error. This thermodynamic consistency provides increased confidence in the reliability of the measurements.

IV. CONCLUSIONS

The thermodynamic properties of the three purest samples of molybdenum are very consistent in both the normal and the superconducting state. Pure molybdenum appears to have the reversible transition of a type I superconductor. The transition width is apparently quite sensitive to very small traces of impurities, which also seem to affect the specific heat in both normal and superconducting states as well. We have deduced several thermodynamic properties from specific heat measurements in the neighborhood of and well below the critical temperature and compared them with the theoretical predictions. The average width of the energy gap at 0°K as deduced from our specific heat measurements is consistent with the BCS value. Anisotropy of the energy gap or possible existence of two gaps may be indicated by the experimental data for C_{es} at the lowest temperatures, which are larger than the values from the BCS theory. A λ-type anomaly in the transition in zero field could not be detected, in agreement with the measurements on other superconductors.

ACKNOWLEDGMENTS

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Thermal Mixing between Spin Systems in Solids

M. Goldman*

Centre d'Etudes Nucléaires de Saclay, Gif-sur-Yvette, Seine-et-Oise, France

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The present work is a study of thermal mixing in zero field between protons and bromine nuclei in paradibromobenzene, induced by rf irradiation at a frequency close to the bromine quadrupole resonance frequency. Experiments have been conducted at 77 and 4.2°K. This mixing leads to the cooling of the dipole-dipole interactions to a temperature which depends on the relative couplings to the lattice of the different interactions—dipolar and quadrupolar—experienced by the spin system. The ordering of the dipolar interactions is transferred to Zeeman interactions by adiabatic magnetization, which results in an enhanced proton polarization with respect to its thermal-equilibrium value. A detailed theory of the thermal mixing, together with experimental results obtained with paradichlorobenzene, has been published in a preceding article. The present work pays special attention to the dynamics of the evolution of the spin system during the thermal contact. This evolution proceeds from two distinct phenomena: The first is the establishment of a spin temperature in the rotating frame by rf-induced thermal mixing between dipole-dipole and quadrupole interactions. The second is a variation of this temperature at a rate and toward a steady-state limit determined by the respective spin-lattice relaxation times of the dipole-dipole and quadrupole interactions. The experiments performed at 4.2°K with paradibromobenzene verify this two-step evolution. They also demonstrate that even very low concentrations of paramagnetic impurities provide the dominant relaxation mechanism for the dipole-dipole interactions, resulting in a drastic decrease of the dynamic polarizations obtainable by this method.

I. INTRODUCTION

In a preceding article[1] with A. Landesman, referred to hereafter as I, we have presented a method of dynamic polarization of a nuclear spin species I, in solids, through its thermal mixing in zero field with a second spin species S which is subjected to quadrupole interactions. One of the features of this method, on which emphasis was given throughout the analysis made in (I), is that under suitable conditions—gyromagnetic ratio γ_S of the spins S smaller than the gyromagnetic ratio γ_I of the spins I, and spin-lattice relaxation entirely originating from the coupling of the lattice with the spins S only—the resulting polarizations are larger than the maximum polarization which can be expected from a "solid effect," i.e., the final ratio of populations between the levels of the spins I is larger than the Boltzmann ratio $\hbar\omega_Q/kT$ corresponding to the quadrupole splitting of the spins S. Experiments performed on paradichlorobenzene at liquid-nitrogen temperature qualitatively verified the correctness of the theory and

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* On leave during the 1964–65 academic year at Washington University, Department of Physics, St. Louis, Missouri.

[1] M. Goldman and A. Landesman, Phys. Rev. **132**, 610 (1963).

actually led to proton polarizations larger than those produced by a solid effect.

The present work describes a series of thermal mixing experiments performed on paradibromobenzene, mainly at liquid-helium temperature, which displays new aspects of the thermal mixing process.

The situation here is opposite to that analyzed in (I) in paradichlorobenzene: at 4.2°K, the spin-lattice relaxation time of the spins I, the protons, due to paramagnetic impurities is far shorter than the quadrupole relaxation time of the spins S, the bromine nuclei, due to their coupling with the lattice vibrations.

The proton polarizations obtainable under these conditions are much lower than those produced by a solid effect. The experiments show that the theory of thermal mixing works equally well in this situation and, because of the length of all relaxation times at low temperature, it is possible to observe separately the two phenomena occurring during the thermal contact: establishment of a spin temperature, and evolution of this temperature under the influence of the spin-lattice relaxation.

The method of dynamic polarization by thermal mixing also provides an easy technique for measuring the proton spin-lattice relaxation time at low fields, from which information can be drawn as to the paramagnetic impurities responsible for this relaxation. Such an investigation has been made and is described in a following article.

We begin by briefly recalling the principle of thermal mixing.

II. PRINCIPLE OF THERMAL MIXING

We consider a crystal with two nuclear spin species I and S. The nuclei I have a spin $\frac{1}{2}$; the nuclei S have a spin $\frac{3}{2}$ and a pure quadrupole resonance frequency Ω_0. If this crystal is irradiated in zero dc field with a rf field of frequency Ω, such that the difference

$$\Delta=\Omega_0-\Omega$$

is comparable to the quadrupole resonance linewidth, we must use an interaction representation chosen in such a way that the evolution of the system in this representation is governed by a time-independent effective Hamiltonian. The use of this interaction representation is completely analogous to the use of a rotating frame in the case of Zeeman interactions.[2–5] We may then use, with very slight changes, the theories developed by Redfield[2] and Provotorov[5] for the Zeeman case.

The effective Hamiltonian of the system in the interaction representation is

$$\mathcal{H}^*=Q+\mathcal{H}_D'+Z=\mathcal{H}_0^*+Z. \qquad (1)$$

Q is a reduced quadrupole interaction for the spins S, corresponding to the splitting Δ between their states $|\pm\frac{3}{2}\rangle$ and $|\pm\frac{1}{2}\rangle$.

$\mathcal{H}_D'$ is the part of the dipolar interactions which is time-independent in this representation.

Z is the part of the Zeeman interaction of the spins S with the applied rf field which is time-independent in the same representation.

We restrict ourselves to the case when

$$\mathrm{Tr}Z^2 \ll \mathrm{Tr}Q^2,\ \mathrm{Tr}\mathcal{H}_D'^2.$$

Then Z can be considered as a small perturbation of the principal Hamiltonian $\mathcal{H}_0^*$, which is a sum of two commuting operators Q and $\mathcal{H}_D'$. Following Provotorov,[5] we assume that after a time of the order of T_2, the system can be described by attributing distinct temperatures to these operators. The density matrix of the system is then, in the high-temperature limit

$$\sigma \propto 1-\alpha Q-\gamma\mathcal{H}_D', \qquad (2)$$

where α and γ are inverse temperatures.

The perturbation Z, which commutes neither with Q nor with $\mathcal{H}_D'$ will produce an exponential evolution of these two inverse temperatures α and γ to a common value β, with a time constant θ. This mixing time θ is inversely proportional to H_1^2 and to the normalized line shape of the quadrupole resonance absorption. Provided that θ is far shorter than the spin-lattice relaxation times, which corresponds to the strong saturation condition, we can neglect relaxation during this mixing process.

Starting with initial values α_i and γ_i, the limit β is a weighted average:

$$\beta=(\alpha_i\,\mathrm{Tr}Q^2+\gamma_i\,\mathrm{Tr}\mathcal{H}_D'^2)/(\mathrm{Tr}Q^2+\mathrm{Tr}\mathcal{H}_D'^2),$$

obtained by taking into account the "heat capacities" $\mathrm{Tr}Q^2$ and $\mathrm{Tr}\mathcal{H}_D'^2$ of Q and $\mathcal{H}_D'$.

We introduce a local frequency ω_D', defined by

$$\omega_D'^2/\Delta^2=\mathrm{Tr}\mathcal{H}_D'^2/\mathrm{Tr}Q^2.$$

This local frequency plays the same role as the local field used in pure Zeeman cases.

We then have

$$\beta=(\alpha_i\Delta^2+\gamma_i\omega_D'^2)/(\Delta^2+\omega_D'^2). \qquad (3)$$

The system is now described by a single spin temperature

$$\sigma \propto 1-\beta\mathcal{H}^*.$$

The inverse spin temperature then varies slowly under the effect of spin-lattice relaxation toward a steady state value β_∞ which results from a balance between the relaxation rates of the quadrupole and the dipolar parts. The quadrupole term Q is relaxed toward the inverse temperature $\beta_L(\Omega_0/\Delta)$, where β_L is the inverse lattice temperature, with relaxation time $T_1^{(S)}$. The dipolar term $\mathcal{H}_D'$ is relaxed toward the inverse lattice

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[2] A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

[3] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England, 1961), Chap. XII.

[4] I. Solomon and J. Ezratty, Phys. Rev. **127**, 78 (1962).

[5] B. N. Provotorov, Zh. Eksperim. i Teor. Fiz. **41**, 1582 (1961) [English transl.: Soviet Phys.—JETP **14**, 1126 (1962)].

temperature β_L, with relaxation time T_D. The relaxation time in the rotating frame is then given by the formula

$$\frac{1}{T_1}=\left(\frac{\Delta^2}{T_1^{(S)}}+\frac{\omega_D'^2}{T_D}\right)\Big/(\Delta^2+\omega_D'^2). \tag{4}$$

The steady-state value β_∞ is given by the equation

$$\beta_\infty=\frac{\beta_L(\Omega_0/\Delta)(\Delta^2/T_1^{(S)})+\beta_L(\omega_D'^2/T_D)}{(\Delta^2/T_1^{(S)})+(\omega_D'^2/T_D)}.$$

Neglecting the second term in the numerator, which is small in the range of interest where $\Delta\sim\omega_D'$, we get

$$\beta_\infty=\beta_L\frac{\Omega_0\Delta}{\Delta^2+\omega_L^2}, \tag{5}$$

where

$$\omega_L^2=(T_1^{(S)}/T_D)\omega_D'^2. \tag{5'}$$

This inverse temperature is maximum when $\Delta=\omega_L$, and is then equal to

$$(\beta_\infty)_{\max}=\beta_L(\Omega_0/2\omega_L)\gg\beta_L. \tag{6}$$

The net result of the thermal contact is an important cooling of the dipole-dipole interactions. The increase of order reflected by this cooling can be transferred to Zeeman interaction of the spins I by performing an adiabatic magnetization up to a field H large compared with ω_D/γ_I, where ω_D is a local frequency for the spins I, defined by the relation

$$\omega_D^2=\mathrm{Tr}\mathcal{H}_D'^2/\mathrm{Tr}I_Z^2.$$

If N_I and N_S are the numbers of nuclei of species I and S, respectively, this frequency ω_D is related to the local frequency ω_D' previously used by the relation:

$$\omega_D/\omega_D'=(N_S/N_I)^{1/2}. \tag{7}$$

The spin temperature achieved in field H for the spins I after adiabatic magnetization is

$$\beta(H)=\beta(0)(\omega_D/\gamma_I H).$$

The corresponding polarization is

$$P=\tfrac{1}{2}\hbar\beta(H)\gamma_I H=\tfrac{1}{2}\hbar\beta(0)\omega_D,$$

$$P=\tfrac{1}{2}\hbar\beta_L\omega_D(\Omega_0\Delta/\Delta^2+\omega_L^2). \tag{8}$$

Its maximum value is

$$P_{\max}=\tfrac{1}{2}(\hbar\Omega_0/kT_L)(\omega_D/2\omega_L).$$

It differs from the maximum polarization following a solid effect by the factor

$$G=\omega_D/2\omega_L=(\omega_D/2\omega_D')(T_D/T_1^{(S)})^{1/2}. \tag{9}$$

This enhancement factor G can be larger than unity if two conditions are fulfilled:

(1) The gyromagnetic ratio of the spins I must be far larger than that of the spins S: $\gamma_I\gg\gamma_S$.

(2) The quadrupole relaxation of the spins S must largely exceed the relaxation of the spins I due to paramagnetic impurities.

The first condition allows one to neglect the dipole-dipole interaction between pairs of spins S. The secular dipolar interaction then consists of two parts:

$$\mathcal{H}_D'=\mathcal{H}_{I-S}'+\mathcal{H}_{I-I}'$$

and we have further

$$\mathrm{Tr}(\mathcal{H}_{I-S}')^2\ll\mathrm{Tr}(\mathcal{H}_{I-I}')^2\simeq\mathrm{Tr}\mathcal{H}_D'^2.$$

From the second condition, only the part $\mathcal{H}_{I-S}'$ is in contact with the lattice, and its partial relaxation time $T_D^{(IS)}$ is comparable to the relaxation time $T_1^{(S)}$ of the quadrupole part. The spin-lattice relaxation time of the total dipole-dipole interaction $\mathcal{H}_D'$ is then

$$T_D=T_D^{(IS)}(\mathrm{Tr}\mathcal{H}_D'^2/\mathrm{Tr}\mathcal{H}_{I-S}'^2)\gg T_1^{(S)}.$$

Since ω_D and ω_D' are of comparable value, we see from (9) that $G\gg1$. G is actually of the order of[1]

$$G\sim\tfrac{1}{2}(\gamma_I/\gamma_S).$$

The experiments performed on paradichlorobenzene at 77°K, reported in (I), verified the main features of the theory and actually led to enhancement factors G, with respect to the solid effect, as large as 8.

The thermal-mixing experiments performed with paradibromobenzene, which are described in the present work, make use of a quadrupole splitting of the order of 270 Mc/sec, substantially larger than that of paradichlorobenzene, and are conducted at helium temperature as well as at nitrogen temperature. They provide in a somewhat different situation, additional verification of the theory of thermal mixing.

III. EXPERIMENTAL METHODS

We have performed thermal mixing experiments between protons and bromine-79 in paradibromobenzene.

The isotopic abundance of ^{79}Br is approximately 50% and its gyromagnetic ratio is approximately $\frac{1}{4}$ of the proton gyromagnetic ratio.

The thermal-mixing experiments involve three major steps: (i) sample preparation, (ii) measurement of the frequency, line width, and relaxation time of the pure quadrupole resonance absorption, (iii) realization and observation of the thermal mixing, which we describe in turn.

Sample Preparation

The samples are cylinders of approximately 10 mm diam and 20 mm length.

The commercial products are purified by two or three successive vacuum sublimations.

Most samples used were slowly grown single crystals in order to avoid strains and reduce the inhomogeneous broadening of the quadrupole line to a minimum.

The crystal growth is performed under vacuum by slow solidification of the melt in a temperature-gradient oven.

It is a necessary precaution to operate under vacuum since otherwise the air dissolved in the melt gives rise to bubbles occluded in the crystal, which might result in strains and quadrupole inhomogeneous broadening. Crystallization is achieved in a time of the order of two to ten hours.

Preparation of samples of paradi-iodobenzene and metadi-iodobenzene has also been tried, but these compounds are unstable and release iodine which distorts the crystal lattice and causes a very severe broadening of the quadrupole line.

Quadrupole Resonance

We have used a marginal oscillator-type quadrupole spectrometer. In order to perform measurements in liquid helium, the coil—typically three or four turns of 12 mm diam—is sealed to a rigid coaxial line about 3 ft. long. When in parallel with a capacitor, this circuit has a series of resonance frequencies; the spectrometer is forced to oscillate in the suitable range—from 260 to 300 Mc/sec—by using a tuned-plate-tuned-grid arrangement, the plate circuit of which has only one resonance frequency. The tube is a 5718 miniature triode. The spectrometer is frequency modulated at 318 cps with a varicap capacitor. The mean dc frequency can be swept over a range of 1 to 2 Mc/sec with the same varicap capacitor. The high frequency is crystal detected at the cathode, and detection is followed by audio-frequency amplification. For oscilloscope observation, it is necessary to use a twin-T filter to remove the amplitude modulation which accompanies frequency modulation. The displayed line is then the derivative of the absorption line. For lock-in detection, a much smaller frequency modulation depth is required, which brings the parasitic amplitude modulation to a level which does not necessitate the use of a filter and permits the recording of the first derivative of the absorption line.

Frequency measurements are performed by observing beats with the second harmonic of an auxiliary oscillator, the fundamental frequency of which is directly measured with a frequency meter.

Only very long spin-lattice relaxation times can be measured with this spectrometer by observing the absorption signal amplitude on the run, at various times after saturation.

Thermal Mixing

The experimental setting used for realizing and observing thermal mixing is very similar to that described in (I).

The sample is irradiated in zero field with a rf field of frequency close to the quadrupole resonance frequency of the spins S (of the order of 271 Mc/sec for ^{79}Br in paradibromobenzene) during a given time. The rf field is then turned off and a dc magnetic field is increased to about 200 G in a fraction of a second; this achieves an adiabatic magnetization of the spins I, the protons, and decouples them from the spins S. During a second increase of the magnetic field from 200 to 300 G in 0.5 sec, the proton signal is observed by fast passage in a crossed-coil spectrometer operating at 1100 kc/sec.

The magnetic field is produced by a pair of Helmholtz coils.

The irradiation coil consists of 4 spaced turns of 12 mm diam. The power dissipated by irradiation is varied between 1 and 5 W in the experiments performed in liquid nitrogen and is, at most, of 50 mW in the experiments performed in liquid helium. The spectrometer transmitter coils produce a rotating field of the order of 0.5 G and are operated only by 0.5-sec pulses for the fast passage observation in order to reduce the power dissipated in the cooling liquid.

IV. EXPERIMENTAL RESULTS

Quadrupole Resonance

The quadrupole resonance line widths of single crystals of paradibromobenzene at room temperature range between 6 and 8 kc/sec. They are actually not very different in polycrystalline samples. These widths do not vary appreciably when the samples are slowly cooled from 300 to 77°K in a time of 3 to 4 h, nor by a fast cooling from 77 to 4°K. But after a sudden cooling from air to liquid nitrogen, the line widths increase up to 18 kc/sec.

Paradi-iodobenzene and metadi-iodobenzene samples have quadrupole line widths of about 30 kc/sec at room temperature, and exceeding 100 kc/sec at nitrogen temperature. This broadening is thought to originate from the iodine atoms released in the lattice by decomposition. As explained in I, an important inhomogeneous broadening of the quadrupole line drastically reduces the effectiveness of the thermal mixing for polarizing the spins I, and we actually never observed any proton polarization in thermal mixing experiments performed with these compounds.

In Table I are quoted the quadrupole resonance frequencies of ^{79}Br in paradibromobenzene at several temperatures.

We did not measure the quadrupole relaxation time

TABLE I. Quadrupole resonance frequency of ^{79}Br in paradibromobenzene at several temperatures.

Temperature (°K)	Resonance frequency Mc/sec
298	267.903±0.003
77	271.117±0.006
4.2	271.506±0.003
1.2	271.506±0.006

at 77°K. By comparison with paradichlorobenzene, for which the quadrupole relaxation time is equal to 560 msec at this temperature,[6] the quadrupole relaxation time of ^{79}Br in paradibromobenzene must be roughly of the order of 10 msec, taking into account the factor 8 between the respective quadrupole interactions and assuming that the molecular vibrations are not very different in these two compounds.

At 4.2°K, the quadrupole relaxation time is equal to

$$T_1 = 40 \pm 5 \text{ min}.$$

Thermal Mixing

Thermal mixing experiments between protons and ^{79}Br have been conducted at 77 and 4.2°K.

The results of proton polarization by thermal mixing at 77°K are just a duplicate of those obtained with paradichlorobenzene and described in (I).

Figure 1 shows, for a particular experiment, a plot of the proton fast passage signal amplitudes, observed at 300 G as a function of the frequency at which the crystal was irradiated when in zero field, and displays an over-all agreement with formula (8). The relaxation time in the rotating frame is, at this temperature, a fraction of a second.

At 4.2°K, the thermal mixing experiments show that the spin-lattice relaxation time T_D of the dipole-dipole part $\mathcal{H}_D'$ is of the order of 20 to 80 sec, depending on the samples. Since at the same temperature, the quadrupole spin-lattice relaxation time is equal to 40 min, this leads, from formula (9) to a value of the factor G far smaller than unity, and the proton polarizations obtainable are very low.

The experiments which demonstrate this circumstance consist in starting the thermal contact with such prepared initial conditions that the quadrupole term is at a definite temperature and the dipolar term at infinite temperature. As a function of the time of thermal contact, the inverse temperature of the dipolar part is observed to increase first, due to the achievement of a single spin temperature in the rotating frame under the influence of the rf field, and then to decrease to a finite limit, due to spin-lattice relaxation.

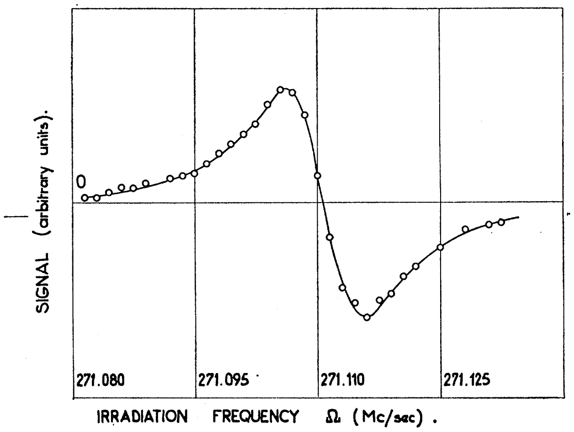

Fig. 1. Fast-passage signal amplitudes of protons in paradibromobenzene at 77°K, as a function of irradiation frequency in zero field.

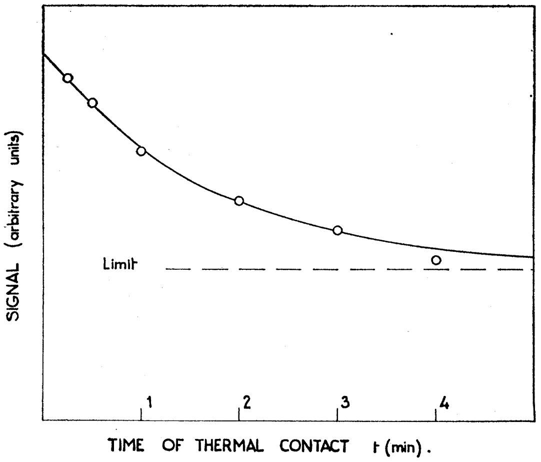

Fig. 2. Proton fast-passage signal amplitudes observed in sample A at 4.2°K, as a function of time of thermal contact in zero field at 18 kc/sec from quadrupole resonance. The solid curve is a plot of the equation

$$h(t)/h(\infty) = 1 + 1.25 \exp(-t/104).$$

The experimental sequence is the following:

(1) The quadrupole term is saturated, i.e., its temperature is made infinite by a 2-min irradiation in zero field at the exact quadrupole resonance frequency, namely, 271.506 Mc/sec.

(2) The sample then spends a given time (5 to 10 min) in high field (200 to 300 G); thermal contact is now interrupted between the quadrupole and the dipolar terms, and the temperature of the quadrupole term decreases to a definite value under the influence of spin-lattice relaxation.

The dipolar term is meanwhile saturated by repeated nonadiabatic fast passages performed on the protons; saturation is complete when fast passage signal of the protons becomes unobservable.

(3) The initial condition now corresponding to a definite temperature for the quadrupole term and an infinite temperature for the dipolar term, thermal contact is established between these parts by irradiating the sample in zero field with a rf field of frequency 271.524 Mc/sec at 18 kc/sec from resonance, i.e., corresponding to $\Delta = 18$ kc/sec. Thermal contact is maintained a time t, which is varied from one experiment to the other.

(4) At the end of this thermal contact period, the magnetic field is switched on and the proton signal is observed by fast passage.

Figures 2, 3, and 4 display the observed signal amplitudes as a function of the time of thermal contact for

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[6] A. Hirai, J. Phys. Soc. Japan 15, 201 (1960).

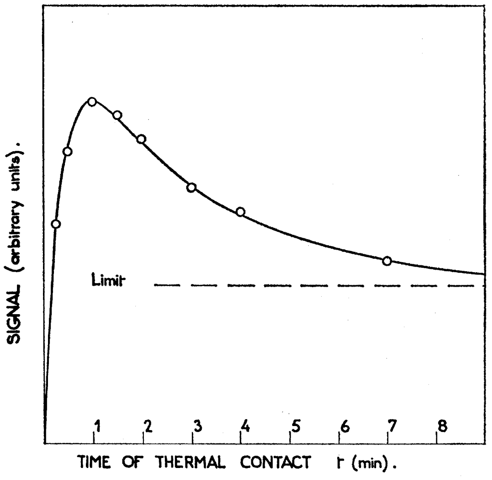

FIG. 3. Proton fast-passage signal amplitudes observed in sample B at 4.2°K as a function of time of thermal contact in zero field at 18 kc/sec from quadrupole resonance. The solid curve is a plot of the equation

$$h(t)/h(\infty)=1+1.44\exp(-t/160)-2.44\exp(-t/20).$$

three different samples, referred to hereafter as samples A, B, C, using different rf field amplitudes.

The initial phase of increase of the signal, observed in Figs. 3 and 4 corresponds to the thermal mixing between quadrupole and dipolar terms under the influence of the irradiation field.

The initial alignment of the spins S is a fraction $k<1$ of their thermal equilibrium alignment. The corresponding initial inverse temperature of the quadrupole term in the rotating frame is

$$\alpha_i=k\beta_L\Omega_0/\Delta.$$

Thermal mixing increases the inverse temperature of the dipolar term from zero to a value β, which, from formula (3), is equal to

$$\beta=k\beta_L(\Omega_0\Delta/(\Delta^2+\omega_D'^2)). \qquad (10)$$

The shorter mixing time θ actually corresponds to the larger rf field amplitude. We did not attempt any quantitative investigation.

The subsequent decrease of the signal corresponds to the evolution due to spin-lattice relaxation. The rate of this decrease and the very low value of the steady-state polarization actually prove, from formulas (4) and (5), that

$$T_1^{(S)}/T_D\gg 1.$$

The relaxation time in the rotating frame is then

$$T_1=T_D(\omega_D'^2+\Delta^2)/\omega_D'^2. \qquad (11)$$

Direct measurements of T_D have been performed in the following way:

(1) Initial conditions are achieved by following steps (1) and (2) of the preceding experiment.

(2) A 15-sec thermal contact is realized in zero field at $\Delta=18$ kc/sec.

(3) Irradiation is switched off and the sample is allowed to stay in zero field during a time t.

(4) The dc magnetic field is switched on and the proton signal is observed by fast passage. This signal decays exponentially as a function of t, with time constant T_D.

Table II collects the observed values of θ, T_1, and T_D for the three samples. For samples A and C, for which both T_1 and T_D have been measured, we have

TABLE II. Mixing times, relaxation times in the rotating frame at $\Delta=18$ kc/sec, and dipolar relaxation times at 4.2°K in three different samples of paradibromobenzene, using different irradiation rf field amplitudes.

Sample and corresponding figures	Mixing time (sec)	Relaxation time T_1 (sec)	Dipolar relaxation time T_D (sec)
A (Fig. 2)	...	104	49
B (Fig. 3)	20	160	...
C (Fig. 4)	3.8	48	25

$$T_1\simeq 2T_D$$

which, from formula (11) corresponds to

$$\omega_D'\simeq\Delta=18\text{ kc/sec}.$$

A direct measurement of ω_D' has been attempted by verifying formula (10). Starting with the same initial conditions as before, 15 sec thermal mixings are performed with different values of Δ by irradiating the sample at different distances from quadrupole resonance. Figure 5 is a plot of the observed proton-signal amplitudes as a function of Δ. It displays a poor agree-

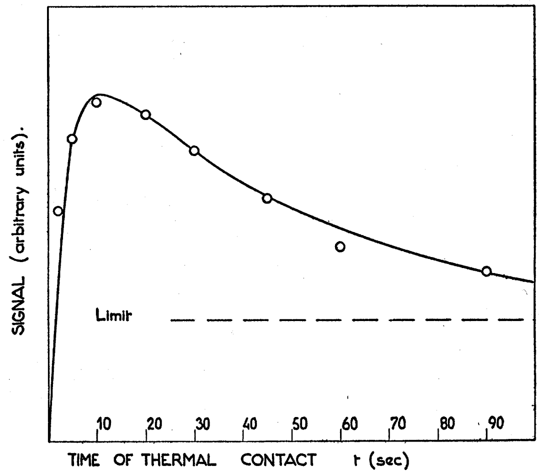

FIG. 4. Proton fast-passage signal amplitudes observed in sample C at 4.2°K as a function of time of thermal contact in zero field at 18 kc/sec from quadrupole resonance. The solid curve is a plot of the equation

$$h(t)/h(\infty)=1+2.6\exp(-t/48)-3.6\exp(-t/3.8).$$

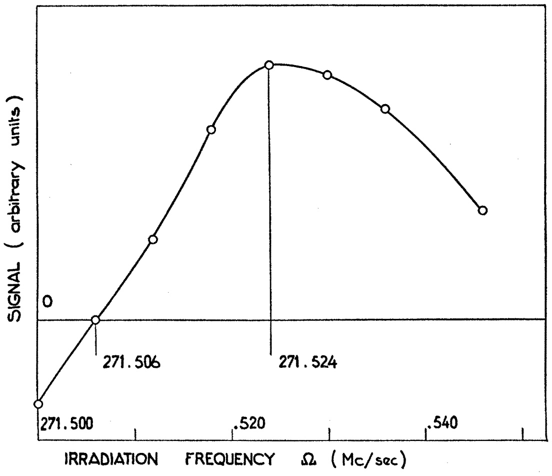

FIG. 5. Proton fast-passage signal amplitudes following 15-sec thermal contact in zero field as a function of irradiation frequency.

ment with Eq. (10) for two reasons: As Δ becomes smaller, the relaxation time T_1 becomes shorter and the signal is decreased with respect to formula (10) by spin-lattice relaxation; when Δ becomes large, the thermal mixing time θ increases sharply, and the dipolar inverse spin temperature does not reach the value β in 15 sec. However, the maximum of the experimental curve should not be severely shifted from the maximum predicted by Eq. (10), and this maximum occurs at $\Delta=\omega_D'\simeq 18$ kc/sec, consistent with the former result. From Eq. (7), since there are four times more protons than ^{79}Br nuclei, the local frequency ω_D pertaining to the proton system is

$$\omega_D \simeq 9 \text{ kc/sec},$$

which corresponds to a local field

$$H_L=\omega_D/\gamma_I\simeq 2.1 \text{ G}.$$

The variation of the dipolar relaxation time T_D found among several samples suggests that this relaxation time is due to the coupling of the protons with paramagnetic impurities.

Much stronger evidence that this is actually the case is provided by studying the variation of the proton spin-lattice relaxation time as a function of magnetic field. Such a study has been performed on sample *C*, for which $T_D=25$ sec. In addition to displaying evidence for this impurity-controlled relaxation of the protons, it gives information on the impurities responsible for this relaxation and provides a check of the relaxation theories. This is why it is described in a separate article. Anticipating these results, a rough figure can be given for the paramagnetic impurity concentration in this particular sample.

$$N\sim 10^{-7} \text{ impurities/molecule}.$$

V. CONCLUSION

The thermal mixing experiments performed with paradibromobenzene at liquid-helium temperature clearly exhibit the occurence of two separate phenomena during the thermal contact. The first is the evolution of the spin system under the influence of rf irradiation toward the establishment of a single spin temperature in the rotating frame; this is a pure spin mechanism, with no influence of the lattice, which qualitatively verifies Provotorov's theory[5] of rf induced thermal mixing between different parts of the spin Hamiltonian.

The second is the evolution of the spin temperature of the system in the rotating frame under the influence of its coupling with the lattice. The experimental results emphasize the importance, as regards the rate of this evolution and the steady-state value toward which it leads, of the relative strengths of the couplings with the lattice of the quadrupole part and of the dipolar part, in a situation opposite to, and thus complementary to, the situation met with in paradichlorobenzene.

These experiments establish the increased importance of paramagnetic impurities at low temperature in the thermal mixing, even at very low concentrations, which appears to be the major factor hampering the use of thermal mixing as a practical method for obtaining large nuclear dynamic polarizations.

As a by-product, the polarization of the protons by thermal mixing, increasing their magnetic resonance signal well above the noise level, allows the measurement of their relaxation time in low fields, as exemplified in another article.

The experiments on paradibromobenzene, together with the experiments on paradichlorobenzene provide at least qualitative confirmations of many detailed features of the theory of a phenomenon in which the concept of spin temperature play a dominant part.

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