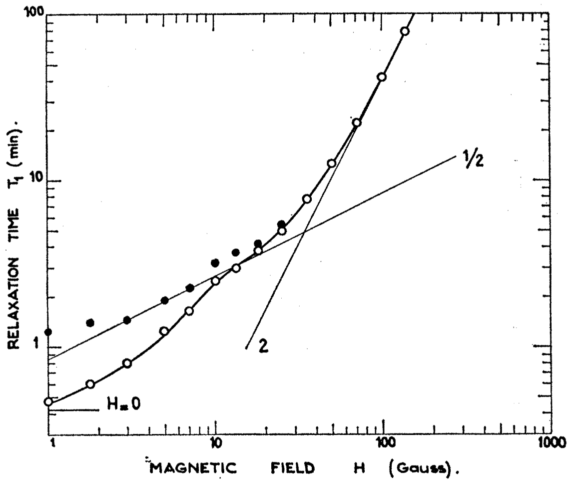

FIG. 1. Proton spin-lattice relaxation time as a function of magnetic field in paradibromobenzene at 4.2°K. The black dots are the proton Zeeman relaxation times calculated from the experimental values. The straight lines have slopes $\frac{1}{2}$ and 2.

If H_L is the local field of the protons, we have

$$(H^2+H_L^2)/T_1=H_L^2/T_D+H^2/T_{1z}. \qquad (12)$$

From the thermal mixing study performed on paradibromobenzene and described in the preceding article, an approximate value is derived for the local field

$$H_L \simeq 2.1\ \mathrm{G}.$$

If we assume that the dipole-dipole spin lattice relaxation time is field-independent, and thus equal to the zero-field value of 25 sec, it is then possible from Eq. (12) to calculate for each value of the spin-temperature relaxation time T_1 the corresponding Zeeman relaxation time T_{1z}. These calculated values correspond to the black dots on Fig. 1. At fields sufficiently larger than H_L, T_1 does not appreciably differ from T_{1z}.

In fact, the dipole-dipole relaxation time does depend on magnetic field: It is contributed to by the operators S_zI_z and $S_zI_\pm$ of the electron-nucleus interactions, and only the first of these operators gives rise to field-independent relaxation transitions. To have an order of magnitude for this variation, we have calculated the field dependence of the dipole-dipole relaxation time for a powder, in the case when the electronic fields seen by two neighboring nuclei are uncorrelated, using the method described in the Appendix of Ref. 7. This relaxation time turns out to decrease by about 12% from zero field to high field. Since the contribution of the dipole-dipole relaxation time to the total relaxation time decreases when the field is increased, as seen from Eq. (12), the error introduced in T_{1z} by ignoring the field dependence of T_D is substantially smaller than the above figure and can be neglected, considering the accuracy of the measurements.

The proton Zeeman relaxation times T_{1z} are reproduced on Fig. 2 for clarity. They are consistent with a variation of T_{1z} proportional to $H^{1/2}$ at low field, and to H^2 at high field as shown by the straight lines of slopes $\frac{1}{2}$ and 2 on this log-log plot. No credit can be given to the points at the lowest fields, and no significance to their departure from the $H^{1/2}$ law, since at these low fields the contribution of T_{1z} to T_1 is small and the accuracy of the calculation of T_{1z} is very poor. These limit behaviors of T_{1z} prove that the proton spin-lattice relaxation time is indeed due to paramagnetic impurities. A lower limit can be ascribed to the electronic relaxation time τ from the experimental results: Indeed, at low fields $T_{1z}\propto C^{-1/4}$ and, from Eq. (2), $T_{1z}\propto H^{1/2}$ only as long as $\omega_I\tau\gg 1$. The highest field at which T_{1z} may possibly depart from the proportionality to $H^{1/2}$ is about 3 G. For this field, we have thus:

$\omega_I\tau \geqslant 1$, which corresponds to:

$$\tau \geqslant 1.5\times 10^{-5}\ \mathrm{sec}.$$

At the field H_0 at which the straight lines of slopes $\frac{1}{2}$ and 2 intersect, we must have, from Eqs. (6) and (8):

$$4.67b^3=3b_0^3, \quad \text{i.e., } 1.16b=b_0.$$

Since $b\propto H^{-1/2}$, we know the ratio b/b_0 at all fields and we can calculate F/b from Eq. (11). The solid curve in Fig. 2 is the theoretical curve calculated from Eqs. (10) and (11), using the value $b/b_0=1/1.16$ at the field H_0. The over-all fit of the experimental points to this curve strongly suggest the plausibility of the following conclusions:

(1) The transition from the low field region, where $T_{1z}\propto H^{1/2}$, to the high field region, where $T_{1z}\propto H^2$, is correctly described by Khutsishvili's theory, which implies that the diffusion coefficient decreases sharply over a very small distance and that the diffusion barrier is well defined.

(2) The results are consistent with the existence of only one species of paramagnetic impurity. Indeed, if several impurities with different relaxation times τ contribute with comparable importance to the proton relaxation time, the transition of the latter from the region of slope $\frac{1}{2}$ to the region of slope 2 must occur in a broader field range than observed, since the field corresponding to the turning point is different for each impurity. However, there is no reason why there should be only one impurity species. From the fact that only one impurity seems to contribute to the proton relaxation time in the field range investigated, it is possible to put a limit on the concentration and the relaxation times of the other kinds of impurities. For instance, if N and τ are the concentration and relaxation time of the impurity responsible for the observed relaxation times of the protons, a noticeable departure from the theoretical curve can be expected from an additional impurity of relaxation time $10^{-1}\tau$ at concentration $0.03N$, or from an additional impurity of relaxation time 10τ at concentration $0.7N$.

It is also to be noted that the theory of relaxation seems to be still correct at surprisingly low fields.

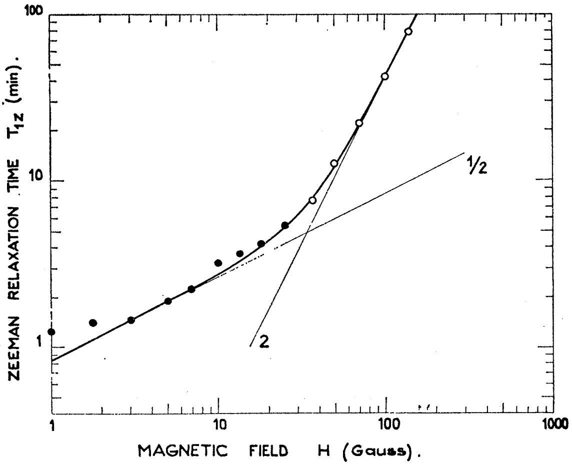

FIG. 2. Proton Zeeman spin-lattice relaxation time as a function of magnetic field in paradibromobenzene at 4.2°K. The solid curve is calculated from Eqs. (10) and (11) and fitted to the intersection point of the straight lines of slopes $\frac{1}{2}$ and 2.

Without any other information on the impurities, no definite proof can be given of the correctness of these conclusions, since they depend on each other. It only seems more probable for the above conclusions to be valid than for the experimental fit to theory to be merely accidental.

As an additional rough look for consistency we can compare the value of $b_0{}^4D$ as obtained from the order-of-magnitude calculation of b_0 and D, with the upper limit of $b_0{}^4D$ derived from experiment. The proton linewidth in paradibromobenzene is of the order of 2 G so that $T_2 \simeq 2.10^{-5}$ sec. Since the electronic relaxation time $\tau \gtrsim 1.5\times10^{-5}$ sec is comparable with T_2, the electron-nucleus interactions are not averaged, and the diffusion barrier b_0 is obtained from Eq. (8). If we suppose that the electronic Landé factor is 2, the distance at which the electronic field seen by a nucleus is equal to 2 G is

$$b_0 \simeq 17\text{ Å}.$$

In order to calculate D, we need the internuclear spacing a. The proton lattice in paradibromobenzene is far from regular and no theory of spin diffusion has been done in that case. However, following a very rough procedure, we use Eq. (4), choosing for a the internuclear distance in a fcc lattice with the same proton concentration as paradibromobenzene.

Then $a \simeq 4$ Å and

$$D \simeq 2.5\times10^{-12}\text{ cm}^2\text{ sec}^{-1}.$$

The estimated value of $b_0{}^4D$ is then

$$b_0{}^4D_{\text{est}} \simeq 2\times10^{-39}.$$

On the other hand, at the field $H_0 = 35$ G, at which the straight lines of slopes $\frac{1}{2}$ and 2 intersect, we have $b_0 = 1.16b$, i.e.,

$$b_0{}^4D = 0.39C = 0.39\times(\tfrac{2}{5})\times\hbar^2\gamma_S{}^2S(S+1)/H_0{}^2\tau.$$

If we assume the electronic Landé factor to be $g=2$ and its spin to be $S=\frac{1}{2}$, we find, from $\tau \gtrsim 1.5\times10^{-5}$ sec, that

$$b_0{}^4D_{\text{exp}} \lesssim 2.5\times10^{-39}.$$

Owing to the crude way b_0, D, and C can be calculated, the only conclusions are that there is no obvious discrepancy between theory and experiment, and that the values

$$b_0 = 17\text{ Å},$$
$$D = 2.5\times10^{-12}\text{ cm}^2\text{ sec}^{-1},$$
$$\tau = 1.5\times10^{-5}\text{ sec},$$

are not unreasonable.

Using these values, an estimate of the impurity concentration can be made with the help of Eq. (5). The result is

$$N \sim 7.10^{14}\text{ impurities/cm}^3,$$
$$\sim 10^{-7}\text{ impurity/molecule}.$$

This figure may be correct to within a factor 10^2.

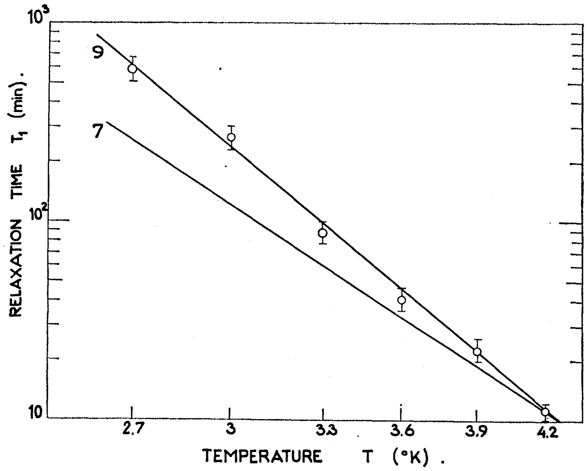

FIG. 3. Proton spin-lattice relaxation time at 50 G as a function of temperature, plotted as $\ln T_1 = f(\ln T)$. The straight lines of slopes -9 and -7 correspond to the temperature dependence of the relaxation by a Raman process of a Kramers system and a non-Kramers system, respectively.

In another series of experiments, we have measured the proton spin-lattice relaxation time at 50 G as a function of temperature from 2.7 to 4.2°K. This field is in the region where $T_1 \propto C^{-1} \propto \tau$, and the temperature dependence of T_1 is the same as that of the electronic relaxation time τ. Figure 3 is a plot of $\ln T_1$ as a function of $\ln T$. By comparison with the straight lines of slopes -9 and -7, it is seen that the temperature dependence of $T_1 \propto \tau$ is consistent with the proportionality

$$T_1 \propto \tau \propto T^{-9}$$

characteristic of the relaxation of a Kramers doublet by a Raman process. Figure 4 is a plot of $\ln T_1$ as a function of $1/T$, and shows that the temperature dependence of $T_1 \propto \tau$ is also consistent with the proportionality

$$T_1 \propto \tau \propto \exp(-E/kT)$$

characteristic of electronic relaxation by an Orbach process with $E/k \simeq 31$°K.

A choice between these two processes would have been possible by measuring T_1 in a wider temperature range, but measurements above 4.2°K necessitate a different cryogenic setup and measurements below 2.7°K seem hardly feasible, since both the bromine quadrupole relaxation time and the proton relaxation time increase prohibitively. However, it may seem a little more probable that the variation $T_1 \propto T^{-9}$ is real instead of being accidental.

B. High-Temperature Measurements

The proton spin-lattice relaxation times have been measured at 300°K from 100 to 12 000 G. Before describing the results, we try to estimate what they can be expected to be.

If we suppose that the impurities have Kramers

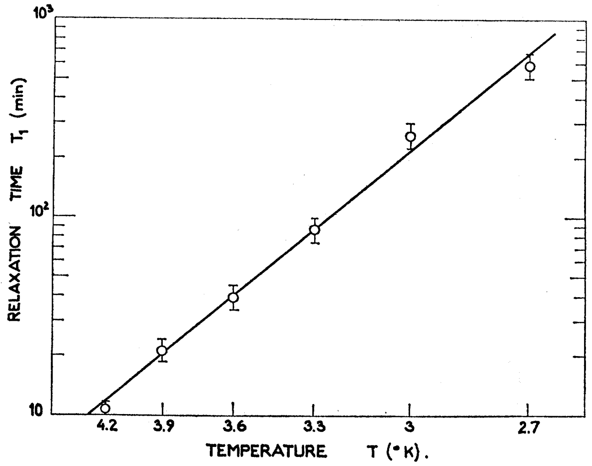

FIG. 4. Proton spin-lattice relaxation time at 50 G as a function of temperature, plotted as $\ln T_1 = f(1/T)$. The straight line corresponds to an activation energy $E/k \simeq 31$°K.

degeneracy, and if we use a Debye vibration spectrum which must be a poor approximation in the case of paradibromobenzene, the temperature dependence of the relaxation time τ is given by

$$\frac{1}{\tau}\propto\int_0^{k\Theta}\frac{\omega^8\exp(-\omega/kT)d\omega}{[1-\exp(-\omega/kT)]^2}.$$

Θ is the Debye temperature, which is probably between 50 and 100°K. At 4.2°K, for which we use the subscript a, we have $T_a \ll \Theta$, and then

$$(\tau_a)^{-1}\propto 8!T_a{}^9.$$

At 300°K, for which we use the subscript b, we have $T_b \gg \Theta$ and then

$$(\tau_b)^{-1}\propto T_b{}^2\Theta^7/7.$$

Thus, for $\Theta \sim 70$°K, we have

$$(\tau_a/\tau_b)\sim 7.10^6$$

which, if $\tau_a \simeq 1.5\times10^{-5}$ sec corresponds to $\tau_b \sim 2.10^{-12}$ sec, we then expect that $\omega_I\tau_b \ll 1$ at all practical fields, and that C is so small that b is far smaller than the diffusion barrier b_0'. Since $\tau_b \ll T_2$, the electron-nucleus interactions are decreased by the electronic Boltzmann factor, and b_0' turns out to be comparable to the internuclear distance. Moreover, since $\omega_S\tau_b \sim 1$, the contribution to T_{1b} of the operators I_+S_+ and I_+S_- of the electron-nucleus interactions may become non-negligible. From a very rough estimate, the proton relaxation time at 300°K, T_{1b}, is expected to be field-independent and of the order of a few hundred minutes. Since at this temperature, $T_{1b}\propto\tau_b{}^{-1}$, whereas at 4.2°K and high field $T_{1a}\propto\tau_a$, if we have two kinds of impurities of different relaxation times, the proton relaxation time can be entirely due to the impurity with the shorter relaxation time at low temperature, and to the impurity with the longer relaxation time at high temperature. Measurements at only two temperatures are unable to decide if this actually happens. The proton relaxation time measurements at room temperature are thus not expected to give valuable new information on the paramagnetic impurities responsible for the proton relaxation at low temperature; they may be of some use inasmuch as they exhibit new relaxation mechanisms, ineffective at low temperature.

Figure 5 is a plot of $1/T_1$ versus magnetic field H on a log-log scale. The experimental values correspond to the open circles. The variation of T_1 is correctly described by the equation

$$T_1{}^{-1}=A+BH^{-2} \qquad (13)$$

with $A=2.5\times10^{-3}$ min^{-1} and $B=4\times10^4$ min^{-1} G^2 as derived from the straight lines. The black dots are obtained by subtracting 2.5×10^{-3} from the experimental points and the solid curve corresponds to Eq. (13). The relaxation time at 100 G, not noted on the figure, also fits this curve.

The field-independent limit $A^{-1}=400$ min can be, with no inconsistency, accounted for by the impurities responsible for the proton relaxation at low temperature. As for the field-dependent relaxation rate $T_1{}^{-1}=BH^{-2}$, it cannot be due to these same impurities. Indeed, let us select, for instance, the field of 5 G at 4.2°K and the field of about 300 G at 300°K for both of which the relaxation time is 2 min. If relaxation is due to the same impurity, we have

$$(T_{1a})^{-1}=4\pi NF_aD=(T_{1b})^{-1}=4\pi NF_bD$$

whence $F_a=F_b$. In the field of 5 G at 4.2°K, we are in

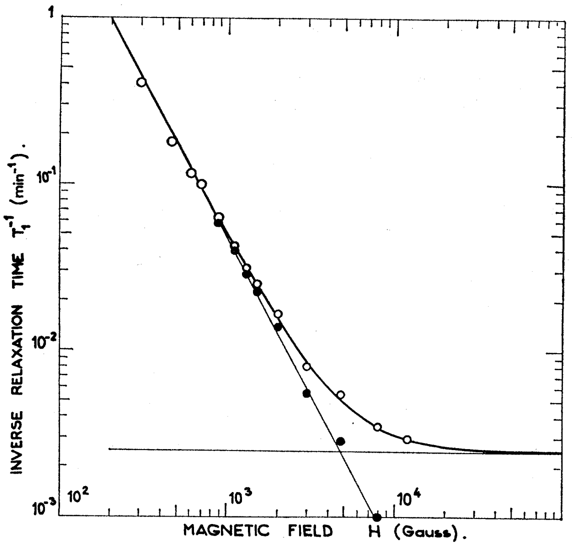

FIG. 5. Proton spin-lattice relaxation time as a function of magnetic field in paradibromobenzene at 300°K. The black dots are obtained by substracting 2.5×10^{-3} from the experimental values. The solid curve corresponds to the equation

$$T_1{}^{-1}=2.5\times10^{-3}+4\times10^4H^{-2}.$$

the region where $T_{1a} \propto H^{1/2}$ so that $F_a \gg b_0$ and, since $b_0' < b_0$, we have also $F_b \gg b_0'$. The field of 300 G at 300°K should be in a region where $T_{1b} \propto H^{1/2}$, which is not the case. This relaxation can be due to another kind of paramagnetic impurity. If this is the case, the relaxation time τ of this impurity cannot be shorter than T_2, since otherwise the diffusion barrier would be comparable to the lattice spacing and, by comparison to the results obtained at 4.2°K, the transition between the region of $T_1 \propto H^{1/2}$ and the region of $T_1 \propto H^2$ would take place at a field of a few thousand gauss.

The proton relaxation at 300°K and low fields can be due to an impurity only if the relaxation time of this impurity is longer than

$$\tau \gtrsim 10^{-5} \text{ sec, which implies,}$$

taking into account the values of T_1, an impurity concentration

$$N \gtrsim 10^{-5} \text{ impurity per molecule.}$$

On the other hand, the dipole-dipole interactions between the protons and the bromine nuclei, modulated by the bromine quadrupole relaxation transitions, provide an effective relaxation mechanism for the protons. Since the bromine quadrupole resonance frequency is far higher than the proton resonance frequency at the fields where T_1 is measured, the effective operators for relaxing the proton is $I_+ S_Z$, with a properly chosen Z axis for the bromine spin, and the transition probability is proportional to $(\omega_I^2 \tau)^{-1}$. Proton spin diffusion plays no part in this process, which then gives rise to a proton relaxation time proportional to $T_1 \propto H^2$. The bromine quadrupole relaxation time in paradibromobenzene is a fraction of a millisecond at room temperature, and an approximate calculation leads to proton relaxation times quite comparable to the observed values. The proton relaxation rate BH^{-2} is very likely due to this mechanism.

V. CONCLUSION

In a single crystal of paradibromobenzene, the impurity content of which is unknown, the proton relaxation time at 4.2°K exhibits the field dependence predicted by the theory of nuclear relaxation by paramagnetic impurities: T_1 is proportional to $H^{1/2}$ at low field, which corresponds to the domain of diffusion-limited relaxation; T_1 is proportional to H^2 at high field, which corresponds to the domain of free diffusion relaxation. These features of the theory are safe enough to make it certain that the proton relaxation is due to paramagnetic impurities. The transition between these domains follows the behavior derived by Khutsishvili for a simplified model in which the spin diffusion coefficient is constant down to a distance b_0 from the impurity and then drops suddenly to zero. Any smoother variation of the diffusion coefficient as approaching the impurity should result in a broader transition region. If several kinds of impurities, with different relaxation times, contribute comparably to the proton relaxation rate, this must also result in a broadening of the transition region. On the other hand, the *a priori* calculated value of the diffusion barrier b_0 is only a few times the average internuclear spacing and it is by no means evident that the theory, which treats the lattice as a continuum, should be applicable. It is possible that the discontinuous character of the lattice makes the transition region steeper than predicted by Khutsishvili's theory, and that the agreement with this theory is due to the contributions of several kinds of impurities. If we reject this fortuitous fit to theory as improbable, we must accept the following conclusions:

(1) The theory of relaxation by paramagnetic impurities is correct at very low fields.

(2) The proton relaxation is due only to one kind of paramagnetic impurity.

(3) The spin diffusion coefficient D decreases sharply over a small distance as approaching the impurity, which adds some consistency to the definition of a diffusion barrier b_0.

Owing to the complexity of the proton lattice and to the lack of other knowledge of the impurities, no quantitative comparison can safely be made between theory and experiment.

A limited amount of information is derived as to the paramagnetic impurities: They probably have a Kramers degeneracy, and their spin-lattice relaxation time at 4°K is probably due to a Raman process. Their spin-lattice relaxation time at 4.2°K is comparable to $\tau \sim 1.5 \times 10^{-5}$ sec and their concentration is comparable to $N \sim 10^{-7}$ impurity/molecule.

The field-dependent relaxation process observed at room temperature is consistently accounted for by the dipole-dipole interactions between protons and bromine nuclei. This relaxation mechanism differs from the relaxation mechanism by paramagnetic impurities insofar that, because of the high concentration of relaxing nuclei, spin diffusion plays no part in it. It is also very analogous to the "scalar relaxation of the second kind" by a nuclear spin species observed in liquids[11,12] the difference being that, since the lattice is rigid, the dipole-dipole coupling is effective.

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