PHYSICAL REVIEW VOLUME 112, NUMBER 3 NOVEMBER 1, 1958

Dynamics of Interacting Spin Systems*

Robert T. Schumacher
Carnegie Institute of Technology, Pittsburgh, Pennsylvania

(Received July 3, 1958)

The dynamics of the approach of two spin systems to the same spin temperature is examined. It is found that for two spin systems in a rigid lattice interacting weakly with the lattice and with each other, differential equations governing the time rate of change of the spin temperatures can be derived. The derivation assumes the validity of the concept of spin temperature and the validity of the principle of detailed balance applied to eigenstates of the spin Hamiltonians of the systems. The spin mixing experiments of Abragam and Proctor provide evidence for the correctness of the differential equations thus derived. Additional experiments on spin-lattice relaxation times in NaBr, NaI, and NaCl are reported and interpreted in terms of the differential equations developed here. It is shown that under certain conditions the presence of a second spin system can shorten the relaxation time of a spin system even at rather high values of the external field.

I. INTRODUCTION

The recent work by Abragam and Proctor[1] (hereafter referred to as AP) has demonstrated the utility and validity of the concept of spin temperature as applied to nuclear spin systems in rigid lattices. They have also demonstrated that two spin systems at initially different spin temperatures may be allowed to interact ("mix") with each other at sufficiently small magnetic fields, and that as a consequence of this interaction the two systems reach the same spin temperature. It is the purpose of this paper to investigate the time scale for this mixing under various circumstances and the effect of the spin system interaction on the measured spin-lattice relaxation time of either of the spin systems.

The one experiment done by AP on LiF which included the effects of spin-lattice relaxation is particularly relevant to this investigation. The lithium resonance was saturated at a high-magnetic field while the fluorine magnetization remained untouched. The sample was removed to a field of about 75 gauss for a known time and then the lithium spin temperature (magnetization) was measured at the high field. AP chose to fit their data by the expression $1/T_s^{\mathrm{Li}} \propto \exp(-t/100)[1-\exp(-t/6)]$, with t in seconds. It was explicitly mentioned by them that the time constant "6 seconds" represents the thermal mixing time of the fluorine and lithium spin systems, and the 100-second time constant is the spin-lattice relaxation time of the lithium (and fluorine) spin system. The present investigation derives from certain well-defined assumptions differential equations obeyed by two spin systems interacting weakly with each other and the lattice. The solutions to these equations are in the form of the sum of two exponentials, and the meaning of the time constants as given by AP is verified. The same experiment has been performed by Little[2] on LiF, except he measured the time dependence of the fluorine spin temperature. His results are qualitatively quite in agreement with the differential equations to be proposed here and are in agreement with one's expectations on the basis of the AP experiment on the lithium system.

In Sec. II we shall derive the equations mentioned above. Section III will describe some experiments on some sodium halide crystals which test qualitatively some of the predictions of these equations which have not been previously tested by AP.

II. THEORY

It is the object of the calculation described here to obtain differential equations obeyed by the spin temperatures of two spin systems interacting weakly with each other and the lattice. The systems under consideration have as their prototype the alklai halides—a rigid lattice with equivalent lattice sites occupied by two kinds of nuclei. We assume that each of the systems may be described by an unperturbed Hamiltonian of the form

$$\mathcal{H}=\mathcal{H}_z+\mathcal{H}_D, \tag{1}$$

where $\mathcal{H}_z=-\gamma\hbar H_0\sum_j I_{zj}$, and $\mathcal{H}_D$, the dipole-dipole Hamiltonian, includes interactions between like nuclei as well as those interactions between unlike nuclei which do not involve spin flips in either spin system. The Hamiltonian $\mathcal{H}$ refers to either spin system in the sample; when required, distinction between the two systems will be made by a superscript 1 or 2. The spin-lattice interaction and the remaining part of the spin-spin interaction between unlike nuclei are treated as weak perturbations of (1) for each of the systems.

The starting point of the calculation is exactly that of Slichter and Hebel.[3] Let $E=\mathrm{Tr}[\rho(T_s)\mathcal{H}]$ be the energy of either spin system, where

$$\rho(T_s)=\exp(-\mathcal{H}/kT_s)/\mathrm{Tr}[\exp(-\mathcal{H}/kT_s)].$$

Then $dE/dt=(dE/dT_s)(dT_s/dt)$ may be rewritten in terms of $1/T_s$ and solved for $(d/dt)(1/T_s)$:

$$\frac{d}{dt}\left(\frac{1}{T_s}\right)=\frac{dE/dt}{-T_s^2dE/dT_s}. \tag{2}$$

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* Assisted in part by a grant from the National Science Foundation.

[1] A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1958).

[2] W. A. Little, Proc. Phys. Soc. (London) **B70**, 785 (1957).

[3] C. P. Slichter and L. C. Hebel (to be published). L. C. Hebel, thesis, University of Illinois, 1957 (unpublished).

Now $E=\sum_n p_n E_n$, where E_n is an eigenvalue of $\mathcal{H}$: $\mathcal{H}|n\rangle=E_n|n\rangle$.

The population of the eigenstate $|n\rangle$ is given by

$$p_n=\frac{\exp(-E_n/kT_s)}{\sum_n \exp(-E_n/kT_s)}. \tag{3}$$

To find dE/dt we note that $dE/dt=\sum_n (dp_n/dt)E_n$, and that for weak perturbations dp_n/dt may be written as a rate equation involving transition probabilities. The validity of such a procedure seems well established in the case of spin-lattice interactions, and Slichter and Hebel[3] show that this procedure leads to the familiar relaxation time description of the approach of the spin system to equilibrium. We make here the additional assumption that such a rate equation governs the interaction between the two spin systems.[4] Labeling the spin systems by superscripts (1) and (2), we write

$$\frac{dp_n}{dt}=\sum_m \left[W_{mn}^{(1)}p_m-W_{nm}^{(1)}p_n\right]+\sum_{m,r,s}\left[W'_{ms,\,nr}p_m q_s-W'_{nr,\,ms}p_n q_s\right]. \tag{4}$$

The first (single) summation involves the interaction of spin system (1) directly with the lattice. $W^{(1)}$ is determined by the spin-lattice relaxation mechanism for the spin species (1). The calculations involving this term are done in reference 3, and the term will not be pursued further here. $W'_{ms,\,nr}$ represents the probability per unit time that a transition will occur between states $|m\rangle$ and $|n\rangle$ of system (1) and states $|s\rangle$ and $|r\rangle$ of system (2) via the dipole interaction between the systems. q_s is the occupation probability of the eigenstate $|s\rangle$ of the Hamiltonian (1) for the second spin system and p_n the analogous quantity for eigenstate $|n\rangle$ of (1) for the first system. Since the two spin systems are characterized by the two spin temperatures $T_s^{(1)}$ and $T_s^{(2)}$, we have

$$\frac{p_n}{p_m}=\exp\left[-(E_n^{(1)}-E_m^{(1)})/kT_s^{(1)}\right],\quad\text{and}\quad \frac{q_r}{q_s}=\exp\left[-(E_r^{(2)}-E_s^{(2)})/kT_s^{(2)}\right]. \tag{5}$$

We have assumed that only the dipole-dipole interaction, and not the lattice, is involved in W', so we have $W'_{ms,\,nr}=W'_{nr,\,ms}$. This also requires that $E_n^{(1)}-E_m^{(1)}=E_s^{(2)}-E_r^{(2)}$ for the states labeled by n, m, r, and s. Otherwise W' vanishes. Substituting (5) into (4) and expanding the exponential in the usual high-temperature approximation, we find for the contribution to dp_n/dt due to W' alone:

$$\frac{dp_n}{dt}=\sum_{m,r,s} W'_{nr,\,ms}p_m q_r \times\frac{(E_n^{(1)}-E_m^{(1)})}{k}\left(\frac{1}{T_s^{(1)}}-\frac{1}{T_s^{(2)}}\right). \tag{6}$$

Hence

$$\begin{aligned}\frac{dE^{(1)}}{dt}&=\sum_n \frac{dp_n}{dt}E_n\\&=\sum_{nmrs} W'_{nr,\,ms}p_m q_r\frac{E_n^{(1)}}{k}(E_n^{(1)}-E_m^{(1)})\\&\quad\times\left(\frac{1}{T_s^{(1)}}-\frac{1}{T_s^{(2)}}\right)=\sum_{nmrs} W'_{nr,\,ms}\\&\quad\times(E_n^{(1)}-E_m^{(1)})^2\left(\frac{1}{T_s^{(1)}}-\frac{1}{T_s^{(2)}}\right)\frac{1}{2k\mathcal{N}_1\mathcal{N}_2},\end{aligned} \tag{7}$$

where $\mathcal{N}_i$ is the total number of spin states of spin system $i=1$ or 2.

The other pertinent derivative of E, dE/dT_s, has been calculated by Slichter and Hebel. They find that

$$\frac{dE^{(1)}}{dT_s^{(1)}}=\frac{1}{k(T_s^{(1)})^2}\frac{\mathrm{Tr}[(\mathcal{H}^{(1)})^2]}{\mathcal{N}_1}. \tag{8}$$

With the aid of (8), (7), and the spin-lattice terms from Slichter and Hebel, (2) may be written

$$\frac{d}{dt}\left(\frac{1}{T_s^{(1)}}\right)=-R_1\left(\frac{1}{T_s^{(1)}}-\frac{1}{T_L}\right)-R_{12}\left(\frac{1}{T_s^{(1)}}-\frac{1}{T_s^{(2)}}\right), \tag{9a}$$

where

$$R_{12}=\frac{\sum_{mrns} W'_{nr,\,ms}(E_n^{(1)}-E_m^{(1)})^2}{2\,\mathrm{Tr}[(\mathcal{H}^{(1)})^2]\mathcal{N}_2},$$

$$R_1=\frac{\sum_{nm} W_{nm}^{(1)}(E_n^{(1)}-E_m^{(1)})^2}{2\,\mathrm{Tr}[(\mathcal{H}^{(1)})^2]},$$

and T_L is the temperature of the lattice. By interchanging (1) and (2), the second spin system can be seen to obey

$$\frac{d}{dt}\left(\frac{1}{T_s^{(2)}}\right)=-R_2\left(\frac{1}{T_s^{(2)}}-\frac{1}{T_L}\right)-R_{21}\left(\frac{1}{T_s^{(2)}}-\frac{1}{T_s^{(1)}}\right), \tag{9b}$$

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[4] L. Van Hove, Physica 21, 517 (1955) has considered in detail the conditions which must be satisfied by the system described by $\mathcal{H}$ and by the perturbation in order that such a rate equation may be used. We have not investigated in detail whether all his criteria are exactly satisfied by (1) and its perturbations. However, the most obviously important of his criteria seem to be satisfied. The spectrum of eigenstates $|n\rangle$ of (1), and its spectrum of eigenvalues E_n form nearly a continuum of states and energies, and we limit ourselves to very weak perturbations.

where

$$R_{21}=\frac{\sum_{nrms} W'_{nr,\,ms}(E_r^{(2)}-E_s^{(2)})^2}{2\,\mathrm{Tr}[(\mathcal{H}^{(2)})^2]\mathfrak{N}_1},$$

$$R_2=\frac{\sum_{rs} W_{rs}^{(2)}(E_r^{(2)}-E_s^{(2)})^2}{2\,\mathrm{Tr}[(\mathcal{H}^{(2)})^2]}.$$

Since, as mentioned above, W' vanishes unless $(E_r^{(2)}-E_s^{(2)})=(E_n^{(1)}-E_m^{(1)})$, we can solve simply for the ratio R_{21}/R_{12} in the high-field region where most of the energy of each spin system is in the Zeeman term. Under these circumstances we get

$$\frac{R_{21}}{R_{12}}=\frac{\mathrm{Tr}[(\mathcal{H}^{(1)})^2]\mathfrak{N}_2}{\mathrm{Tr}[(\mathcal{H}^{(2)})^2]\mathfrak{N}_1}\cong\frac{\mathrm{Tr}[(\mathcal{H}_z^{(1)})^2]\mathfrak{N}_2}{\mathrm{Tr}[(\mathcal{H}_z^{(2)})^2]\mathfrak{N}_1}$$
$$=\frac{N_1\gamma_1^2I_1(I_1+1)}{N_2\gamma_2^2I_2(I_2+1)}\equiv\mu. \quad (10)$$

μ is the ratio of the heat capacity of the two systems at the same spin temperature.

Equations (9) represent the main results of this investigation.[5] The derivation made use of two explicit assumptions: each system is described by a spin temperature, and the interaction of each spin system with the other and with the lattice is weak enough to allow the use of the rate Eq. (4). This last requirement may be written R_1, $R_2 \ll \Delta\nu_1$, $\Delta\nu_2$ where $\Delta\nu_1$ and $\Delta\nu_2$ are the line widths of the nuclear resonances of the two nuclei, and also $R_{12}, R_{21} \ll \Delta\nu_1, \Delta\nu_2$. The last inequality is certain to be satisfied only in external fields large compared to the local fields in the sample, so the ratio (10) is always satisfied in the range of external fields for which Eqs. (9) are likely to be valid.

The solutions of the coupled Eqs. (9) may be written

$$1/T_s^{(1)}=Ae^{m_+t}+Be^{m_-t}+C, \quad (11a)$$

$$1/T_s^{(2)}=A'e^{m_+t}+B'e^{m_-t}+C', \quad (11b)$$

where A, B, and C depend on initial conditions, and A', B', and C' are determined by Eqs. (9). Here

$$m_\pm=-\tfrac{1}{2}R_1[1+g+(1+\mu)h\pm S],$$

where $g=R_2/R_1$, $h=R_{12}/R_1$, and

$$S=[(g-1)^2+(\mu+1)^2h^2+2h(\mu-1)(g-1)]^{\frac{1}{2}}. \quad (12)$$

Equations (9) and their solutions (11) pass all the necessary trivial tests. If R_1 and R_2 vanish and the initial spin temperatures are not equal the systems approach a final common temperature determined by their relative heat capacities and by conservation of the total energy within the spin systems. That this happens in fact was determined by the experiments described in AP. Equations (11) also provide precise meanings for the exponents in the expression AP fit to their data on LiF in the experiment described in the introduction of this paper. Data for the behavior of the fluorine system under nearly identical circumstances were published by Little.[2] Unfortunately the spin lattice relaxation mechanism in LiF is field dependent in an unknown manner, so neither R_1, R_2, nor their ratio is known for LiF at 75 gauss. This prevents quantitative comparison of $m_\pm$ with the experiments.

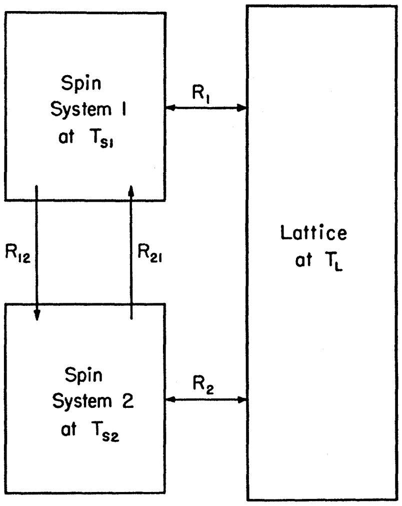

FIG. 1. Shown schematically are the two spin systems at spin temperatures T_{s1} and T_{s2}, respectfully, coupled to the lattice at T_L by "heat leaks" of magnitude determined by the relaxation rates R_1 and R_2. The systems exchange energy at rates determined by R_{12} and R_{21}.

We conclude this section by remarking that Eqs. (9) suggest an obvious phenomenological model.[6] This model is represented in Fig. 1. The spin systems are thermodynamic systems which are in weak contact with a heat reservoir, the lattice, at T_L, and are also in weak contact with each other. Consideration of this model even without the quantitative analysis presented above explains immediately many observations presented later in this paper and many of those in AP. In particular, it is evident that if the two systems are coupled more tightly to each other than either system is coupled to the lattice, the systems will quickly attain the same spin temperature and maintain equal spin temperatures as the lattice temperature is approached. Hence they exhibit a common relaxation time.

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[5] Equations similar, but not identical, to Eqs. (9) have been obtained by I. Solomon, Phys. Rev. **99**, 559 (1955). Actually, in the problem solved by Solomon the spin-spin interactions between unlike nuclei and the spin-lattice interactions of each system involved the same mechanism, rather than completely different mechanisms as in the calculation leading to Eqs. (9). A calculation similar in aim to ours has been performed by Little (reference 2).

[6] Equations (9) were originally written by the author by consideration of this model, the experimental results of AP, and the experiments reported here. Professor C. P. Slichter suggested that these equations probably could be derived as indicated in this section.

III. EXPERIMENTS

The experiments described in this section were chosen to test the consequences of the dipolar interaction between unlike spins on the measured spin-lattice relaxation time. Since one expects R_{12} in Eq. (9a) to be strongly field dependent, it would be convenient if neither R_1 nor R_2 were field dependent. This requirement is satisfied by the quadrupole-phonon relaxation mechanism described by Van Kranendonk.[7] Crystals were chosen in which there was good reason to believe both R_1 and R_2 are determined by the quadrupole-phonon interaction. In addition, it was thought appropriate to keep all the characteristics of one of the spin systems reasonably constant while varying the properties of the second spin system. For this purpose the three sodium-halides NaCl, NaBr, and NaI were chosen. Their properties, including high-field spin-lattice relaxation times at room temperature and liquid nitrogen temperature, are summarized in Table I. The liquid nitrogen measurements were made to demonstrate that the crystals were sufficiently free of paramagnetic impurities so that even at low magnetic fields the quadrupole relaxation mechanism was dominant. This phase of the investigation will be discussed more completely below.

(A) Technique

Spin-lattice relaxation times (T_1) were measured by observing the magnitude of the free-induction decay following a short, high-intensity pulse of rf power at the Larmor frequency. The apparatus is conventional nuclear resonance pulse equipment. The rf pulses are derived from a continuous 10 Mc/sec oscillator which also provides a reference voltage on the signal detector which follows a 10-Mc/sec rf amplifier. Thus the detector is linear and sensitive to the relative phases of the signal and the c. w. oscillator.[8] Probably because of the sloppiness of the tail of the high-power pulse, the receiver remained blocked for nearly 20 μsec after the half-power point of the trailing edge of that pulse. Fortunately the duration of the free-induction decay for the resonances investigated here was long enough so that the receiver blocking was not important.

TABLE I. Listed are the relevant spin-lattice relaxation times for the nuclei investigated. Also included for each nucleus is $\gamma^2 I(I+1)$, which is proportional to the spin specific heat of the nuclear spin system involved.

Nucleus	Crystal	$\gamma^2 I(I+1)$	T_1 (300°K)	T_1 (77°K)
Na	NaCl	1.84×10^8	14.2 sec	300 sec
Cl	NaCl	(0.234×10^8)[a]	(4.5 sec)[b]	90 sec
Na	NaBr	1.84×10^8	8.5 sec	130 sec
Br^{81}	NaBr	(1.78×10^8)[a]	0.075 sec	$\sim$1.2 sec
Na	NaI	1.84×10^8	9.5 sec	...
I	NaI	2.45×10^8	0.010 sec	...

[a] Calculated using both isotopes weighted by the known isotopic abundance.
[b] Inferred from the measurements at 77°K. See text for discussion.

In the case of the nuclei with the long relaxation times (Na and Br at 77°K), the high-field T_1's were measured by observing visually the free-induction decay following a pulse which came at a measured time after a string of approximately 90° pulses had reduced the magnetization to zero. In this way it was never necessary to assume that the rf pulses were exactly of the length required to rotate the magnetization vector 90°. The short relaxation times (less than one second) were measured with the aid of a narrow-banding device, the "boxcar."[9] Here care had to be taken that the rf pulses were exactly 90°.

The field dependence of the sodium relaxation times was measured in the following way. The sample was allowed to come to equilibrium on the high field (8900 gauss for sodium at 10 Mc/sec). It was then removed to a predetermined point in the fringe field of the magnet, allowed to remain there for a known time, then returned quickly to the high field where the signal size, which is proportional to M_z, was immediately measured. Exponential behavior of the magnetization as a function of time was always observed when a consistent small correction was applied to the signal to account for the time spent in the high field before the measuring pulse was applied. No irreversible effects which depended on the rate at which the sample was removed from the high to the low field were observed. The value of the fringe field was measured by a commercial flux meter whose range was extended below 50 gauss by use of a Millivac millivoltmeter with a maximum sensitivity of one millivolt full scale. The fringe field values are probably correct to within 10%.

The chlorine resonance was never observed by the pulse apparatus because the fixed frequency of the apparatus was too high to allow the chlorine resonance to be seen in the fields available. In spite of this, the chlorine T_1 at 77°K was inferred in the following manner. The sample was allowed to come to equilibrium at 8900 gauss. Then the sodium resonance was saturated and the sample was immediately removed to a low mixing field for a short time ($\sim$one second), then returned to the apparatus in the high field where the sodium magnetization was measured. The experiments by AP on spin mixing indicate that in this case the magnetization acquired by the sodium system is proportional to the initial magnetization of the chlorine system [see Eq. (18) of their paper]. In the experiment described above the sodium signal following mixing was then proportional to the chlorine magnetization characteristic of 77°K. It was then a simple matter to put the sample in the high field for various known times, repeat the measurement of the chlorine mag-

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[7] J. Van Kranendonk, Physica **20**, 781 (1954).

[8] The circuits comprising the heart of this coherent pulse system were obtained from Dr. John Spokas, then at the University of Illinois.

[9] D. F. Holcomb and R. E. Norberg, Phys. Rev. **98**, 1074 (1955).

netization, and obtain from these data the chlorine T_1. Actually, subsequent experiments have shown that the mixing rate of the sodium and chlorine systems is slow even in fields not too much larger than the local field. For this reason the mixing may not have been complete by the time the sample reached the earth's field, and under these circumstances Eq. (18) of AP is not correct. In spite of this, and without detailed additional analysis, it seems safe to conclude that the time dependence of the signals obtained in the manner described above is characteristic of chlorine relaxation time.

(B) Results and Discussion

It is first necessary to define what is meant by a spin-lattice relaxation time for the sodium nuclei which have been removed to a field in which mixing can take place. Let Eq. (11a) represent the spin temperature of the Na system. For the demagnetization experiments described above we get for the constants of integration:

$$\begin{aligned} A&=-\sigma_1(0)[(1+\mu)h+g-1-S]/2S,\\ B&=\sigma_1(0)[(1+\mu)h+g-1+S]/2S, \end{aligned} \tag{13}$$

where $\sigma_1(0)$ is the reciprocal spin temperature immediately after demagnetization of the sodium system. We have assumed that the field to which the sample has been removed is large compared to the local field, and that $1/T_L$ is small compared to $\sigma_1(0)$. For $h=0$, we find $m_+=-R_2$, $m_-=-R_1$, $A=0$, and $B=\sigma_1(0)$. For $h\neq 0$ we find that $A\ll B$, and $m_+\gg m_-$. So although the spin temperature recovery is not governed by a single exponential, we see that one of the exponentials dies away much faster than the other and has in addition a small coefficient. All attempts to detect the presence of the second exponential have met with failure, since the largest effect is small and occurs rather quickly after demagnetization. For all practical purposes, then, the sodium spin temperature obeys

$$1/T_s^{\mathrm{Na}}=B\exp(m_-t). \tag{14}$$

The spin-lattice relaxation time T_1^{Na} is just $1/m_-$.

Suppose, as is the case for all the crystals considered here, that $g=R_2/R_1>1$. Then as $h=R_{12}/R_1$ increases, $1/m_-$ decreases. As h becomes much larger than g a limiting value of m_- is reached, which implies that T_1^{Na} will never be shorter than

$$(T_1^{\mathrm{Na}})^{-1}=\tfrac{1}{2}R_1(1+K)+\tfrac{1}{2}R_2(1-K), \tag{15}$$

where $K=(\mu-1)/(\mu+1)$.

The sodium T_1 data for the three crystals investigated are presented in Fig. 2. Consider first NaBr. Since the two equally abundant isotopes of bromine have gyromagnetic ratios which closely straddle sodium, it is not surprising that $1/m_-$ begins to shorten at rather high fields.† The shortest T_1 measured here corresponds to $h=5$. The limiting value of T_1 from Eq. (15) is about 200 milliseconds, too short to measure in small field with the present apparatus. The spin-lattice relaxation times of both isotopes of bromine and of sodium at 77°K were about a factor of 15 longer than at room temperature. The limiting value of the low-field T_1 was expected to be about 2 seconds from Eq. (15). This value is about the smallest T_1 that can be measured by the techniques used here. The experiments, which were carried out in fields of 50 and 100 gauss, seemed to indicate a sodium T_1 closer to one second than to two. However, the measurements must be considered to be somewhat unreliable.

An attempt was made to duplicate at 77°K the curve for NaBr in Fig. 2. It was noticed that the sodium relaxation time shortened at higher fields (>2000 gauss) than at room temperature. Two explanations may be offered for this phenomenon. One is that the bromine line widths were increased by the effects of increased static strains when the sample was plunged into liquid nitrogen. This would have the effect increasing W' in Eqs. (9). In support of this, it was noticed that the crystal shattered somewhat when cooled rapidly. The other, perhaps more sensible explanation is simply that with a small R_1 (for sodium) much smaller values of R_{12} may be noticed. If $(R_{12})^{-1}=60$ seconds and $(R_1)^{-1}=10$ seconds, little or no effect on the measured T_1 due to the other spin system will be detected. However, if $(R_{12})^{-1}=60$ seconds, and $(R_1)^{-1}=120$ seconds, the measured T_1 will be appreciably shortened. Since R_{12} is temperature independent and R_1 becomes a factor of 15 smaller between 300°K and 77°K, it is clear that at least part of the shortening of the measured T_1 at about 2000 gauss is from this effect.

The sodium T_1 in NaI shows qualitatively the same features as in NaBr. However, the iodine relaxation rate (R_2^{I}) is about eight times as great as R_2^{Br}. On the basis of this alone one might expect the sodium T_1 to shorten at a much higher field than in NaBr. However, the iodine gyromagnetic ratio, rather than being nearly

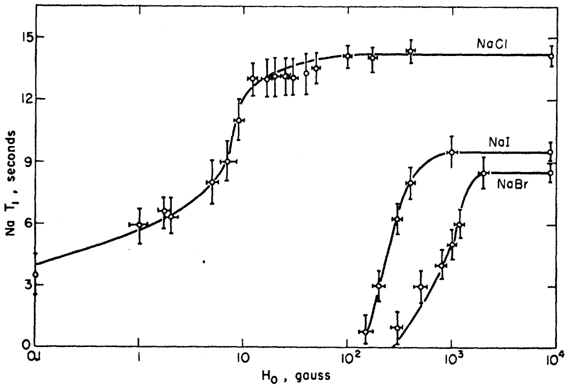

FIG. 2. Room temperature spin lattice relaxation times of Na in NaCl, NaBr, and NaI as a function of external field H_0. The solid curves were simply drawn through the experimental points.

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† *Note added in proof.*—The shortening of a long relaxation time by the mechanism found here has been observed by H. S. Gutowsky and D. E. Woessner, Phys. Rev. Letters 1, 6 (1958).

equal to that of sodium as in the case of bromine, is about three-quarters that of sodium. Hence in the same field W' must be much smaller for NaI than for NaBr. Qualitatively one may argue that at a given field the chance of two nonidentical nuclei being in local fields which allows them to flip while conserving energy is much greater for Na and Br than for Na and I. Of course, W' describes processes which are much more complicated than this, but the qualitative argument should be correct. Measurements were not made on NaI at 77°K since there would be no hope of observing the limiting value of the sodium T_1 because of the extremely short iodine T_1.

The striking feature of the NaCl data is the field independence of the sodium T_1 down to perhaps 40 gauss. We offer this as strong evidence that the sodium T_1 is determined by the quadrupole-phonon mechanism, and not by paramagnetic impurities. Even stronger evidence of the purity of the NaCl crystal is given by the data at 77°K, which show at all fields the essential features of the curve in Fig. 2 with the T_1 scale multiplied by about a factor of 20. Since this ratio is not greatly different from $T_1(77°\mathrm{K})/T_1(300°\mathrm{K})$ for both sodium and bromine in NaBr at 8900 gauss, we conclude that 20 is the ratio characteristic of this T_1 mechanism in NaCl. Van Kranendonk[7] predicts that this ratio should be in the vicinity of 30 for NaCl [Fig. (3) and Eq. (59) of this paper]. However, 77°K is in a region for NaCl in which Van Kranendonk's results apparently are extrapolated between low- and high-temperature calculations. In any event, it was felt justifiable to assume that the chlorine T_1 at room temperature may be found from the 77°K value by dividing by 20. This yields $T_1^{\mathrm{Cl}}(300°\mathrm{K})=4.5$ seconds, the value quoted in parentheses in Table I.

We can now explain the field independence to such low fields of the sodium T_1 in NaCl. Using the now known parameters needed in Eq. (15), we find that the limiting sodium T_1 for $h \gg g$ is 11.5 seconds. So even if R_{12} is large the chlorine system, with its small heat capacity and rather long relaxation time, has a rather small effect on the sodium system. In addition, from a qualitative argument one expects R_{12} to be much smaller for NaCl than in comparable circumstances for NaBr. One reasons that whereas in NaBr when the external field becomes small the sodium and bromine resonances begin to overlap, in NaCl the Cl^{35} (the most abundant isotope) resonance occurs at a frequency a factor of 2.7 below the sodium frequency. This means that although the simplest process one can imagine for an exchange of energy between the Na and Br systems involves $\Delta m_{\mathrm{Na}}=\pm 1$ and $\Delta m_{\mathrm{Br}}=\mp 1$, the simplest process conceivable in NaCl is $\Delta m_{\mathrm{Na}}=\pm 1$, $\Delta m_{\mathrm{Cl}}=\mp 3$. This process must proceed in higher order in perturbation theory and is consequently more rare. Again we realize that W' in general describes much more complicated transitions than visualized here, but we expect the argument to be correct qualitatively.

Since the T_1 measurements at fields less than 8900 gauss are not accurate to better than 10%, it is not clear whether or not the small diminution of T_1 observed below 50 gauss is real. The data at 25 gauss could correspond to $h=R_{12}/R_1 \lesssim 3$. A direct measurement of this mixing rate at 77°K was performed by repeating the type of measurement described above in obtaining the chlorine T_1. It was found that $(R_{12})^{-1}$ is about 10 seconds at 25 gauss and 2 to 4 seconds at 15 gauss. At 40 gauss $(R_{12})^{-1}$ is perhaps 20 to 30 seconds. Qualitatively, then, these direct measurements of R_{12}, and hence h, agree with the rather insensitive sodium T_1 data.

It has been emphasized before that Eqs. (9) cannot be considered to be valid at external fields which are not large compared to the local fields in the sample. The abrupt drop in the sodium T_1 below 15 gauss is not an effect explained by the Eqs. (9). It is rather related to the field dependence of R_1 and R_2 themselves. This has been calculated from the expressions for R by Redfield,[10] and by Slichter and Hebel,[3] for the case of a monatomic metal where the relaxation mechanism involves hyperfine coupling of the nuclei to the conduction electrons. An extension of these calculations to two spin systems and the quadrupole-phonon relaxation mechanism has not been attempted here.

Throughout this research the quantity R_{12}, for which we have an explicit expression, has been treated as a parameter which may be determined, if it is so desired, by the experiments. No attempt has been made to calculate it directly from the explicit expression, although this is possible in principle.

ACKNOWLEDGMENTS

I wish to thank Dr. A. Weiss and Dr. W. I. Goldburg for suggestions made during numerous conversations on this subject. Dr. M. Baranger has been particularly helpful with respect to some aspects of the theory. I have also benefited from discussions and correspondence with Dr. L. C. Hebel and Professor C. P. Slichter. A suggestion by Professor Slichter made possible the existence of Sec. II of this paper.

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[10] A. G. Redfield, IBM J. Research Develop. 1, 19 (1957). Redfield derives an expression for R from a somewhat different point of view than that adopted here.