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Spin Temperature

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The introduction of the concept of spin-temperature into the literature has not been adequately supported by theory and experiment, and it has not been clear when the concept is essential, merely convenient, or possibly inapplicable. In fields high compared to a defined "local field" and where the individual energy levels are equidistant, it is argued that spin temperature is a convenient but unnecessary notion. Where the levels are not equidistant a spin temperature cannot generally be defined. Experiments are cited or described which demonstrate the rapid establishment of a Boltzmann population ratio when three or more levels are equidistant.

It is for low fields, those which are comparable with the local field, that a theoretical examination making use of thermodynamic principles yields new quantitative predictions. In particular, a spin temperature is analytically defined, and its identity with thermodynamic temperature is experimentally established. Studies in "spin calorimetry," or the thermal mixing of two or more spin systems, strengthen the validity of the concept.

INTRODUCTION

ONE distinctive feature of nuclear paramagnetic resonance is that, unlike some other resonance methods, such as those using atomic beams, it deals with ensembles of nuclear spins, coupled to each other by spin-spin interactions, and also loosely coupled to a lattice by a spin-lattice relaxation mechanism.

The lattice acts as a thermostat for the spin system. Once the thermal equilibrium between the two systems has been established for a given value of the dc field H_0 and prior to the application of a rf field H_1, a temperature equal to the temperature of the lattice can be assigned to the spins. This means that the macroscopic properties of the spin system can be predicted by assuming that the populations P_i of its energy levels E_i are given by the Boltzmann exponential law:

$$P_i \sim \exp\{-E_i/kT\}, \qquad (1)$$

where T is the temperature of the lattice. In an operator notation the density matrix of the spin system can be expressed as:

$$\rho \sim \exp\{-\mathcal{H}/kT\}, \qquad (2)$$

where $\mathcal{H}$ is the Hamiltonian of the spin system. This description is still approximately correct in a steady-state nuclear resonance experiment provided the radiofrequency field is sufficiently weak and the sweep of the dc field, H_0, through the resonance line is sufficiently slow.

On the other hand, when either one of the previous conditions is violated, that is for strong rf fields or rapidly varying dc fields, one sometimes uses the concept of a spin temperature as distinct from the lattice temperature, of which negative spin temperatures are the most spectacular example.

However, there does not seem to exist among physicists a universal agreement as to the validity of the concept of spin temperatures, positive or negative. While some consider this concept as perfectly natural and requiring no more justification than, say, the temperature of a crystal lattice or a gas, others think that it lacks the deep physical meaning of thermodynamic temperature and is at best useless and often greatly misleading.

The object of the present paper is to steer a middle course between these two extremes and to outline situations where the existence of a spin temperature is a valid assumption leading to nontrivial predictions which have actually been tested by experiments to be described below. The concept of a spin temperature higher than the lattice temperature is most frequently met with in connection with the saturation of a spin resonance by an intense rf field.[1] However the description of systems with time-dependent Hamiltonians by the methods of statistical mechanics is a difficult problem and there is certainly no simple and rigorous way of defining a temperature for such systems, although it has been attempted in some special cases.[2–4] For this reason, although we admit the possibility of using rf fields to "prepare" the spin system in a given state, we shall not attempt to describe its behavior while the rf field is on.

As most of the previous students of spin temperature have done,[5–8] we shall limit ourselves to the case when the spin-lattice relaxation time T_1 is sufficiently long to allow experiments of duration $\tau \ll T_1$ to be performed, during which the spin system is practically isolated from the lattice. At the same time, we shall want the spins to come into equilibrium with each other

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[1] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

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

[3] C. P. Slichter, Phys. Rev. **99**, 1822 (1955).

[4] J. H. Van Vleck, Suppl. Nuovo cimento, **6**, No. 3, 1082 (1957).

[5] R. V. Pound, Phys. Rev. **81**, 156 (1951).

[6] R. V. Pound and E. M. Purcell, Phys. Rev. **81**, 279 (1951).

[7] R. V. Pound and N. F. Ramsey, Phys. Rev. **81**, 278 (1951).

[8] N. F. Ramsey, Phys. Rev. **103**, 20 (1956).

in a time T_2 much shorter than the duration τ of the experiment. This requires the sample to be a solid where indeed $T_1 \gg T_2$.

An important point which has been particularly stressed by Bloch[9] is that a description of the state of a spin system by a temperature and more generally by the populations of its energy levels can have a meaning only if the density matrix of the system commutes with the Hamiltonian. For instance, it is meaningless to assign populations to the energy levels of a spin system immediately after a 90° pulse. However, in solids, where the off-diagonal elements of the density matrix decay very quickly when the rf field which has produced them has been suppressed, it will be possible to speak in terms of populations once these off-diagonal elements have disappeared.

THEORY

We shall assume a Hamiltonian of the spin system of the form:

$$\mathcal{H}=\mathcal{H}^0+\mathcal{H}^1,$$

where $\mathcal{H}^0=\sum_i\mathcal{H}_i^0$ is the sum of the individual energies of the spins and $\mathcal{H}^1=\sum_{i<k}\mathcal{H}_{ik}^1$ is the sum of the spin-spin interactions. In the following, $\mathcal{H}_i^0$ will be, in general, the Zeeman energy: $\mathcal{H}_i^0=-\gamma_i\hbar H_0 S_i^z$ of the magnetic moment of spin i in an applied dc field H_0, and $\mathcal{H}_{ik}^1$ the dipole-dipole coupling between spins i and k (we shall then call it for brevity a Zeeman system), but we shall see examples of slightly more general systems. The distances between the spins are assumed to be constant in time (rigid-lattice approximation).

In attempting to define a spin temperature two different situations occur which require different approaches, namely the high- and low-field cases.

(1) High-Field Case

When the applied dc field is much larger than the local field produced at a given spin by its neighbors, or, more generally, when $\mathcal{H}^0 \gg \mathcal{H}^1$, it is permissible to speak of the states and energy levels of an individual spin which are the eigenstates and eigenvalues of $\mathcal{H}_i^0$ and to consider the whole sample as a statistical ensemble of such spins, $\mathcal{H}^1$ being a small perturbation coupling the different spins together and establishing a statistical equilibrium between them. This is akin to the Maxwell-Boltzmann description of the states of the molecules of a gas.

(A) $I=\frac{1}{2}$

The situation is particularly simple when the nuclear spin I is equal to $\frac{1}{2}$ and there are only two energy states $+$ and $-$. It is then always possible to define a spin temperature T through the relations:

$$P_+/P_-=\exp\{-\gamma\hbar H_0/kT\}, \tag{3}$$

where $P_\pm$ are the populations of the $\pm$ states. If H_0 is changed sufficiently slowly for the conditions of an adiabatic passage in the quantum mechanical sense to be realized (but still fast compared to T_1), P_+ and P_- do not change, but T defined by (3) varies proportionally to H_0. If an rf field has saturated to a certain extent the resonance of spin I, the ratio P_+/P_- gets nearer to unity and one may speak of an increase of the spin temperature, which becomes infinite for $P_+=P_-$. In the same way, if a 180° pulse or a rapid passage has reversed the magnetic moment of the sample, interchanging P_+ and P_-, one can define a negative spin temperature. Among the transitions which can be induced by the spin-spin interactions, only the simultaneous flip of two neighboring spins in opposite directions is energetically possible and it obviously conserves P_+ and P_-. Thus, in the case of spin $I=\frac{1}{2}$, the definition of a spin temperature is perfectly straightforward but also perfectly trivial.

(B) $I>\frac{1}{2}$

For $I>\frac{1}{2}$, the important physical fact which permits the definition of a spin temperature is the equidistance of the levels $I_z=m$ of a spin in a magnetic field. Its consequences are twofold: first, if at time $t=0$, the populations P_m of these levels form a Boltzmann distribution, $P_m \sim \exp\{-\gamma\hbar H_0 m/kT\}$, this distribution keeps the Boltzmann form when H_0 is changed adiabatically, if one makes the convention that the spin temperature varies proportionally to H_0. Furthermore, if at time $t=0$ the distribution is not of a Boltzmann form, the spin-spin interactions bring it to that form in a time $T_2 \sim (\gamma H_{\mathrm{loc}})^{-1}$. This has already been demonstrated by Bloembergen, Purcell, and Pound[1] for the case of spin $I=1$ but is valid for any spin. This can be seen quite generally as follows: it is a well-known result of statistical mechanics that if a given energy E has to be distributed between N identical systems having individual energy levels, the most probable distribution of populations among these states will be the Boltzmann one. For this distribution to be reached starting from any other initial distribution, a coupling mechanism is required which can transfer energy from one individual system to another and change the populations, keeping the total energy E of the N systems constant. The spin-spin interactions, through the simultaneous opposite flip of two spins, thanks to the equidistance of the levels of the individual spins, do precisely this.

The most convincing evidence of this effect was provided by an ultrasonic experiment already mentioned previously[10] and described in more detail below. Pure quadrupole transitions $\Delta m=2$ of nuclear spins $I=\frac{3}{2}$ of Na^{23} in NaCl, at twice the Larmor frequency, induced by ultrasonic waves, can lead to complete disappearance of the magnetic moment of Na^{23} for sufficiently strong ultrasonic transition probability W,

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[9] F. Bloch, Phys. Rev. **70**, 460 (1946).

[10] A. Abragam and W. G. Proctor, Phys. Rev. **106**, 160 (1956).

according to the formula:

$$M/M_0 = (1+8WT_1/5)^{-1}. \qquad (4)$$

The proof of this formula (unfortunately written in reference 10 with the wrong numerical factor 12/7 instead of 8/5) will be given in Appendix I. Ultrasonic saturation is well suited to demonstrate the role of spin-spin interactions in establishing a Boltzmann distribution because saturation by a magnetic rf field does not in general destroy the Boltzmann character of the distribution of spin populations.

(*C*) *Systems With Nonequidistant Levels*

Examples of such systems are provided by nuclei with quadrupole splitting or paramagnetic ions with fine or hyperfine structure. To be specific, let us consider impurity atoms of phosphorus embedded in a silicon lattice, which have been extensively studied.[11]

(a) *Impurity atoms.*—The electronic spin and the nuclear spin are both $\frac{1}{2}$. The Hamiltonian $\mathcal{H}_i^0$ of the atom i is

$$\mathcal{H}_i^0 = -\gamma_e \hbar H S_i^z - \gamma_n \hbar H I_i^z + A(\mathbf{I}_i \cdot \mathbf{S}_i), \qquad (5)$$

and the variation of its four energy levels with the applied dc field H, given by the well-known Breit-Rabi formulas, is represented in Fig. 1.

The spin lattice relaxation time T_1 (or rather the shortest of the time constants, coupling the populations a', b', b, a of the four spin-levels to the lattice) is of the order of two minutes at 2°K. It is thus possible, after the thermal equilibrium populations have been established at a given value H_0 of the field, to change it adiabatically to a value H, the populations remaining unchanged.

It might be well at this stage to point to a rather obvious but nonetheless frequent confusion originating from the use of the word adiabatic in two different senses: first, adiabatic in the quantum mechanical sense or (as it is sometimes called) in the Ehrenfest sense, describes the evolution of a statistical ensemble when some external parameter is changed in such a way that no transitions are induced and the populations of the various energy levels remain unchanged. Second, adiabatic in the thermodynamic sense describes the reversible change of a system in thermal equilibrium when no heat is allowed to flow in or out of the system. It is obvious that except for very special cases such as the one of equidistant levels, if thermal equilibrium, that is a Boltzmann distribution of populations, exists at time $t=0$, it will *not* remain of the Boltzmann form in an Ehrenfest adiabatic transformation when the energy levels change but not the populations. The two definitions are thus clearly incompatible in general. In the following, adiabatic will mean adiabatic in the Ehrenfest sense, the other type of transformation being called isentropic.

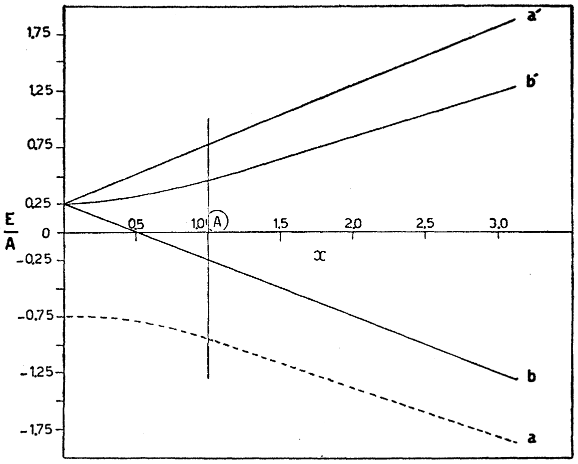

FIG. 1. Variation with the magnetic field of the energy levels of an electronic spin $\frac{1}{2}$ coupled by isotropic hyperfine interaction $A\mathbf{I}\cdot\mathbf{S}$ with a nuclear spin $I=\frac{1}{2}$. The parameter x is equal to $\hbar(\gamma_e+\gamma_n)H/A$.

For the impurity phosphorus atoms with hyperfine structure, in contrast to the pure Zeeman case, the spin-spin interactions are in general unable to change the populations of the various levels. We say in general, because for a special value H^* of the applied field, three levels can become equidistant and a spin temperature between these three levels can be established by the spin-spin interactions as the field sweeps through H^*. This happens for $\hbar(\gamma_e+\gamma_n)H^*=A$ (point A of Fig. 1). The actual value of H^* is 42 oersteds. If we polarize the sample by contact with the lattice in a high field H where the populations are

$$a' \simeq b' \simeq 1-\epsilon, \quad a \simeq b \simeq 1+\epsilon, \quad \epsilon \simeq (\gamma_e \hbar H/2kT) \ll 1,$$

they keep these values until the value H^* of the field is crossed, but at the crossing they undergo an irreversible change, becoming

$$a_1' \simeq 1-\epsilon, \quad b_1' \simeq 1-\tfrac{2}{3}\epsilon, \quad b_1 \simeq 1+\tfrac{1}{3}\epsilon, \quad a_1 \simeq 1+\tfrac{4}{3}\epsilon. \qquad (6)$$

These values are easily computed by assuming at the crossing of H^*, a Boltzmann distribution for the three lower levels, conservation of the total number of atoms, and conservation of energy. This effect has been actually checked experimentally.[11,12] If, starting from a high field where the two electronic transitions $a' \leftrightarrow a$ and $b' \leftrightarrow b$ can be observed, one lowers the field to any value above H^* and then comes back to observe the resonance, the intensities of the two lines are, respectively, proportional to $a-a'$ and to $b-b'$ and thus equal. After the crossing of H^*, however, the intensities of the two lines become proportional to a_1-a_1' and b_1-b_1' and are in the ratio 7/3. Further details on the behavior of impurity atoms can be found in reference 11.

(b) *Crystals with two species of spins.*—As another example of a spin system where the spin-spin inter-

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[11] See A. Abragam and J. Combrisson, Suppl. Nuovo cimento, **6**, No. 3, 1197 (1957) where further references are given.

[12] G. Feher (private communication).

actions are unable to establish a temperature, we consider a substance such as LiF where the nuclear spins of Li^7 and F^{19} have different Larmor frequencies. The usual way to look at it is to consider it as two different systems, the system Li^7 and the system F^{19} (or three systems if the small admixture of Li^6 is not neglected). For each of these systems the levels in high field are equidistant and a spin temperature can be defined which, however, need not be the same for both systems since energy cannot be transferred from one to the other. Thus, raising the temperature of the fluorine system by saturating the resonance of F^{19}, or even making it negative by a rapid passage, will not affect the temperature of the lithium system.

It is possible to draw an analogy, somewhat superficial but perhaps enlightening, between the case of LiF and the case of impurity atoms considered previously, by considering a crystal of Li^7F^{19} (neglecting for simplicity Li^6) as a statistical ensemble of identical systems of a single species. The individual system described by the Hamiltonian $\mathcal{H}_i^0$ is a Li^7 spin *plus* a F^{19} spin associated with it by a constant but otherwise arbitrary lattice vector. The eight energy levels of such a system are given by the formulas:

$$E(m,m')=\hbar H(\gamma_F m+\gamma_{Li} m'),$$

where $m=\pm\frac{1}{2}$ and $m'=\pm\frac{1}{2}, \pm\frac{3}{2}$.

Although not equidistant, they vary linearly with the field and therefore have properties intermediate between those of the Zeeman levels of a single species and those of impurity atoms. If a Boltzmann distribution exists for a given value of the applied field for the 8 levels of our individual systems, it keeps that form as the field varies. On the other hand, if it is *not* of the Boltzmann form, spin-spin interactions cannot bring it to that form. All this is of course also evident by considering Li^7 and F^{19} (and also Li^6) as different systems.

(D) *Conclusion For the High-Field Case*

To conclude, it can be said that in the high-field case, spin temperature is a convenient notion, whose utilization is made possible by the special structure (equidistance) of Zeeman levels. The corresponding formalism is developed in detail by Ramsey[8] with special emphasis on negative temperatures. It must be recognized, however, that in the high-field case the concept of spin temperature, positive or negative, is not indispensable, and that most, if not all of the experimental results could be formulated without making use of it. For instance, if a spin system has been polarized in a field H_0 by contact with a lattice at a temperature T_0 its magnetic moment according to Curie's law is: $M_0=CH_0/T_0$. If then the field is changed adiabatically to a value $H\neq H_0$, the value of the magnetic moment will be $M=CH/T$ where T is the new spin temperature different from T_0. However, since $H\propto T$, $H/T=H_0/T_0$ and $M=M_0$. This could evidently be stated immediately without bothering with spin temperature at all, simply by noticing that in the high-field region the magnetic moment is an adiabatic invariant.

(2) Low-Field Case

(A) *The Gibbs Approach*

It is clear from the previous paragraph that for Zeeman systems, lowering the field from a value H_0 to $H<H_0$ and coming back to H_0 in a time $\tau\ll T_1$, is a reversible operation [as can be checked by measuring $M(H_0)$ by a resonance experiment before and after changing the field], as long as $H\gg H_{\text{local}}$. The obvious question now is what happens if $H\leq H_{\text{loc}}$, in particular if $H=0$. By extrapolating from the high-field case, the following argument may seem plausible: as long as $H\gg H_{\text{loc}}$, because of conservation of energy, the only transitions induced by the spin-spin interactions are opposite flip-flops of neighboring spins which do not change the total magnetic moment M_0. On the other hand, when the applied field falls well below the local field, two neighboring spins can under go all the transitions for which matrix elements exist in their dipole-dipole interactions: flip of a single spin, flip of both spins in the same direction, unprevented now by conservation of energy. One would thus expect a complete disorientation of all the spins and no nuclear resonance signal upon coming back into high field. The passage through zero field would be irreversible.

This argument is certainly wrong for it is in contradiction with experiment. Pound[5] has shown that in a crystal of LiF (T_1 of $Li^7\sim 5$ min) the nuclear resonance signal of Li^7 was unaffected within experimental error if the sample was taken out of the magnet gap into the earth's field for a second or two. Furthermore, Purcell and Pound[6] have shown that even if in the high field H_0 the nuclear magnetization was antiparallel to the field (which was realized by them by reversing the field in a time of a fraction of a microsecond, much shorter than T_2, but which can also be done by a rapid passage or a 180° pulse) the passage through zero field was a reversible operation at the end of which the polarization in high field was still opposite to the field as attested by the sign of the nuclear resonance signal.

The main weakness of the argument which led us to a wrong conclusion resides in an incorrect description of the spin system in low fields. When the interaction $\mathcal{H}^1$ between the spins becomes comparable to $\mathcal{H}^0$, the concept of energy levels of individual spins becomes meaningless and one must speak in terms of energy levels and eigenstates of the whole sample. A statistical description is still possible provided one gives up the Boltzmann-Maxwell point of view to take the Gibbs approach where the macroscopic sample is not any more a statistical ensemble of identical systems (individual spins) but one element of a statistical ensemble representative of its properties. Such a description is by no means restricted to spin systems but has to be used whenever, instead of weakly coupled systems, such as gas molecules, one deals with systems with tight coupling between their constituents such as crystals.

(*B*) *Interpretation of the Work of Pound and Purcell*

To explain their experimental results Pound[5] and Pound and Purcell[6] speak of a spin temperature, positive or negative as the case may be. Unfortunately, although they emphasize the importance of the reversibility of the passage through zero field for the validity of the concept of spin temperature, their discussion is very brief and has led to conflicting interpretations. Thus Purcell[13] himself describes the reversible passage through the earth field as follows:

> "… the transfer from the strong field out to the earth field and back again took place slowly compared to the nuclear precession frequency and therefore *adiabatically*—and here I use the word in the Ehrenfest sense—so that the net magnetization followed the field in direction and returned parallel as it began."

A possible interpretation of this statement can be formulated mathematically as follows: the total Hamiltonian of the spin system, which contains the applied field H as parameter: $\mathcal{H}(H)=\mathcal{H}^0(H)+\mathcal{H}^1$, has, for each value of H, eigenstates $\xi_k(H)$ and eigenvalues $E_k(H)$ which vary continuously as H is changed and which can be calculated in principle if not in practice. The description of the transformation as adiabatic in the Ehrenfest sense can be taken to mean that while the eigenstates and eigenvalues of $\mathcal{H}(H)$ change with the field, their populations remain unchanged. In an operator notation, if we call $\rho(H_0)$ the density matrix assumed to commute with $\mathcal{H}(H_0)$, describing the spin system in the field H_0, and $U(H,H_0)$ the unitary operator which connects $\xi_k(H)$ and $\xi_k(H_0)$ through $\xi_k(H)=U(H,H_0)\xi_k(H_0)$, the density matrix in the field H, $\rho(H)$, is related to $\rho(H_0)$ by

$$\rho(H)=U\rho(H_0)U^{-1}. \tag{7}$$

The assumption of an Ehrenfest adiabatic passage obviously explains the complete reversibility observed in the experiments of Pound and Pound and Purcell and there is nothing in their experimental results to contradict this interpretation. However, as was already pointed out previously, this assumption is incompatible with the existence of a spin temperature. The precise meaning of the latter assumption is that, as the applied field is changed, the state of the system is constantly described by a density matrix:

$$\rho(H)=A\exp\{-\mathcal{H}(H)/kT(H)\}, \tag{8}$$

where the parameter $T(H)$ is precisely the spin temperature. It is clear that, except for the high-field case, (7) and (8) are incompatible. Both assumptions explain the results of Pound and Purcell and further experimental results are needed to decide which one of them, if either, is valid.

From the theoretical point of view, it is very doubtful that for a large system with a quasicontinuous spectrum such as a macroscopic spin system in a weak field, the variation of the applied field H will ever be sufficiently slow in time for the conditions described in standard textbooks,[14,15] as necessary for an adiabatic passage, to be realized. Further discussion of this point would be rather academic for experiment does show that the reversible passage of a spin system through zero (or earth) field is *not* an adiabatic Ehrenfest passage. Such a passage would evidently be reversible whether the initial distribution was of the Boltzmann type or not, and experiments to be described later, where the latter was the case, showed irreversibility in the passage through the earth field.

(*C*) *Consequences of the Assumption of a Spin Temperature*

We now assume that when we change the applied field H, the state of the spin system is correctly described by a temperature, that is by the density matrix (8). This assumption enables us to calculate, at least in principle, all the observable quantities connected with the spin system, provided we know the dependence of the spin temperature $T(H)$ on H. This is easily obtained by writing that the transformation is isentropic: for a change dH of the field, the work dW done by the applied field on the system is equal to the change dU of its internal energy. Since $U=\langle\mathcal{H}\rangle=\mathrm{Tr}\{\rho\mathcal{H}\}$ and $dW=-\langle M_z\rangle dH=-\mathrm{Tr}\{\rho M_z\}dH$, this can be written:

$$\frac{d}{dH}\mathrm{Tr}\{\rho\mathcal{H}\}=-\mathrm{Tr}\{\rho M_z\}, \tag{9}$$

where

$$\rho=\exp\{-\mathcal{H}(H)/kT(H)\}/\mathrm{Tr}\{\exp[-\mathcal{H}(H)/kT(H)]\},$$

$$\mathcal{H}(H)=\mathcal{H}^0(H)+\mathcal{H}^1=-HM_z+\mathcal{H}^1,$$

$$M_z=\hbar\sum_i \gamma_i I_i^z,$$

$$\mathcal{H}^1=\hbar^2\sum_{i<k}\gamma_i\gamma_k r_{ik}^{-3}[(\mathbf{I}_i\cdot\mathbf{I}_k)-3(\mathbf{I}_i\cdot\mathbf{r}_{ik})(\mathbf{I}_k\cdot\mathbf{r}_{ik})r_{ik}^{-2}].$$

The solution of (9) is easily obtained in the case of high temperatures when it is permissible to use a linear expansion of the exponential, which is legitimate in all the experiments to be described here. Making use of the relations:

$$\mathrm{Tr}\{\mathcal{H}^0\}=\mathrm{Tr}\{\mathcal{H}^1\}=\mathrm{Tr}\{\mathcal{H}^0\mathcal{H}^1\}=0,$$

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[13] E. M. Purcell, Physica 17, 282 (1951).

[14] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 207.

[15] R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, New York, 1938), p. 409.

we get

$$\frac{d}{dH}\left\{\frac{1}{kT(H)}\operatorname{Tr}\{H^2M_z^2+(\mathcal{H}^1)^2\}\right\}=\frac{H}{kT(H)}\operatorname{Tr}\{M_z^2\},$$

or

$$dT/T=HdH/(H^2+H_L^2), \tag{10}$$

where H_L is the local field defined by

$$H_L^2=\operatorname{Tr}\{(\mathcal{H}^1)^2\}/\operatorname{Tr}\{M_z^2\}. \tag{10$'$}$$

Equation (10) integrates to

$$\frac{T}{T_0}=\left[\frac{H^2+H_L^2}{H_0^2+H_L^2}\right]^{\frac{1}{2}}. \tag{11}$$

From (11) we can calculate the final spin temperature in the earth's field, in Pound's experiments[5]: H_L, calculated in Appendix II, is for LiF 7.77 gauss, H_0 is 6376 gauss, H^2 the square of the earth's field is negligible compared to H_L^2, itself negligible compared to H_0^2:

$$T=T_0H_L/H_0=(300\times 7.77)/6376=0.37°\text{K}. \tag{11$'$}$$

Equation (11) also enables us to calculate the magnetic moment reached in any field H, in particular in a large field H where it can be measured by a resonance experiment, after the spin system has been polarized in a low field H_0 by thermal contact with a lattice at a temperature T_0:

$$\langle M_z(H)\rangle=\frac{CH}{T}=\frac{CH}{T_0}\frac{[H_0^2+H_L^2]^{\frac{1}{2}}}{[H^2+H_L^2]^{\frac{1}{2}}}, \tag{12}$$

$$C=\operatorname{Tr}\{M_z^2\}/k\operatorname{Tr}\{1\}.$$

If $H^2\gg H_L^2$, then

$$\langle M_z(H)\rangle=C[H_0^2+H_L^2]^{\frac{1}{2}}/T_0. \tag{13}$$

This suggests a rather fundamental experiment designed to prove the identity of spin temperature and thermodynamic temperature.

Let us suppose that we demagnetize into zero field a spin system which has been allowed to come into equilibrium with a lattice at 300°K in a field:

$$H_0=H_L(300/2)=1165 \text{ gauss for LiF}.$$

From Pound's experiment we know that some kind of order must exist in this spin system when it is in zero field, since upon being brought back into H_0 it has the same magnetic moment as before demagnetization. If we are to believe the assumption of a spin temperature, this order is adequately described by a spin temperature which from (11′) should be $T_S=2°\text{K}$. It is easy, however, to produce a situation where the spin system is indeed describable by a genuine thermodynamic temperature of 2°K by letting it come into equilibrium in zero field with a cold lattice at 2°K. The identity of the two temperatures would then be demonstrated by a nuclear resonance experiment at a fixed frequency showing that one gets the same signal from a sample brought to equilibrium in zero field at 2°K, and from a sample polarized in a field $H_L(300/2)$, at 300°K.

Actually, because of the unavoidable change of gain of the apparatus performing experiments at two different lattice temperatures one would get, if the assumption of spin temperature is correct,

$$S(2°,0)=\lambda S(300°,\, H_L\times 300/2), \tag{14}$$

where $S(T,H_0)$ is the signal obtained at a fixed frequency from a spin system prepared by a long contact with a lattice at temperature T in a field H_0 and λ is the change in the gain of the apparatus going from 300°K to 2°K. λ is easily eliminated by making an extra measurement at 2°K polarizing in a field $H_1\gg H_L$, say $H_1\sim 50$ gauss. Since both H_1 and H_0 are in the high-field region where the magnetic moment is an adiabatic invariant, we *know* that

$$S(2°,H_1)=\lambda(300/2)H_1/(H_L\times 300/2)$$
$$\times S(300°,\, H_L\times 300/2)=\lambda S(300°,\, H_L\times 300/2)H_1/H_L.$$

In order to prove (14), it is then sufficient to verify that

$$S(2°,0)=(H_L/H_1)S(2°,H_1). \tag{15}$$

In this way no measurements have to be made at room temperature at all. It is still better to check the general relation (13):

$$S(2°,H_0)\propto[H_0^2+H_L^2]^{\frac{1}{2}}, \tag{15$'$}$$

of which (15) is a special case, by plotting the curve $S(H_0)$. The experiment to be described later shows that the spin temperature assumption is correct.

Finally it can be remarked that in 1932 Waller[16] had shown by a perturbation method that if a system of spins, in thermal equilibrium at a temperature T_0 in zero field, was brought into a small field $H\ll H_L$, its equilibrium magnetic moment was $M=CH/T_0$.

Waller's restriction of small fields can be lifted now and (13) shows that the maximum magnetic moment obtainable in a large field starting from the same initial conditions is $M=CH_L/T_0$.

(*D*) *Validity of the Assumption of a Spin Temperature*

Since, as will be seen later, the assumption of a spin temperature describes correctly the behavior of a Zeeman spin system when the applied field is varied all the way down to zero, it is interesting to inquire whether it was to be expected and why. This is a difficult problem and only a very qualitative discussion will be given. In order to get a unified description of the spin system we shall use the global Gibbs approach throughout, even though in the high-field region the Maxwell-Boltzmann picture of a statistical ensemble of individual, loosely coupled, spins is simpler.

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[16] I. Waller, Z. Physik **79**, 370 (1932).

Statistical mechanics teaches us that a necessary condition for a large system to be able to come into thermal equilibrium starting from a nonequilibrium situation or to remain in thermal equilibrium when some external parameter is slowly varied, is that the total energy of the system be the only constant of motion (good quantum number in quantum statistics). Such a system is called ergodic in statistical mechanics.

In practice the problem is complicated by the existence of *approximate* constants of motion. Let us take as an example the system S of spins $I=1$ with a nonvanishing zero-field quadrupole splitting, coupled together through dipole-dipole interactions:

$$\mathcal{H}=\mathcal{H}^0+\mathcal{H}^1,\quad \mathcal{H}^0=\sum_i\mathcal{H}_i^0,\quad \mathcal{H}^1=\sum_{i<k}\mathcal{H}_{ik}^1,$$
$$\mathcal{H}_i^0=a(I_i^z)^2-\gamma\hbar H I_i^z.$$

Using the individual-spins picture, we have already pointed out that because of the unequal spacings of the levels, their populations P_m were unaffected by spin-spin interactions and remained constant in time. The population of, say, the level $I_z=0$, is the expectation value, taken over the wave function of the whole sample, of the operator: $\mathcal{P}_0=N^{-1}\sum_i[1-(I_i^z)^2]$. Therefore $\mathcal{P}_0$ is a constant of motion for the system S in spite of the fact that it obviously does not commute with $\mathcal{H}^1$ and is not rigorously a good quantum number. The system S might possibly come into thermal equilibrium starting from a nonequilibrlium situation, after a very long time but this is an academic problem. Over the duration of our experiments the operators $\mathcal{P}_m$ *are* constants of motion and S is *not* an ergodic system.

Let us consider now a Zeeman spin system S_0 with a single species of spins. In the low field region it is reasonable to assume that it is an ergodic system without any approximate constants of motion. In the high-field range, because of the nature of the Zeeman splittings, the populations operators $\mathcal{P}_m$ are not even approximate constants of motion. There remains, however, one approximate constant of motion different from the total energy, which is the Zeeman energy $\mathcal{H}^0$. A process in which $\langle\mathcal{H}^0\rangle$ would, say, decrease and $\langle\mathcal{H}^1\rangle$ increase, although not rigorously forbidden, would be extremely slow. Thus S_0 would not be an ergodic system on our experimental time scale but for the fact that, $\langle\mathcal{H}^0\rangle$ being much larger than $\langle\mathcal{H}^1\rangle$, one can say with a good accuracy that $\mathcal{H}^0$ is in fact the total energy and therefore S_0 *is* ergodic.

As H is decreased two things happen: $\langle\mathcal{H}^0\rangle$ becomes smaller and it is less and less correct to consider it as the total energy of the system, but on the other hand the time over which $\mathcal{H}^0$ may be considered as a constant of motion becomes shorter and transfer of energy between $\mathcal{H}^0$ and $\mathcal{H}^1$ becomes faster.

If the critical value H^* of the field, for which the transfer of energy between $\mathcal{H}^0$ and $\mathcal{H}^1$ becomes fast compared to the rate of change of the field, is still large compared to H_L, the system is approximately ergodic through the whole range of H and the demagnetization is a reversible isentropic process, its small irreversibility being of the order of H_L^2/H^{*2}. Since within experimental error the process is reversible, $H^*\gg H_L$.

(E) *Zeeman System With More Than One Spin Species*

The behavior of a Zeeman spin system with two species of spins such as LiF provides an example for the previous discussion. In the low-field range it can be assumed that the total energy is the only constant of motion and that the system is ergodic: as evidence to that effect we may quote the identity of the spin lattice relaxation times of Li^7 and F^{19}, and the audio-frequency experiments of Pound and Ramsey[7] whereby in a field of 42 gauss the application of an audiofrequency field at the Larmor frequency of F^{19} affected the nuclear resonance signal of Li^7, observed subsequently in a high field. It should be emphasized however that these results by themselves demonstrate only the existence of a strong coupling between the nuclear spins of Li^7 and F^{19} in a low field. Further quantitative experimental results, to be given later, are required before concluding that thermal equilibrium exists between the two species.

On the contrary, in a high field there are two distinct approximate constants of motion which are the Zeeman energies $\mathcal{H}^{0\prime}=-\gamma'\hbar H_0 I_z'$ and $\mathcal{H}^{0\prime\prime}=-\gamma''\hbar H_0 I_z''$ of both species of spins (there are three species if Li^6 is taken into account). Therefore the total spin system is *not* ergodic and the demagnetization should be an irreversible process except for special initial conditions. Just as in the case of one species, it is permissible in a high field to consider Li^7 and F^{19} as two distinct ergodic systems each with a temperature of its own. The fact that one does not know how to handle the lithium-fluorine interaction and what temperature, if any, should be assigned to it, is not disturbing for this interaction is very small compared to the Zeeman energies of both systems.

By the mixing field we shall mean the field H^* at which the rate of exchange of energy between Zeeman energy and spin-spin interaction (and thus also between the Zeeman energies of the two species) becomes fast compared to the rate of change of the applied field. If H^* is large compared to the local field, the whole process of demagnetization can be described simply by assuming that above the mixing field we have two distinct spin systems with energies $\mathcal{H}^{0\prime}=-\gamma'\hbar H_0 I_z'$ and $\mathcal{H}^{0\prime\prime}=-\gamma''\hbar H_0 I_z''$ describable by temperatures T' and T'' and that below H^* we have a simple Boltzmann system with a Hamiltonian $\mathcal{H}=\mathcal{H}^{0\prime}+\mathcal{H}^{0\prime\prime}+\mathcal{H}^{1\prime}+\mathcal{H}^{1\prime\prime}+\mathcal{H}^2$, where $\mathcal{H}^{1\prime}$, $\mathcal{H}^{1\prime\prime}$ and $\mathcal{H}^2$ are respectively the $\mathrm{Li}^7-\mathrm{Li}^7$, $\mathrm{F}^{19}-\mathrm{F}^{19}$, and $\mathrm{Li}^7-\mathrm{F}^{19}$ interactions. Once the mixing is accomplished, the subsequent behavior of the spin system is reversible as if it were a single ergodic system at a temperature T. If one includes Li^6, the generalization is obvious.

Starting the demagnetization process at a field H_0 with initial temperatures T_i' and T_i'' for both systems, one arrives at the field H^* with temperatures

$$T'=T_i'H^*/H_0 \quad \text{and} \quad T''=T_i''H^*/H_0.$$

After the mixing, the new temperature T is obtained by writing that the total energy, or, since $H^*\gg H_L$, the expectation value of the Zeeman energy, is conserved.

$$\langle\mathcal{H}^{0'}\rangle+\langle\mathcal{H}^{0''}\rangle\simeq\langle\mathcal{H}\rangle,$$

$$\frac{1}{T'}\operatorname{Tr}\{(\mathcal{H}^{0'})^2\}+\frac{1}{T''}\operatorname{Tr}\{(\mathcal{H}^{0''})^2\}\simeq\frac{1}{T}\operatorname{Tr}\{(\mathcal{H}^{0'})^2+(\mathcal{H}^{0''})^2\},$$

$$\frac{1}{T}=\frac{(N'/T')\gamma'^2I'(I'+1)+(N''/T'')\gamma''^2I''(I''+1)}{N'\gamma'^2I'(I'+1)+N''\gamma''^2I''(I''+1)}, \tag{16}$$

where N' and N'' are the numbers of spins of each species. N' and N'' may be replaced, respectively, by the isotopic abundances p' and p''. Defining μ by

$$\mu=p''\gamma''I''(I''+1)/p'\gamma'I'(I'+1),$$

we have

$$\frac{1}{T}=\left(\frac{1}{T'}+\frac{\mu}{T''}\right)\bigg/(1+\mu)$$

$$=\frac{H_0}{H^*}\left(\frac{1}{T_i'}+\frac{\mu}{T_i''}\right)\bigg/(1+\mu). \tag{16$'$}$$

If we raise the field back to H_0, the common temperature of the total spin system will be $T_1=TH_0/H^*$, given by

$$1/T_1=(H^*/H_0)/T=(1/T_i'+\mu/T_i'')/(1+\mu). \tag{17}$$

If before demagnetization the magnetic moments of the two systems were $M_i'=C'H_0/T_i'$, $M_i''=C''H_0/T_i''$, with $C''/C'=\mu$, then after demagnetization they become $M'=C'H_0/T_1$, $M''=C''H_0/T_1$, or

$$\begin{aligned}M'&=(M_i'+M_i'')/(1+\mu),\\ M''&=\mu(M_i'+M_i'')/(1+\mu).\end{aligned} \tag{18}$$

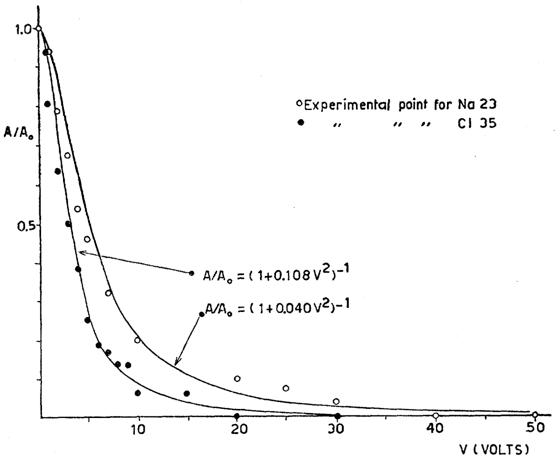

FIG. 2. The attenuation of the magnetization of Na^{23} and Cl^{35} in NaCl in a strong magnetic field as a function of the voltage applied to the attached quartz transducer providing ultrasonic waves at twice the Larmor frequency.

The formulas (17) and (18) call for the following comments:

(*a*) The exact value of the mixing field H^* does not appear in these formulas which are valid provided $H^*\gg H_L$. It may be inferred from this that their validity is more general than that of the very crude model used to establish them and that they might be correct even if the mixing takes place over a range of fields, provided that when it is terminated the Zeeman energy is still much larger than the spin-spin energy.

(*b*) If to start, the two spin systems are at the same temperature $T_i'=T_i''=T_i$ the demagnetization process is reversible just as for a single species and the final temperature T_1 is equal to T_i as demonstrated by (17).

(*c*) The two spin systems can both have negative temperatures since their energies have an upper bound[13] and it is possible to make calorimetry experiments where positive and negative temperatures are exactly on the same footing. Thus it is possible for the equilibrium temperature to be negative after mixing, which is impossible in case of thermal contact between a spin system and a lattice.[8]

(*d*) The confirmation by experiment of (17) and (18) demonstrates conclusively, as mentioned previously, that the demagnetization into low fields is *not* an adiabatic passage in the Ehrenfest sense.

(*F*) *The Dynamics of Isentropic Demagnetization*

The discussion of the previous two sections has led us to the conclusion that, provided the dc field is varied at a sufficiently slow rate (although fast on the T_1 time scale) the behavior of the spin system should be, depending on the initial conditions, either reversible or irreversible, as described by the formula (18). We shall not attempt a quantitative discussion of the difficult problem of the dynamics of the process which for example provides an explanation of the variation of the mixing time with the applied field but will be content to state an approximate criterion for the rate of change of the dc field.

In order for the spin system to be constantly in equilibrium with itself as the dc field changes, we require that the transition probability per unit time of a spin in the local field H_{loc}, $W\simeq\gamma H_{\text{loc}}$, be large compared to the inverse of the time $\theta=H_{\text{loc}}/(dH/dt)$ required to sweep through the width of the spin energy level. This gives the criterion

$$(dH/dt)\ll\gamma(H_{\text{loc}})^2. \tag{19}$$

This criterion is admittedly very crude for neither the definition of H_{loc}, nor the value of γ when more than one species of spins is present, is clearly specified.

If we use tentatively in (19) for H_{loc}^2 the value 60.6 gauss^2 computed for LiF in zero field, the right-hand side of (19) is of the order of 1.5×10^6 gauss/sec for F^{19}, 0.6×10^6 for Li^7 and 0.2×10^6 for Li^6. In spite of the scatter of these values they all lie between 10 000 gauss/sec which was the maximum rate of change of the dc field in our experiment, where the transformation was isentropic, and 10^9 gauss/sec which corresponded to the definitely nonequilibrium reversal of a field of 100 gauss in 0.2 μsec in the experiment of Pound and Purcell on negative temperatures.[6]

Undoubtedly more theoretical work along the lines of Waller's paper[16] is required to get a quantitative description of the dynamics of the process.

EXPERIMENTS

(A) The Experiments at Room Temperature

A variety of experiments performed at room temperature emphasize some aspects of the nature of spin temperature. One of these, the ultrasonic experiment mentioned above in paragraph 1(B), illustrates the role of the spin-spin interactions in establishing and maintaining a Boltzmann distribution between the populations of a spin system with three or more energy levels. The other experiments, some of which have been described briefly earlier,[10] demonstrate the thermal mixing of two spin systems and will be described again in greater detail below.

(*a*) *The Ultrasonic Experiment*

An experiment, differing in its physical form only in unessential features from that described by Proctor and Robinson,[17] has been performed again on Na^{23} and Cl^{35} in a single crystal of NaCl, with the simple difference that more ultrasonic power was available. As in that experiment, ultrasonic waves, supplied to the NaCl crystal at twice the Larmor frequency, caused pure quadrupole transitions between those levels related by $\Delta m=2$. The populations of the four equally spaced levels of these nuclei in a magnetic field were then inferred by examination, using ordinary pulsed techniques, of the magnetization $\langle I_z\rangle$ immediately after exposure to ultrasonic waves.

As the analysis in reference 17 shows, ultrasonic waves cannot cause the complete saturation of the magnetic energy levels which were considered to be connected only by either (a) pure magnetic dipole or (b) pure electric quadrupole relaxation processes. [A further analysis of the same nature, shows that for an arbitrary mixture of the two processes (a) and (b), values of the limiting magnetization for intense ultrasonic waves, lie intermediate to the two pure cases.] We have, however, been able to increase the energy density of ultrasonic waves in the crystal to such an extent that the polarization disappears completely. This result is to be expected if one also takes into account in the differential equations which describe the level populations the spin-spin interactions which lead to a Boltzmann distribution in a time $\sim T_2$. A simple derivation of this result is given in Appendix I.

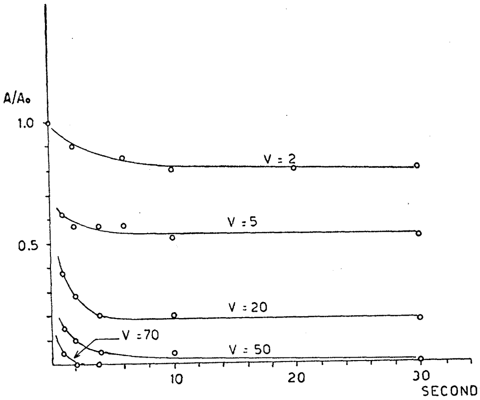

FIG. 3. Attenuation of the polarization of Na^{23} as a function of time, measured from the beginning of the ultrasonic pulse, for different voltages applied to the quartz transducer.

The expression (A4) of Appendix I for the relative polarization is plotted in Fig. 2 along with the experimental points for Na and Cl. The transition probability W required by Eq. (4) goes as the energy density of ultrasonic waves in the crystal, and hence as the square of the voltage applied to the quartz transducer. Meaningful data concerning the ratio of the electric perturbations caused by the ultrasonic distortion for Cl^{35} to Na^{23} are immediately available from Fig. 2 but that will not be discussed further here. Although the agreement is satisfying, it is not conclusive, since one must judge, whether the asymptotic polarization is rigorously zero or only (1/25) M_0, as the pure dipole relaxation case requires. However, there remains yet another criterion: the time dependence of the saturation. The primitive theory, which neglects the spin-spin coupling, leads, as one can readily understand, to a time dependence which is characterized by two time constants. For example, for high values of W, one would expect a rapid attenuation with a time constant $1/(2W)$ to an asymptote $M/M_0=0.2$, which value can be calculated by ignoring all relaxation processes. The attenuation would then be carried below this level at a rate given by T_1 since it is the thermal relaxation processes which would be responsible for the difference of the final asymptotic value from 0.2. However, the correct time dependence for the saturation is easily obtained from formula (A2) and one finds that the approach to the limiting value is characterized by a single time constant $(T_1^{-1}+8W/5)^{-1}$. Figure 3 shows the approach to the limiting polarization for various voltages applied to the ultrasonic crystal; the rapid saturation of the levels for high voltages in times much shorter than T_1 removes any remaining question in this respect.

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[17] W. G. Proctor and W. A. Robinson, Phys. Rev. **104**, 1344 (1956).

(*b*) *Experiments With Thermal Mixing*

As has been pointed out above, the experiment of Pound[5] demonstrates that some order must exist in the spin system when the sample has been removed to zero field, since upon replacing it, in the strong field, the original polarization is obtained again. We have been able to show, in our experiment at low temperature, that this order is the same as that obtained by thermal contact with a cold lattice. Hence it is not surprising that the experiments to be described below show that it is possible for one spin system to communicate this order to another.

Our mixing experiments have in general been performed using LiF as a sample material. At room temperature, our sample showed a thermal relaxation time of 1.4 min for F, and 4.5 min for Li^7; in zero field, the relaxation time of the common spin system was only 6 seconds. The two species (we are ignoring Li^6 for the time being) could be prepared in any one of three well-known states, namely those characterized by polarizations of M_0, 0 and $-M_0$. M_0 was of course obtained by simply allowing the species in question to rest several relaxation times in a strong field, which, in our experiments, was always the resonance field for 8 Mc/sec. $-M_0$ was obtained by reversing the polarization by fast passage. A polarization of zero was best obtained by saturating the species in question by modulating the field over the resonance value, using the same value of H_1 as in the fast-passage polarization reversals; since the reversals were not complete, several seconds of modulation at 40 cps would destroy the polarization.

With two species in the desired states, the process of mixing was performed by removing the crystal from the spectrometer probe located between the poles of the electromagnet to a distance of about one meter from the gap and then restoring it to the probe. This operation required about one second. The two spin systems, isolated from each other by the different spacing of their energy levels in a strong field, lose their identities in weak or zero fields, and find, in a time T_2, a common temperature. Subsequent examination always showed polarizations characteristic of a common spin temperature after mixing.

Our experiments are summarized in Table I. The first two columns show the initial states, relative to M_0, for the species in question; the last two columns show the final states, again measured relative to their respective equilibrium polarizations, after mixing.

TABLE I. Summary of nuclear calorimetric experiments at room temperature. The observed values, averages of several measurements, are reproducible to about 10%.

Expt.	(M/M_0) before mixing Fluorine	 Lithium	(M/M_0) after mixing Fluorine	 Lithium
(a)	1	1	0.95	0.95
(b)	1	0	0.42	0.51
(c)	0	1	0.42	0.43
(d)	1	−1	0.27	0.20
(e)	−1	1	0.05	0.00
(f)	0	−1	−0.16	−0.17
(g)	−1	0	−0.29	−0.34
(h)	−1	−1	−0.71	−0.73

Since the spin temperature after mixing is the same for each species, it is clear that the ratio M/M_0, of the polarization to the equilibrium polarization must be the same for each. We have consequently expressed the experimental results in Table I in this fashion, so that an appraisal of the experiments may be most rapidly made. Experiments (a) and (h) will be recognized as the reversible processes observed by Pound, and by Pound and Purcell, and appear here as the special case of the mixing together of two systems at the same temperature. Experiments (d) through (g) are believed to be the first examples of "calorimetry" carried out with one of the systems initially in a negative temperature state. The discussion in paragraph (2*E*) leads easily to an extension of formulas (17) and (18), which will include more than two nuclear species. They become

$$T^{-1}=\textstyle\sum_j(C^j/T_i^j)/\sum_j C^j, \tag{17'}$$

$$M^k=C^k\textstyle\sum_j M_i^j/\sum_j C^j. \tag{18'}$$

Equation (17′) resembles the expression for the computation of the common temperature in ordinary calorimetry, except that here the temperature appears inversely. Hence $C^j=p^jI^j(I^j+1)(\gamma^j)^2$ may, by this analogy, be called the "spin specific heat."

Equation (18′) restates (17′) in terms of the observable polarizations M^k. Introducing $m=M/M_0$, Eq. (18′) takes the form

$$m^{\text{any species }k}=\textstyle\sum_j m_i^jC^j/\sum_j C^j, \tag{18''}$$

which will have to be used in order to be able to examine the results presented in Table I more critically. We shall need the various spin "specific heats"; thus

$$C(\mathrm{F}^{19})=(1.00)(4005.5\times 2\pi)^2(\tfrac{1}{2})(\tfrac{3}{2})=471\times 10^6,$$

and similarly $C(\mathrm{Li}^7)=374\times 10^6$ and $C(\mathrm{Li}^6)=2.3\times 10^6$. One observes immediately that $C(\mathrm{Li}^6)$ is negligible; hence

$$m^{\mathrm{Li,F}}=0.56m_i^{\mathrm{F}}+0.44m_i^{\mathrm{Li}}. \tag{18'''}$$

Although the accuracy of the data does not justify a serious examination on the basis of Eq. (18‴), one may observe that the polarizations of either species after mixing should be approximately the arithmetic mean of the initial polarizations, with a little extra weight given to the fluorine.

It is principally the relaxation which takes place during the operations forming an experiment which make the data deviate so far from the predictions. In order to lend emphasis to this statement, we would like briefly to describe the course of one "spin calorimetric" experiment, namely experiment (f). In this description, we shall note at various stages the spread of times recorded for a number of rehearsals. We remark that these operations were not performed at once, but required considerable practice. We shall, for brevity, allow H_{Li}^* and H_{F}^* to stand for the resonance fields of Li and F, respectively, at 8 Mc/sec, namely 4840 gauss and 2000 gauss.

Experiment (f) ran as follows: after allowing the sample to polarize for about 20 minutes at a field slightly above H_{Li}^*, the field was dropped suddenly ($t_0=0$) to a value slightly above H_{F}^*. The 40-cps, 5-gauss peak-to-peak modulation was turned on and the field was manually driven through H_{F}^* to a somewhat lower value, observing the destruction of the F polarization enroute (11 to 15 seconds). After turning the modulation off, the sample was removed from the probe for mixing and restored to it (17 to 24 seconds). The u-mode was readjusted; the magnetic field raised through H_{F}^*, reading on the oscilloscope the amplitude of the one-shot F fast-passage signal (25 to 33 seconds). The field was then further raised to H_{Li}^*, reading similarly the amplitude of the Li^7 signal (33 to 46 seconds).

In the units of Table I, the amplitudes of the F and Li signals would ideally be expected to be -0.44. It is not surprising, in view of the relaxation times, to find deviations from this value as large as those observed. Indeed, by assuming suitable average fields and typical intervals for each, the observed values for each species could very nearly be predicted.

It has been assumed, in arriving at the quantitative predictions above, that $H^* \gg H_L$. In seeking to check this inequality, we have not only been able to confirm it, but, where the mixing rate was slow, to measure its rate. Figure 4 shows the amplitude of the Li^7 signal, in experiment (b) measured at 8 Mc/sec, as a function of the time that the sample was held at a poisition in space, located by wooden guides and about 30 cm beyond the rims of the pole shoes, where the field was measured by a commercial field measuring instrument to be 75±10 gauss. The solid curve shows that the mixing rate can be characterized by a time constant $T_m = 6$ seconds, and furthermore that T_1 for the common system is about 100 seconds. At 40 gauss, $T_m=0$ while $T_1=40$ seconds; near zero field, $T_m=0$ while $T_1=6$ seconds.

Experiment (b) of Table I could have been performed with the same outcome, however long the thermal relaxation time of Li^7 in high field. This suggests a possibly useful method of polarizing a nuclear system with a very long thermal relaxation time, that is, it could be "pumped" into a polarized state by cooling it at regular intervals by thermal contact with a system with a shorter T_1. This was strikingly demonstrated by using a powdered sample of CsCl for which $T_1(\mathrm{Cl}^{35})=3.5$ seconds, $T_1(\mathrm{Cs})=9$ minutes, but $T_1(\text{common})=20$ seconds in the earth's field. Commencing with both systems unpolarized, the sample was quickly removed from and restored to the magnetic field at six-second intervals for a total time of two minutes, after which the Cs showed a polarization of $0.7M_0$, which otherwise would have taken about ten minutes to achieve.*

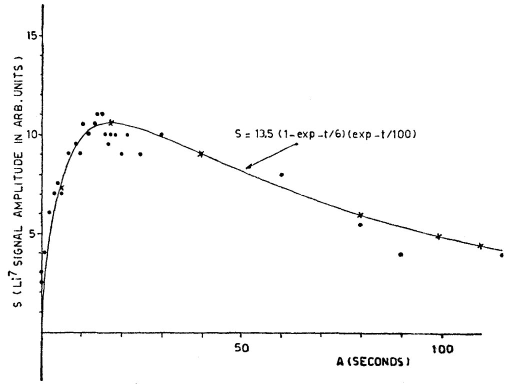

FIG. 4. The observed amplitude of the Li^7 signal *vs* the time that the LiF crystal was held at 75 gauss. The solid line shows how the experimental points can be described by a mixing time constant of 6 seconds and a common relaxation time of 100 seconds.

A second demonstration concerns the polarization of Li^6. It was estimated that the fast passage signal from Li^6 would be visible on the oscilloscope screen if that system could be polarized in a field H_0 of about 12 kilogauss and at the temperature of liquid air, a difficult prospect in view of an estimated relaxation time of one week (see Sec. D below). We found, however, that Li^6 could be polarized into this state by taking only the time to polarize Li^7 and F at 77°K and H_0, and to mix them with Li^6. The Li^6 essentially takes on its whole equilibrium polarization since its specific heat is negligible compared to those of the other two.

Evidence of the very long T_1 which practically precludes the observation of Li^6 by ordinary methods is given by the following experiment. We allowed the LiF sample to rest in the strong field H_0 at 77°K for about 15 minutes. After a quick mixing which returned the sample back at the magnet gap, but not into the liquid air Dewar, we permitted the sample to warm and the magnet itself to be used during the course of the day for other experiments, under the restriction that the field should always remain above several hundred gauss. At the end of the day, about six hours later, the Li^6 signal showed a polarization characteristic of H_0 and 77°K. The same was performed again, but with the change that the polarizations of F and Li^7 were reversed before mixing; we found hours later a polarization of Li^6, characteristic of H_0 and -77°K.

It is interesting to speculate that in favorable cases it may be possible to measure the magnetic moment and the thermal relaxation time of an isotope which is not otherwise observed by measuring its heating effects upon an observed isotope.

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* *Note added in proof.*—An early observation of a similar pump-up effect was made by Holzman, Anderson, and Koth, [Bull. Am. Phys. Soc. Ser. II, 2, 31 (1957)] in fused silica. However the interpretation given by the authors was different.

(B) The Experiments at Low Temperature

This experiment was designed to check the validity of expression (13), given again as (15′). Following the argument which culminates in these expressions, if the fixed frequency signal from the Li^7 spin system, to choose a specific example, in a single crystal of LiF, prepared in thermal equilibrium with its lattice at 2°K in a polarizing field H_0, depends upon the magnitude of H_0 in the manner predicted, the identity of spin and thermodynamic temperature will have been proven.

To check the predicted behavior, laboratory polarizing fields from zero to several times H_L, say up to 50 gauss, were used. The fixed frequency selected for the observations was 8 Mc/sec, or 4840 gauss, chosen simply as a matter of convenience. To make the observations at this field, several hundred times larger than the polarization fields, the measurements had to be made quickly; for such measurements the method of fast passage is ideally suited. The experimental method, idealized, was consequently to permit the sample to reach equilibrium at the chosen weak field, the lattice temperature being 2°K, and then to raise the magnetic field suddenly to a value greater than 4840 gauss, making a fast-passage observation on Li^7, "on the fly."

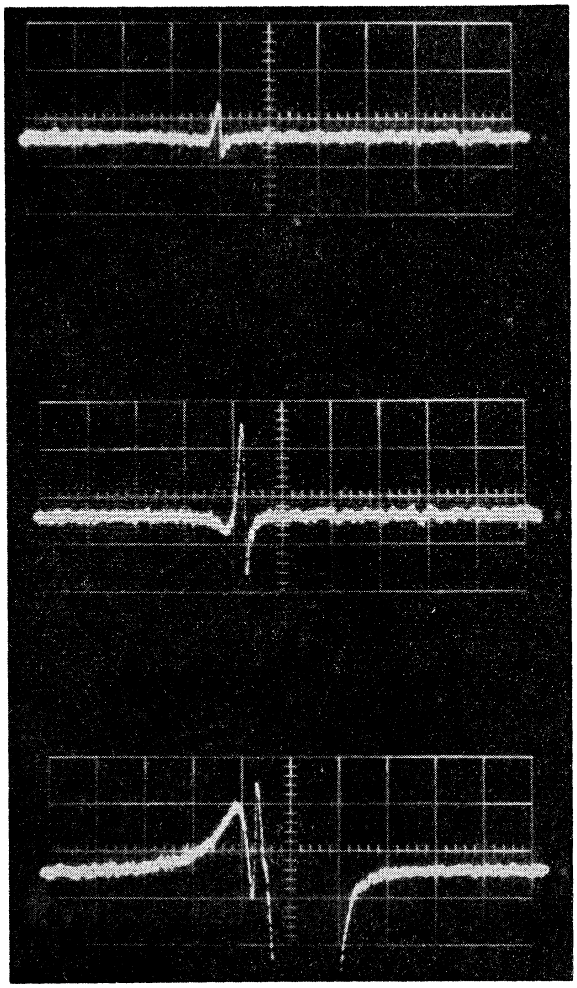

FIG. 5. Three characteristic fast-passage signals: (upper) Li^7, after reaching thermal equilibrium in zero field, (middle) Li^7, after reaching equilibrium in 25 gauss, (lower) F, occurring on the tail of a large proton signal. The trace proceeds from right to left.

In practice, simple as the experiment appears at first glance, there were many experimental difficulties, not all of which will be described below. Indeed, the experiment was only made feasible by the fortunate circumstance of having in our possession a crystal of LiF which possessed, in fields comparable with H_L a relaxation time T_1 of approximately 12 seconds, while at 4800 gauss T_1 was 15 hours. Twelve seconds was short enough to allow the nuclear systems (coupled together) to reach the lattice temperature without exhausting the supply of liquid helium and the experimenters' patience, and yet long enough to measure and thus be reassured that the polarization measured for one low field was characteristic of that field and not some higher field passed through enroute for observation. On the other hand, an extremely long T_1 was required at high fields, since otherwise the growth of the magnetization while the field was at high values for observation, would give corrections which would be large compared to the quantity being measured.

The 15 hours relaxation time, at 4800 gauss and 2°K, although not of direct import for our experiment, could be measured accurately in a short time in the following way. As described below, the equilibrium signal at 50 gauss, where the magnetization could be expected to be linear with field strength, is easily measured, the equilibrium signal being reached in a few minutes. Also, the rate of growth of the signal at 4800 gauss was easily measured: one first permitted the signal to grow to a large value at a field above the resonant field. Then, by reversing the polarization by fast passage in dropping to 4800 gauss, just below resonance, one observed the growth of the signal in pairs of fast passage observations, always returning to 4800 gauss. In this way, (dS/dt), the rate of growth of the signal, can be measured for values near zero signal, and we found 0.1 unit/second, after making a small correction for the incomplete polarization reversals due to the imperfect fast passages. Dividing this value into the value of the signal found at 50 gauss, and multiplying by 4800/50, one learns that for our sample $T_1(Li^7, 4800 \text{ gauss}, 2°K)$ is closely equal to 15 hours.

The measurement of T_1 at low or zero field was, however, more difficult and illustrates the role played by mixing of the spin systems at low fields. One first polarized both species strongly, although by no means completely in a high field, always at 2°K. The direction of the magnet current was then reversed, carrying the laboratory field through zero, so that the two systems would be well mixed, and to a value yielding a field of 2000 gauss where the F^{19} signal was rapidly observed by two fast passages. The magnetic field was then dropped to low or zero field by a practiced maneuver involving another current reversal where it was allowed to rest for a specified time, after which the field was again raised to 2000 gauss to observe the attenuation of the F^{19} polarization for the interval. It is assumed that the rapid excursion of the magnetic field to 2000 gauss for the measurements of the initial signal amplitude did little to change the spin-temperature. By ignoring the step in which the systems were initially mixed, only chaotic results could be obtained. One notes that the relaxation time in low fields could be measured by examining either species; F^{19} was chosen since the magnet current manipulations were simpler.

Since fast-passage observations were to be made, only the *u*-mode signal was available. For this reason we constructed a low-temperature crossed-coil probe which will be described below. A fast-passage observation requires as well a large H_1 which unfortunately entails the generation of heat in the probe. Experiments showed that lattice heating effects were readily observable if the transmitter were on while the magnetic field were at some small value. However, the effects of such heating were made negligible in our experiments by turning on the transmitter only after high fields had been reached, where the long T_1 effectively isolated the spin system from the lattice. The following detailed experimental method was finally evolved:

The sample was allowed to rest in the magnetic field for which the measurement was to be taken, for at least ten relaxation times. The transmitter, for reasons of stability, was in operation, but detuned during this time. At a given warning, the field was raised sharply to 4800 gauss, just under the resonance value, where it rested 15 seconds. During this time, the transmitter was retuned, and the leakage phase adjusted to a *u* mode. At a second warning, the camera shutter was opened, and the field was raised uniformly by a manual control through the resonance field in synchronism with the horizontal trace of the oscilloscope, 5 seconds in duration. The resulting photographic trace of the oscilloscope screen were examined by magnifying glass; unless accidental noise spikes distorted the signal to be measured, the trace was kept for measurement.

Characteristic traces are illustrated in Fig. 5. The signals do not have the characteristic shape of fast passage signals because ac coupling is used in the audio amplification. However, as long as the procedure for observing the signals remained the same, some measure of the magnitude of the signal, whatever its shape, would be a measure of the nuclear polarization. We have arbitrarily used the peak-to-peak measure of the signal for plotting.

Figure 5 (upper) shows the signal observed for zero polarizing field and consequently is of considerable interest in itself. As will be described below, only 13% of the magnitude of this signal can be ascribed to polarization accrued during the high-field observation process. Figure 5 (middle) shows a signal obtained from a polarizing field of 25 gauss.

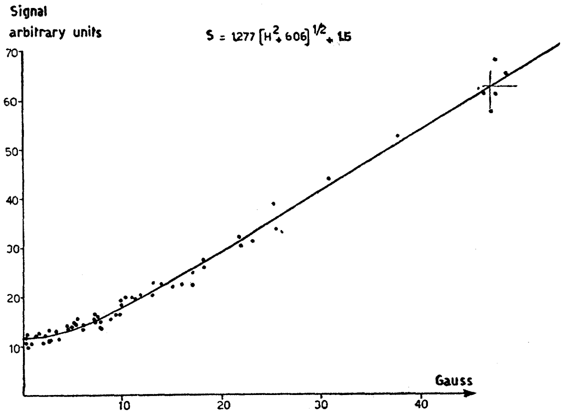

FIG. 6. The fast-passage signal amplitude of Li^7, measured in arbitrary units at 8 Mc/sec, as a function of the magnetic field in which the LiF sample reached equilibrium at 2°K. The smooth curve is given by the analytical expression, arrived at as described in the text.

The experimental results are summarized by the points of Fig. 6. Here the amplitude of the signals observed (actually millimeters on the oscilloscope screen) is given as a function of the field in which the sample reached equilibrium. All the data were taken on the same day using two consecutive helium transfers. Every signal amplitude measured appears in Fig. 6.

From the scatter of points at the lower fields, and from Fig. 5 one may estimate a signal-to-noise ratio. One sees, however, from the scatter of points at the higher fields that the variations in the rapidly operated transmitter and receiver affected the over-all gain seriously.

The magnetic fields appearing as abscissas in the data of Fig. 6 were the residual magnetic fields in the gap of the magnetic after the current had been turned off following a systematic pattern of current reversals. The fields were measured by a large flip-coil which had been calibrated against a smaller flip-coil, the latter having been calibrated in a field measured by proton resonance. Some of the scatter in Fig. 6 may also be due to the relatively inexact way in which the magnetic fields were measured.

The expression (15′) for the signal observed at 4800 gauss may be rewritten as

$$S=k[H^2+H_L^2]^{\frac{1}{2}}+b, \qquad (15'')$$

where now b has been added to describe the additional amplitude picked up at high fields during the rise and 15-sec tuning-times. k is the gain, as explained above, to be measured at a field where the expression (15″) for S is practically linear in H_0.

Since the time of rise of the magnetic field is short, about two seconds, the constant b is given adequately by $b=(15\text{ seconds})\times(dS/dt$ at 4800 gauss$)$. As already described, the latter quantity was measured to be 0.1 unit/second so that $b=1.5$ units.

To set the gain reasonably precisely, six points were measured in the quasi-linear region near 50 gauss and their center of gravity chosen to determine the constant k in (15″). Making allowance for b, we find that $k=1.277$. Upon taking the value for H_L^2 from Appendix 2, (15″) can be written as

$$S=1.277(H^2+60.6)^{\frac{1}{2}}+1.5, \qquad (15''')$$

where the constants have been supplied from measurements made only at 50 gauss and at 4800 gauss. The expression (15‴) is drawn also in Fig. 6, the distribution of experimental points about this curve provides a satisfying agreement between theory and experiment. We emphasize that this curve is not the best hyperbola drawn through the experimental points—it is the theoretical expression using independently measured or computed constants.

It has been drawn through the experimental points making use only of the lattice constant of LiF; the magnetic moments, spins, and abundances of Li^6, Li^7, and F; the gain of the apparatus, and the thermal relaxation time of Li^7 in our sample at 4800 gauss and 2°K.

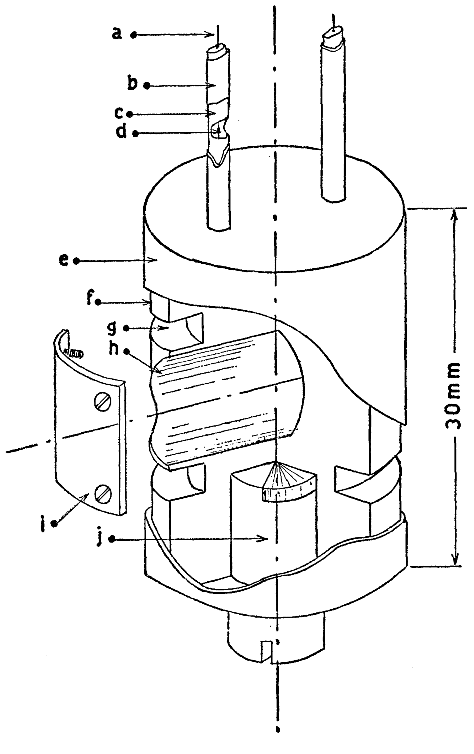

Fig. 7. The low-temperature crossed-coil probe, with cuts. (a) Central co-axial brass wire; (b) outer coaxial brass sleeve; (c) insulating material, taken from commercial coaxial cable; (d) silver solder joint, brass to copper wire; (e) brass envelope; (f) Lucite coil-form; (g) cut for transmitter winding; (h) cylindrical hole for receiver winding; (i) cover plate; (j) paddle. For simplicity, no coils have been drawn in.

The local field H_L is a quantity which is characteristic of the crystal and not of the nucleus observed. It was felt, nevertheless, to be worthwhile to make a similar determination of H_L using F^{19}. Although the signals at the same radio-frequency should be about 20% larger for F, the data are less precise for two reasons. First, the relaxation time at 2000 gauss was only 45 minutes, so that b would have been much larger, and secondly the tail of the large proton signal (due to the short relaxation time of the protons in the Lucite coil form for the most part) shown in Fig. 1(c) interfered with the F signal in a manner which depended upon the rate of sweeping, which was manually controlled. Nevertheless, sufficiently exact experimental results, which will not be reproduced here, could be obtained for it to be asserted that the same value of H_L was obtained.

(C) Some Aspects of the Apparatus

The room temperature experiments described immediately above were all performed using the Varian Model 4200 Wide Line Spectrometer and its associated 12-in. Magnet system. At 8 Mc/sec an H_1 equal to 1.0 gauss was used with which the level populations could be examined, reversed by fast passage, or saturated.

In the low-temperature experiment, the Varian probe was replaced by a simple crossed-coil probe, which could be submerged in liquid helium. Since fast-passage observations were desired, a relatively high H_1 requirement and the necessity of using u-mode observation dictated the crossed-coil method. The probe could be conveniently matched to the rest of the spectrometer at one frequency, giving $H_1=0.3$ gauss, with 50 volts across the transmitter winding.

The probe is illustrated in Fig. 7. The two transmitter windings, approximately of Helmholtz dimensions, were supported on a Lucite form and resonated by the cable and lead capacitances and a small variable capacitor to 8 Mc/sec, as was the receiver coil. The whole was shielded by a cylindrical brass envelope and supported by the 0.2-mm walled cylinders forming the return conductors for the two radio-frequency windings. To avoid magnetic shielding due to the superconductivity of ordinary solder at these temperatures and at low fields, this alloy could not be used. The copper wire making up the coils were joined with the central brass wire of the coaxial supports by a small silver-solder joint, as shown, and which was the only solder employed in the probe. The two cylinders were pressure-fitted into the brass envelope and the ends of both coils were held fast to the envelope by one of the screws which held the cover plate to the opening for the sample. The LiF sample was held securely within the receiver coil by melting a small amount of paraffin about it; the sample was oriented so that the magnetic field would lie along the [1,1,0] direction of the crystal, reducing the line width and thus enhancing the signal amplitude. Since in a high field the relaxation times depend on the orientation of the field with respect to the crystal,[18] all the values given in this paper refer to the [1,1,0] direction.

The "paddle"[19] ensured that the residual leakage phase from the receiver coil would be 180° out of phase with the transmitter voltage. In a "tuning box," the circuit of which will not be given here, it was then possible to reduce the *u*-mode leakage to zero by a simple network of small capacitances which added some current from the transmitter to the receiver input. The *u* leakage was controlled by a simple high impedance *RC* network which added a small amount of current at 90° to the transmitter voltage phase into the receiver input.

The probe was contained in the usual double-Dewar system for use with liquid helium. The vapor pressure of the helium was reduced until the lambda-point was reached, and the manometric measurements showed that the temperature was closely 2°K. Since this number is not of critical import in our arguments, it was not determined with precision. We found that one filling of helium would last about four hours while being pumped. All the data shown in Fig. 6 were obtained on the same day with two consecutive fillings.

(D) Digression on the Spin-Lattice Relaxation Times

As a by-product of our study of spin temperature, some experimental results have been obtained for the spin lattice relaxation times of lithium and fluorine, in various fields and for various temperatures, and it seemed worthwhile to discuss here the most significant of these results.

(*a*) *High-Field Measurements*

All measurements of relaxation times were made near a frequency of 8 Mc/sec, that is in a field of 2000 gauss for F^{19} and 5000 gauss for Li^7. For our sample, we found, at room temperature,

$$T_1(\mathrm{F}^{19})=1.4\ \mathrm{min},\quad \text{and}\quad T_1(\mathrm{Li}^7)=4.5\ \mathrm{min};$$

at 2°K,

$$T_1(\mathrm{F}^{19})=50\ \mathrm{min},\quad \text{and}\quad T_1(\mathrm{Li}^7)=15\ \text{hours}.$$

The absolute values of these times are of little intrinsic interest since their magnitude is greatly influenced by the content of paramagnetic impurities and should vary considerably from one sample to another, or even with the orientation of the magnetic field with respect to the crystal.[18] On the other hand, for their ratios we find

$$\left(\frac{T_1(\mathrm{Li}^7)}{T_1(\mathrm{F}^{19})}\right)_{300^\circ\mathrm{K}}=3.2,\quad \left(\frac{T_1(\mathrm{Li}^7)}{T_1(\mathrm{F}^{19})}\right)_{2^\circ\mathrm{K}}=18.$$

This can be understood by assuming that at room temperature the relaxation of Li^7 is at least partly due to its quadrupole moment whereas at 2°K it is entirely due to the coupling of its magnetic moment with the paramagnetic impurities, the quadrupole mechanism becoming negligible at very low temperatures.

In Bloembergen's theory of relaxation by paramagnetic impurities,[20] for a given impurity content the magnetic relaxation time T_1 depends in a complicated way on two constants: T_1' which represents the relaxation time of a nuclear spin in the neighborhood of the impurity at a fixed distance from it, and D which is the spin diffusion constant. Therefore, although elementary considerations may show how D or T_1' vary with temperature or with the spin species (Li^7 or F^{19}), no quantitative interpretation of the experimental results for T_1 can be given without considerable calculation.

For the relaxation time of Li^6, whose signal could be observed, thanks to the thermal mixing described previously, we have no experimental data except the fact that it is longer than one day. On the theoretical side, the quadrupole moment of Li^6 is very small, $Q(\mathrm{Li}^6)\sim Q(\mathrm{Li}^7)/100$ and the quadrupole relaxation time at room temperature should be of the order of $4.5\times(100)^2$ min, or one month. Its magnetic relaxation time must be very long as well because of its small magnetic moment and its small isotopic content $C\sim 7\%$ which makes the spin diffusion very slow. A conservative estimate is

$$T_1(\mathrm{Li}^6)_{300^\circ\mathrm{K,\ magnetic}}\sim C^{-2}(\gamma_{\mathrm{F}^{19}}/\gamma_{\mathrm{Li}^6})^2T_1(\mathrm{F}^{19})_{300^\circ\mathrm{K}} \sim \text{one week}.$$

(*b*) *Low-Field Measurements*

The sharp decrease of T_1 in low fields as well as the equality of relaxation times of Li^7 and F^{19} have already been pointed out by Pound[5] and Pound and Ramsey.[7] It might be well to remark, since the explanation does not seem to have appeared in print,[21] that the decrease in the relaxation time is a confirmation of Bloembergen's theory of spin diffusion: for sufficiently low fields a spin flip can take place between a Li spin and an F spin, thus considerably increasing the spin diffusion constant D.

It is remarkable that at 2°K, T_1, for our sample, is still only approximately 12 sec, in zero field. Thus the decrease of T_1 from high field to low field is much sharper at 2°K where, for F^{19}, $[T_1(2000\ \text{gauss})/T_1(0\ \text{gauss})]=250$ than at room temperature where the same ratio is only 14, in spite of the fact that the change in spin diffusion coefficients is independent of the lattice temperature. A possible qualitative explanation of this fact is contained in Bloembergen's theory of relaxation. The inverse of the relaxation time $1/T_1'$ of a nuclear spin in the vicinity of a paramagnetic

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[18] R. V. Pound, J. Phys. Chem. **57**, 743 (1953).

[19] Bloch, Hansen, and Packard, Phys. Rev. **70**, 474 (1946).

[20] N. Bloembergen, Physica **15**, 386 (1949).

[21] R. V. Pound (private communication).

impurity is proportional to $\tau/(1+\omega^2\tau^2)$, where τ is the relaxation time of the paramagnetic impurity itself and ω the nuclear Larmor frequency. At 2°K, $\omega\tau \gg 1$ and $1/T_1'$ increases as ω^{-2} as one lowers the field. This does not mean that the over-all relaxation time T_1 for the whole sample decreases in the same ratio, but it certainly should decrease somewhat on account of this phenomenon. On the other hand, at room temperature $\omega\tau \ll 1$ and T_1' is independent of ω. Finally we would like to mention the possibility of a connection between spin lattice relaxation through paramagnetic impurities and a phenomenon previously described: the abnormally small value of the low-field signal (up to 10 gauss), if the rf field is applied, even for a few seconds, *before* the raising of the dc field to 4500 gauss. It is not clear whether during such a short interval the rf heating could raise the temperature of the lattice sufficiently to explain this decrease of the signal. If not, it is possible that this decrease is caused by some kind of negative Overhauser effect through the saturation by the rf, of the electronic spins of the paramagnetic impurities which for a frequency of 8 Mc/sec resonate in a field of the order of 3 gauss. It is hoped that the reality of such an effect may be investigated both, theoretically and experimentally, in the future.

Relaxation times have also been measured at room temperature in CsCl where in high field $T_1(\mathrm{Cl}^{35}) = 3.5$ sec, $T_1(\mathrm{Cs}^{137}) = 9$ min, and in zero field $T_1(\mathrm{Cl}) = T_1(\mathrm{Cs}) = 20$ sec. The change of T_1, going from high into low field is of a different nature than in LiF. The relaxation mechanism is certainly quadrupole for Cl^{35} (if not for Cs^{137}, which has a very small quadrupole moment) and the increase in the spin diffusion constant has nothing to do with the change of T_1, since this change is an *increase* for Cl^{35}. This increase is understandable since in zero field the quadrupole mechanism of Cl is the thermal link between the lattice and the combined system CsCl which has a much larger heat capacity than the Cl system alone.

(E) Digression on the Rapid Passage Problem

In the course of the experiment described here, the rapid passage method has been used systematically to measure the polarization of a spin system, or to produce negative temperatures in high fields by reversing the magnetic moment of the sample. A satisfactory theory of the rapid passage for spins interacting very weakly with their surroundings or with each other, as for instance in liquid samples, was given by Bloch.[9] Redfield[2] pointed out that one of Bloch's conditions for rapid passage, $\tau \ll T_2$, where τ is the time necessary to sweep through the line, was too severe and should be replaced by $\tau \ll T_1$, thus making rapid passage possible in solids for values of dH/dt easily obtained in practice. However, no satisfactory theory of the rapid passage in solids has been given so far, especially for cases when the rf field is small compared to the local field. This is not surprising in view of the difficulty of the problem and we shall be content with a very crude model which will enable us to explain at least qualitatively a rather striking effect, namely the saturation by rapid passage of the signal of Li^6. As everywhere in this work we shall assume the coupling with the lattice to be negligible for the duration of the experiment. In a rapid passage there are two quantities of interest, the magnitude of the signal, and what we might call the turnover efficiency, which is the ratio of the magnitude of the polarization after the passage to that before and which is measured by the ratio of the signal from two consecutive rapid passages. We wish to understand why this efficiency, of the order of 0.9 for Li^7, was very small for Li^6. No Li^6 signal was visible from a second rapid passage, which in view of the fact that the signal-to-noise ratio from the first passage was approximately 4, means that the turnover efficiency was smaller than $\frac{1}{4}$. This occurred for the same rf field and of necessity the same local field as for Li^7 and for a wide range of rates of change of the dc field. For simplicity let us make the assumption, approximately correct in LiF, that the local field at a Li nucleus is due to its unlike neighbors, the fluorine spins. If these unlike neighbors did not flip between themselves, the situation would be the same as in an inhomogeneous applied field and the turnover efficiency would always be one. In fact, because of the fluorine flips, in the rotating frame of coordinates each Li spin sees a time-dependent field H' which is the sum of the usual slowly varying effective field H_{eff} and of the z component of the fast varying local field. Far from resonance, H' is parallel to H_0 on one side of resonance and antiparallel on the other. The condition for a complete reversal of the magnetization is Bloch's condition that the Larmor frequency $\gamma H'$ be large compared to the relative rate of change of H'. Since both H' and its rate of change, controlled by the mutual flips of fluorine spins, are the same for Li^6 and Li^7 while $\gamma_{\mathrm{Li}^7} \gg \gamma_{\mathrm{Li}^6}$, it is not surprising that this condition is approximately fulfilled in Li^7 and violated in Li^6. By the same token one should expect a smaller turnover efficiency for Li^7 than for F^{19}, since their local fields are comparable and their γ widely different. This is confirmed by experiment since this ratio is 0.92 for F^{19} and 0.87 for Li^6. These numbers could be measured precisely by observing the signals $S_1, S_2 \cdots S_{n+1}$ from $n+1$ consecutive rapid passages and taking for the turnover efficiency $[S_{n+1}/S_1]^{1/n}$.

APPENDIX 1. ULTRASONIC SATURATION AND SPIN TEMPERATURE

Let $n_{\frac{3}{2}}, n_{\frac{1}{2}}, n_{-\frac{1}{2}}, n_{-\frac{3}{2}}$ be the populations of the levels $I_z = m$ of Na^{23} irradiated by ultrasonic waves at twice the Larmor frequency and let W be the corresponding transition probability per unit time, between the levels $\frac{3}{2} \leftrightarrow -\frac{1}{2}$ and $\frac{1}{2} \leftrightarrow -\frac{3}{2}$.

The rates of change of these populations are given by the following equations:

$$\begin{aligned} dn_{\frac{3}{2}}/dt&=-W(n_{\frac{3}{2}}-n_{-\frac{1}{2}})+F_{\frac{3}{2}}(n_m)+G_{\frac{3}{2}}(n_m),\\ dn_{\frac{1}{2}}/dt&=-W(n_{\frac{1}{2}}-n_{-\frac{3}{2}})+F_{\frac{1}{2}}(n_m)+G_{\frac{1}{2}}(n_m),\\ dn_{-\frac{1}{2}}/dt&=-W(n_{-\frac{1}{2}}-n_{\frac{3}{2}})+F_{-\frac{1}{2}}(n_m)+G_{-\frac{1}{2}}(n_m),\\ dn_{-\frac{3}{2}}/dt&=-W(n_{-\frac{3}{2}}-n_{\frac{1}{2}})+F_{-\frac{3}{2}}(n_m)+G_{-\frac{3}{2}}(n_m).\end{aligned} \tag{A1}$$

The terms F_m and G_m represent the contributions to the rates of change of the populations from the spin lattice relaxation and the spin-spin coupling, respectively. We shall not require their exact expressions which depend in particular on the type of spin-lattice relaxation mechanism assumed (magnetic dipole or electric quadrupole). Multiplying the first equation by $\frac{3}{2}$, the second by $\frac{1}{2}$ etc., and adding them together, we get on the left-hand side $d\langle I_z\rangle/dt$. On the right-hand side, the sum $\frac{3}{2}F_{\frac{3}{2}}(\ )+\cdots+(-\frac{3}{2})F_{-\frac{3}{2}}$ represents the contribution to the rate of change of $\langle I_z\rangle$ from the spin-lattice relaxation mechanism, which, if we assume a single spin-lattice relaxation time, can be written as

$$-(\langle I_z\rangle-I_0)/T_1.$$

Similarly $\frac{3}{2}G_{\frac{3}{2}}+\cdots-\frac{3}{2}G_{-\frac{3}{2}}$ represents the contribution to $d\langle I_z\rangle/dt$ from the spin-spin interaction and this should be zero since, because of conservation of energy, the spin-spin interaction is unable to change $\langle I_z\rangle$. We are thus left with the equation:

$$\frac{d\langle I_z\rangle}{dt}=-\frac{\langle I_z\rangle-I_0}{T_1}-2W\{(n_{\frac{3}{2}}-n_{-\frac{3}{2}})+(n_{\frac{1}{2}}-n_{-\frac{1}{2}})\}.$$

Since the spin-spin interactions constantly maintain a Boltzmann distribution between the various populations:

$$\begin{aligned} n_{\frac{3}{2}}-n_{-\frac{3}{2}}&=3(n_{\frac{1}{2}}-n_{-\frac{1}{2}}),\\ \langle I_z\rangle&=\tfrac{3}{2}(n_{\frac{3}{2}}-n_{-\frac{3}{2}})+\tfrac{1}{2}(n_{\frac{1}{2}}-n_{-\frac{1}{2}})\\ &=(10/2)(n_{\frac{1}{2}}-n_{-\frac{1}{2}})=(10/6)(n_{\frac{3}{2}}-n_{-\frac{3}{2}}),\end{aligned} \tag{A2}$$

$$\frac{d\langle I_z\rangle}{dt}=-\frac{\langle I_z\rangle-I_0}{T_1}-\left(\frac{8W}{5}\right)\langle I_z\rangle.$$

The limiting value of $\langle I_z\rangle$ obtained when $d\langle I_z\rangle/dt=0$ is

$$\langle I_z\rangle=I_0/(1+8WT_1/5). \tag{A3}$$

Since the signal amplitude A is proportional to $\langle I_z\rangle$, we have

$$A/A_0=\langle I_z\rangle/I_0=(1+8WT_1/5)^{-1}. \tag{A4}$$

APPENDIX 2. CALCULATION OF THE LOCAL FIELD H_L IN LiF

We want to calculate

$$H_L{}^2=\mathrm{Tr}\{(\mathcal{H}^1)^2\}/\mathrm{Tr}\{M_z{}^2\},$$

where

$$M_z=\sum_k \hbar\gamma_k I_k{}^z,\quad \mathcal{H}^1=\sum_{j<k}\mathcal{H}_{jk}{}^1,$$

$$\mathcal{H}_{jk}{}^1=\hbar^2\gamma_j\gamma_k r_{jk}{}^{-3}\{(\mathbf{I}_j\cdot\mathbf{I}_k)-3(\mathbf{r}_{jk}\cdot\mathbf{I}_j)(\mathbf{r}_{jk}\cdot\mathbf{I}_k)r_{jk}{}^{-2}\},$$

$$\mathrm{Tr}\{(\mathcal{H}^1)^2\}=\sum_{j<k}\mathrm{Tr}\{(\mathcal{H}_{jk}{}^1)^2\}=\tfrac{1}{2}\sum_{j\neq k}\mathrm{Tr}\{(\mathcal{H}_{jk}{}^1)^2\}.$$

$\mathrm{Tr}\{(\mathcal{H}_{jk}{}^1)^2\}$ is easily calculated if we remark that its value is independent of the direction of the vector $\mathbf{r}_{jk}$ which can then be taken as the z axis, leading for $\mathcal{H}_{jk}{}^1$ to the expression:

$$\mathcal{H}_{jk}{}^1=\gamma_j\gamma_k r_{jk}{}^{-3}\{I_j{}^xI_k{}^x+I_j{}^yI_k{}^y-2I_j{}^zI_k{}^z\},$$

and

$$\mathrm{Tr}\{(\mathcal{H}_{jk}{}^1)^2\}=\mathfrak{N}\times\tfrac{2}{3}\gamma_j{}^2\gamma_k{}^2r_{jk}{}^{-6}I_j(I_j+1)I_k(I_k+1).$$

where $\mathfrak{N}=\prod_j(2I_j+1)$ is the number of levels of the whole system.

Since

$$\mathrm{Tr}\{M_z{}^2\}=\tfrac{1}{3}\mathfrak{N}\hbar^2\sum_j\gamma_j{}^2I_j(I_j+1),$$

we obtain

$$H_L{}^2=\Big[\hbar^2\sum_{j\neq k}\gamma_j{}^2\gamma_k{}^2r_{jk}{}^{-6}I_j(I_j+1)I_k(I_k+1)\Big]\Big/\sum_j\gamma_j{}^2I_j(I_j+1).$$

In the case of LiF we have a lattice of the NaCl type where the lattice sites of the Cl kind are filled by nuclei of F^{19} and those of the Na kind by nuclei of Li^7 and Li^6 in the proportions $p=0.926$ and $1-p=0.074$. We find:

$$\textstyle\sum_j\gamma_j{}^2I_j(I_j+1)=N\{\gamma_1{}^2I_1(I_1+1)+p\gamma_2{}^2I_2(I_2+1)+(1-p)\gamma_3{}^2I_3(I_3+1)\},$$

where $2N$ is the total number of spins and

$$\begin{aligned} &\mathrm{F}^{19}:\quad I_1=\tfrac{1}{2},\quad \gamma_1=2\pi\times4005.5,\\ &\mathrm{Li}^7:\quad I_2=\tfrac{3}{2},\quad \gamma_2=2\pi\times1654.7,\\ &\mathrm{Li}^6:\quad I_3=1,\quad \gamma_3=2\pi\times\ 626.5.\end{aligned} \tag{A5}$$

$$\begin{aligned} &\sum_{j\neq k}\gamma_j{}^2\gamma_k{}^2r_{jk}{}^{-6}I_j(I_j+1)I_k(I_k+1)\\ &\quad=NS_1[\gamma_1{}^4I_1{}^2(I_1+1)^2+p^2\gamma_2{}^4I_2{}^2(I_2+1)^2\\ &\quad+(1-p)^2\gamma_3{}^4I_3{}^2(I_3+1)^2+2p(1-p)\gamma_2{}^2\gamma_3{}^2I_2(I_2+1)\\ &\quad\times I_3(I_3+1)]+NS_2\times2\gamma_1{}^2I_1(I_1+1)\\ &\qquad\times[p\gamma_2{}^2I_2(I_2+1)+(1-p)\gamma_3{}^2I_3(I_3+1)],\end{aligned} \tag{A6}$$

where $S_1=\sum'r_k{}^{-6}$ is the sum taken from one lattice point of the Na kind to all the other lattice points of the Na kind and $S_2=\sum''r_k{}^{-6}$ is the sum from one lattice point of the Na kind to all the points of the Cl kind. We find $S_1=114.5/a^6$ and $S_2=422/a^6$, where a is the dimension of the cubic unit cell. In LiF, $a=4.01$ A and we get $H_L{}^2=60.6$ gauss², $H_L=7.77$ gauss.

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Polarization of Electrons Scattered by Thin Gold Foils

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The polarization of electrons by scattering from thin gold foils has been observed in a double-scattering experiment. The azimuthal asymmetry in the distribution of the twice-scattered electrons was measured in the energy range from 80 to 190 kev and for scattering angles of 60, 90, and 120 degrees. The observed asymmetries are somewhat smaller than would be expected from the calculations of Mohr and Tassie for the screened field of gold but the predicted increase in asymmetry for increasing scattering angles is confirmed.

INTRODUCTION

On the basis of the Dirac theory of the electron, Mott[1] has shown that polarization effects should be observable in a double-scattering experiment. The expected effect is an azimuthal asymmetry in the angular distribution of the twice-scattered electrons.

The early experiments failed to confirm the Mott theory of electron polarization; the apparent reason in most cases being that inadequate precautions were taken against plural or multiple scattering. Shull, Chase, and Myers[2] later reported agreement with the theory for 400-kev electrons twice-scattered through 90°. More recent experiments have been conducted in Japan by Ryu[3] and he reports polarization asymmetries of the expected sense over a range of energies and for several different scattering angles. His results, however, show consistently smaller asymmetries than predicted from the theory and it is not clear whether these discrepancies are due to deficiencies of the theory or of the experiments.

The present experiments were carried out in the hope of clarifying this situation somewhat through the use of a different experimental technique. The results, obtained some months ago, have attained added significance as a result of recent experiments on the polarization of electrons from beta emitters, which confirm the nonconservation of parity in weak interactions.[4]

SUMMARY OF THE THEORETICAL RESULTS

In the Mott treatment of double scattering, the intensity of the twice-scattered electrons is found to be of the form,

$$I(\theta_1,\theta_2,\phi_2)=A(\theta_1,\theta_2)[1+\delta(\theta_1,\theta_2)\cos\phi_2],$$

so that

$$\frac{I(\theta_1,\theta_2,0)}{I(\theta_1,\theta_2,\pi)}=\frac{1+\delta}{1-\delta},$$

where θ_1 is the angle between the incident unpolarized beam and the chosen once-scattered beam, θ_2 is the angle between the once-scattered beam and the twice-scattered beam, ϕ_2 is the azimuthal angle of the twice-scattered beam about the direction θ_1, A is a function independent of ϕ_2, and δ is the polarization asymmetry factor.

Numerical values of δ as a function of the energy of the incident electrons were first obtained by Mott for double scattering at 90° from unscreened gold nuclei and similar calculations were later made by Bartlett and Watson[5] for mercury. These results show a broad maximum in δ of approximately 0.07 in the neighborhood of 130 kev and a monotonic decrease on each side

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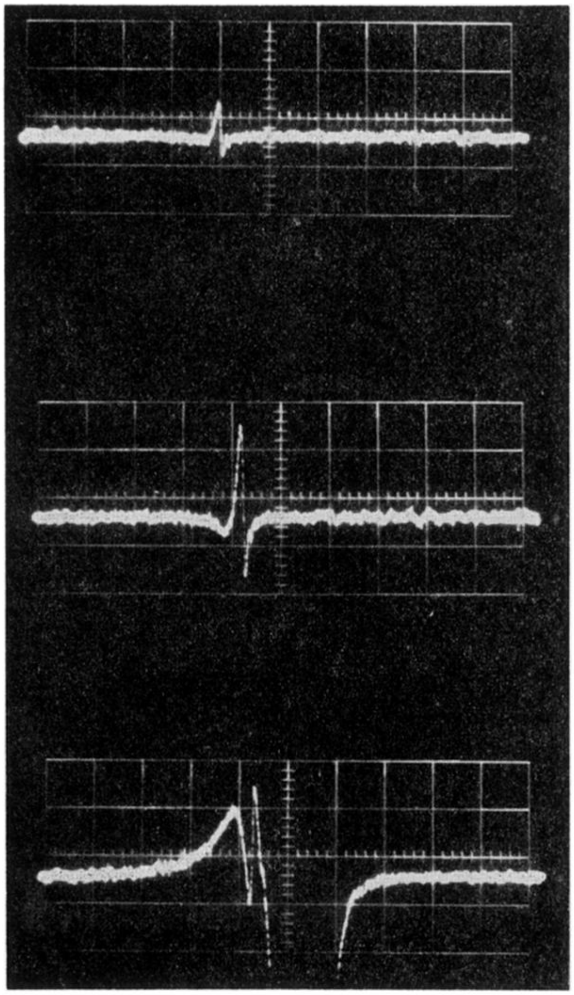

FIG. 5. Three characteristic fast-passage signals: (upper) Li^7, after reaching thermal equilibrium in zero field, (middle) Li^7, after reaching equilibrium in 25 gauss, (lower) F, occurring on the tail of a large proton signal. The trace proceeds from right to left.