View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by The University of Utah: J. Willard Marriott Digital Library

PHYSICAL REVIEW VOLUME 135, NUMBER 4A 17 AUGUST 1964

Low-Field Relaxation and the Study of Ultraslow Atomic Motions by Magnetic Resonance*

CHARLES P. SLICHTER AND DAVID AILION

Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois

(Received 30 March 1964)

Conventional resonance enables one to study motion of atoms by measurement of linewidth when the mean time τ between jumps is less than $1/\Delta\omega$, where $\Delta\omega$ is the rigid lattice linewidth, or by measurement of the spin-lattice relaxation time, T_1, when $\tau\sim 1/\omega_0$, where ω_0 is the Larmor frequency. We describe a new technique applicable when $\tau<T_1$. It is therefore applicable to the study of very slow motion. The method is analogous to measuring T_1 with $\omega_0=0$. However, we are able to keep ω_0 in the megacycle region by performing the experiments in the reference frame rotating at the Larmor frequency. Analysis of the technique requires solution of the problem of the effect of infrequent motion on the nuclear relaxation time when the applied static field is comparable to the local field. The relaxation time is then comparable to τ, indicating that jumps are strong "collisions" for the spins. The case of strong "collisions" is not treated in the conventional treatment of Bloembergen, Purcell, and Pound. We solve the problem by use of the concept of spin temperature and the sudden approximation. Explicit formulas are given for the nuclear relaxation in the laboratory for weak static fields, and in the rotating frame for alternating fields of the order of or less than the local field. We treat both diffusional motion and molecular reorientation.

I. INTRODUCTION

SOME of the most striking phenomena of nuclear magnetic resonance are related to the bodily motion of the nuclei themselves. It is this motion which gives rise to the characteristic narrow lines of liquids as contrasted to the broad lines of solids.[1] In many instances this motion provides one of the most important mechanisms for the nuclear spin system to reach thermal equilibrium with the lattice. This time, called the spin-lattice relaxation time T_1, may become hours in length in insulating materials when all motion is frozen out. The direct connection between atomic motions on the one hand, and the linewidth and relaxation time on the other, have made magnetic resonance one of the most important techniques for studying atomic motion.

Ordinarily, we may characterize motions by the mean time τ an atom sits between jumps. Conventional theory shows that we can observe the motional narrowing of the resonance when τ is less than $(T_2)_{\text{R.L.}}$ where $(T_2)_{\text{R.L.}}$, the spin-spin relaxation time, is the inverse of the rigid lattice line breadth. The spin-lattice relaxation is most effective when τ is of the order of the Larmor period. Since $(T_2)_{\text{R.L.}}$ is of the order of 100 μsec and the Larmor period is typically 10^{-8} sec, we can use conventional resonance techniques to observe motions when τ is less than about 100 μsec.

In this paper[2] we describe a new technique which enables us to use resonance to observe motion when $\tau<T_1$. Since $T_1\gtrsim(T_2)_{\text{R.L.}}$, this technique enables us to observe slower motions than were previously possible by resonance. In some instances T_1 may be hours in length. In such a case, this technique may enable one to observe jump rates of the order of one lattice distance an hour. In a succeeding paper we describe the experimental verification of the theory for the case of self-diffusion in lithium metal.[2] For that case we measure as our longest τ one of several tenths of a second. Combining our data with those of Holcomb and Norberg, whose shortest measured τ was about 2×10^{-9} sec, we have measurements of τ covering a range of 10^8. Our measurements, in fact, extend the data of Holcomb and Norberg by about 10^4.

As we shall show, the technique is very similar to adiabatic demagnetization.[3] It is performed, however, in a rotating reference frame[4] bringing about the important experimental simplifications that the "adiabatic demagnetization" is actually done in a strong applied field of the order of 10 000 G.

One of the principal problems involved in the theoretical interpretation is associated with the fact that in an ordinary experiment on adiabatic demagnetization, the final applied field H_0 is comparable to or less than the local field arising from neighboring nuclei. As a result, one cannot make the usual approximation that the Zeeman energy (coupling to H_0) is large compared to the dipolar energy. If the atomic motion is very rapid (τ short), the effect of the dipolar coupling is greatly diminished, and it can be treated as a weak perturbation. The relaxation theory has been worked out for this case by Bloembergen, Purcell, and Pound, and the fact that their theory works even for low fields has been verified by Brown.[5] However, if the motion is very slow (τ long), the full effectiveness of the dipolar coupling is felt. Then, when H_0 is comparable to or less than the

* Supported in part by the U. S. Atomic Energy Commission.

[1] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948), hereafter referred to as BPP.

[2] A preliminary account of this research together with the experimental verification for the case of diffusion in lithium metal has appeared in Phys. Rev. Letters **12**, 168 (1964).

[3] For an excellent review of the concepts of spin temperature and adiabatic demagnetization, both in the laboratory and rotating frames, see the article by L. C. Hebel, in *Solid State Physics*, edited by F. Seitz and D. C. Turnbull (Academic Press Inc., New York, 1963), Vol. 15.

[4] C. P. Slichter and W. C. Holton, Phys. Rev. **122**, 1701 (1961); A. G. Anderson and S. R. Hartmann, *ibid.* **128**, 2023 (1962).

[5] R. M. Brown, Phys. Rev. **78**, 530 (1950).

dipolar coupling, one has no good knowledge of the energy eigenvalues, nor the eigenfunctions of the system. The assumption of strong-field eigenstates underlying the Bloembergen, Purcell, and Pound theory of relaxation, as, for example, employed by Torrey,[6] is no longer valid. An additional problem is that the BPP theory, depending as it does on the use of perturbation theory, is based on "weak collisions." It takes many "collisions" for a spin to relax. That it takes many jumps to relax a spin is evidenced by the fact that the relaxation time is much longer than τ. In our case, the relaxation time is comparable to τ. Since only about one jump is needed to relax a spin, the "collisions" are strong. A perturbation theory approach will therefore not be applicable. Fortunately, however, two circumstances are present which enable us to treat the problem.

The first circumstance is that a low H_0 enables the Zeeman and dipolar systems to couple strongly, establishing a common spin temperature. By assuming that the relaxation processes disturb the system slowly compared to this internal coupling, we can characterize the spin system by a temperature. The second circumstance is that the actual duration of a jump is so short that we can assume all spins have the same orientation just after a jump that they did before. That is, the sudden approximation applies. As we shall see, these two circumstances enable us to put the relaxation time in the form of a diagonal sum, so that we can evaluate it using any complete set of eigenfunctions, and do not therefore need to solve the weak-field Hamiltonian. The technique of diagonal sums in magnetism is due to Waller and to Van Vleck, who has exploited it in a notable sequence of papers.[7] They were the first people to apply the technique to a relaxation time calculation. Our considerations are most directly based on the work of Redfield[8] and of Hebel and Slichter.[9] They were, however, still concerned with a weak-collision case (relaxation of nuclei by conduction electrons).

Lowe has independently recognized that ultraslow atomic motions can be observed by virtually the same experimental technique as we employ. He and Look[10] have observed the effect in glycerine and gypsum. Since Lowe has applied a BPP type of theory to analyze the data, his theoretical expressions apply when the relaxation time is much longer than τ, which ordinarily occurs when the alternating field H_1 is large compared to the local field.

In Sec. II we outline the physical basis for the technique. In Sec. III we show how to treat relaxation in low applied fields, extending the theory of Torrey and BPP to applied fields comparable to the local field. In Sec. IV we give the general theory of the relaxation time in the presence of an alternating field H_1 which is comparable to the linewidth. The theory of Sec. IV is applied to treat diffusion in Sec. V and to treat molecular reorientation in Sec. VI.

II. THE BASIC THEORY

Consider a system of nuclei interacting with an applied static field H_0 and with one another.[3] We have then a Hamiltonian

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

$$\mathcal{H}_z=-\gamma\hbar H_0\sum_j I_{zj}\,, \tag{2}$$

$$\mathcal{H}_d=\tfrac{1}{2}\sum_{i,j}\frac{\gamma^2\hbar^2}{r_{ij}{}^3}\left[\mathbf{I}_i\cdot\mathbf{I}_j-\frac{3(\mathbf{r}_{ij}\cdot\mathbf{I}_i)(\mathbf{r}_{ij}\cdot\mathbf{I}_j)}{r_{ij}{}^2}\right], \tag{3}$$

where $\mathbf{r}_{ij}$ is the internuclear vector from nucleus i to j, γ is the gyromagnetic ratio, H_0 the applied field (taken to be in the z direction).

The energy $\bar{E}$, entropy σ, and the magnetization $\langle\mathbf{M}\rangle_{\rm av}$ can all be computed from the density matrix ρ, assuming that the spin system has a temperature θ. In particular

$$\begin{aligned}\rho&=\exp(-\mathcal{H}/k\theta)/Z\,,\\ \langle\mathbf{M}\rangle_{\rm av}&=\mathrm{Tr}\rho\mathbf{M}\,,\\ \bar{E}&=\mathrm{Tr}\mathcal{H}\rho\,,\\ \sigma&=(\bar{E}+k\theta\,\ln Z)/\theta\,,\end{aligned} \tag{4}$$

where the partition function Z is

$$Z=\mathrm{Tr}\,\exp(-\mathcal{H}/k\theta)\,. \tag{5}$$

In the high-temperature approximation, one finds readily

$$\begin{aligned}\langle\mathbf{M}\rangle_{\rm av}&=C\mathbf{H}_0/\theta\,,\\ \bar{E}&=-C(H_0{}^2+H_L{}'^2)/\theta\,,\\ \sigma&=kN\,\ln(2I+1)-[C(H_0{}^2+H_L{}'^2)/2\theta^2]\,,\end{aligned} \tag{6}$$

where C is the Curie constant, $N\gamma^2\hbar^2I(I+1)/3k$, N the number of nuclei/unit volume, I their spin, and where $H_L{}'^2$ is a quantity we call the "local field," defined by the equation

$$CH_L{}'^2=(1/k)[\mathrm{Tr}\mathcal{H}_d{}^2/(2I+1)^N]. \tag{7}$$

Explicit expressions for $H_L{}'^2$ can be worked out since the trace can easily be evaluated [see Eq. (30) below].

Let us now consider an adiabatic demagnetization. We start at a large field H_{00}, much larger than the local field, with a sample magnetized in thermal equilibrium at the lattice temperature θ_l. If we turn H_0 slowly to zero, and may neglect any coupling to the lattice, the entropy σ remains constant. Using Eq. (6), we find that

---

[6] H. C. Torrey, Phys. Rev. **92**, 962 (1953); **96**, 690 (1954). See also H. A. Resing and H. C. Torrey, *ibid.* **131**, 1102 (1963).

[7] See, for example, J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937), and I. Waller, Z. Physik **79**, 370 (1932).

[8] A. G. Redfield, IBM J. Res. Develop. **1**, 19 (1957); A. G. Anderson and A. G. Redfield, Phys. Rev. **116**, 583 (1959).

[9] L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959).

[10] A preliminary account of experiments on glycerine and gypsum was presented by D. C. Look and I. J. Lowe at the Fourth Omnibus Conference on the Experimental Aspects of Nuclear Magnetic Resonance Spectroscopy in March 1963 (unpublished).

we reach a temperature θ given by:

$$\theta = H_L'\theta_l/H_{00}. \tag{8}$$

According to Curie's law, the magnetization in zero field is zero. If we slowly turn H_0 back up to H_{00}, we recover the full magnetization without need for contact with the lattice. In this process the order (entropy) has remained the same at all parts of the cycle. In the strong field, the order manifests itself as an alignment of spins along H_0. In zero applied field, the order consists of the alignment of spins along the direction of their local fields. Since the local fields are, in general, random in direction, no bulk magnetization results. (Of course if $\gamma\hbar H_{00}\approx k\theta_l$, there might be a ferromagnetic or antiferromagnetic arrangement when H_0 is zero, so the local fields would not be random. Since we always work in the region $\gamma\hbar H_{00}\ll k\theta_l$, we can consider the local fields as random.) Since the dipolar interaction falls off rapidly with distance, the local field arises from near neighbors. We may say that the order is short range when $H_0=0$, and that the process of demagnetization has changed the order from long range to short range.

As long as the system is isolated from the lattice, the order remains the same. Thus we would recover the full magnetization in raising H_0 to its initial value H_{00}. The process of spin-lattice relaxation, representing as it does a heat flow from the lattice to the spins, will destroy the order in low field, since it will heat the cold spins toward the lattice temperature. We may say that the order can be maintained for a time of order T_1.

Let us now consider what would happen if, when $H_0=0$, the atoms began jumping to new positions as is the case with self-diffusion. The actual time an atom is moving is of the order of 10^{-12} sec, much shorter than any precession periods of the nuclei. During this time, the spins do not change their spatial orientation. A nucleus which was lined up parallel to its local field before jumping finds itself in a different local field after the jump. If the new local field were completely random relative to the old one, a jump would produce a complete loss of order. There is some maintenance of order of course, since a nucleus jumps only one lattice distance ordinarily, but it is still a good approximation to say that we can maintain the dipolar order only for a time τ.

We have the circumstance, then, that when $\tau<T_1$, we can observe the effects of atomic motion since they limit the time for which order can be maintained in the demagnetized state. The loss of order could be studied by observing the amplitude of $\langle M_z\rangle_{\mathrm{av}}$ following remagnetization as a function of the time spent in zero applied field.

The technique we have described is actually feasible for sufficiently long T_1's. However, since the simplest method to observe the magnetization is by means of magnetic resonance, we have a conflict between the need for zero field, to produce a motional destruction of order, and the need for a strong field to observe a resonance. By means of a trick, we produce an important experimental simplification. We apply an alternating field H_1. In this case, provided H_1 is sufficiently strong so that

$$\gamma^2H_1^2T_1T_2\gg 1, \tag{9}$$

we can leave H_0 on and do the adiabatic demagnetization in the rotating reference system[4]—that is, in the reference system rotating with H_1 in the same sense as the nuclear precession. The experimental details are explained in a subsequent paper.[2]

The analysis of relaxation in the rotating frame involves considerations similar to that of relaxation in the laboratory in the absence of H_1. We begin by discussing the latter.

III. RELAXATION IN WEAK FIELDS

Nuclear relaxation in weak applied fields was first treated by Redfield[8] and by Hebel and Slichter,[9] using the idea of spin temperature. Since they were concerned with weak collisions, they employed conventional time-dependent perturbation theory. We must therefore generalize their ideas. Our method of generalization is closely related to the method used by Slichter and Holton[4] an by Lurie and Slichter[11] to discuss sudden switching of the alternating field.

We consider that our Hamiltonian is just that of Eq. (1) consisting of a Zeeman and a dipolar part. These parts couple together strongly compared to the coupling to the lattice. The individual atomic jumps cause changes in the dipolar energy, disturbing the spin system from internal thermal equilibrium. We assume that the time between jumps is sufficiently long that the spin system has time to re-equilibrate between jumps. Thus, at the time of each jump, the spin system is characterized by a temperature. This means approximately that $\tau>T_2$, and places us in the range of τ's for which the linewidth of a resonance would be at its rigid lattice value.

The actual time a spin takes to carry out a jump is very short compared to all precession periods of the nuclei. Therefore, in each jump the dipole energy changes, but the Zeeman energy does not. The jump therefore disturbs the equilibrium in the spin system. As the system comes to a new equilibrium, the Zeeman and dipolar systems exchange energy until a new spin temperature is reached. That is, the Zeeman energy does not change during the jump, but it does change subsequently.

Let us therefore work out a general expression, using these ideas, for the rate of change of the dipolar energy due directly to the jumping. We shall consider that there are N_0 jumping units, and that there is a mean time τ_0 between jumps. For example, if we are dealing with diffusion via vacancies, N_0 might be taken as the number of vacancies N_v, and τ_0 as the mean time between vacancy jumps τ_v. Since an atom must jump whenever a vacancy jumps, these quantities are related

[11] F. M. Lurie and C. P. Slichter, Phys. Rev. **133**, A1108 (1964).

to the number of atoms N_a and the mean time between atomic jumps τ_a by the equation

$$N_a/\tau_a = N_v/\tau_v . \tag{10}$$

If, on the other hand, we are dealing with molecular reorientation, N_0 could be taken as the number of molecules and τ_0 the mean time between reorientational jumps.

In general there is more than one kind of jump. For example, a vacancy may possess G neighboring positions into which it might jump with equal probability. Or a molecule may have several orientations which it might be in initially, and from each initial position a smaller number into which it might go finally. Let us therefore consider that there are, in general, G distinct types of such jumps. In each jump the dipolar Hamiltonian changes from an initial value $\mathcal{H}_{di}$ to a final value $\mathcal{H}_{df}$ since it depends on the relative coordinates of the nuclei. To distinguish between the G types of jumps, we write $\mathcal{H}_{dig}$ and $\mathcal{H}_{dfg}$ where g runs from 1 to G.

On the assumption that the system is described by a temperature, we know that the density matrix before the jump is

$$\rho = \exp[-(\mathcal{H}_{dig}+\mathcal{H}_z)/k\theta]/Z . \tag{11}$$

The assumption that the spins jump so rapidly that the spin orientation does not change during the jump tells us that ρ just after the jump is given by Eq. (11) also. We have, therefore, that the average change in dipolar energy in jump g is

$$(\Delta E)_g = \mathrm{Tr}(\mathcal{H}_{dfg}-\mathcal{H}_{dig})\rho$$

$$= \frac{1}{k\theta Z_\infty}\mathrm{Tr}[(\mathcal{H}_{dig})^2-(\mathcal{H}_{dig}\mathcal{H}_{dfg})], \tag{12}$$

in the high-temperature approximation, where Z_∞ is the partition function at infinite temperature. The average energy change $\langle\Delta E\rangle_{\mathrm{av}}$ for the jump of a single unit is then

$$\langle\Delta E\rangle_{\mathrm{av}} = \frac{1}{G}\sum_g (\Delta E)_g . \tag{13}$$

Since there are N_0 jumping units, the average rate of change of the dipolar energy due to jumping is

$$\partial\langle\mathcal{H}_d\rangle/\partial t = (N_0/\tau_0)\langle\Delta E\rangle_{\mathrm{av}} . \tag{14}$$

Since both $\langle\Delta E\rangle_{\mathrm{av}}$ and the dipolar energy $\langle\mathcal{H}_d\rangle$ are inversely proportional to the dipolar temperature θ, we can write Eq. (14) as

$$\partial\langle\mathcal{H}_d\rangle/\partial t = -\langle\mathcal{H}_d\rangle/T_d , \tag{15}$$

where the minus sign is introduced since $\langle\Delta E\rangle_{\mathrm{av}}$ is positive but $\langle\mathcal{H}_d\rangle$ negative for positive θ, and where

$$1/T_d \equiv -(N_0/\tau_0)(\langle\Delta E\rangle_{\mathrm{av}}/\langle\mathcal{H}_d\rangle) . \tag{16}$$

The traces of Eq. (12) can be evaluated, enabling us to compute $\langle\Delta E\rangle_{\mathrm{av}}$ and therefore T_d.

Equation (15) implies that $\langle\mathcal{H}_d\rangle$ relaxes towards zero, whereas we know in fact it should relax towards a value $\langle\mathcal{H}_d\rangle_l$ corresponding to $\theta=\theta_l$, the lattice temperature. This discrepancy arises because we have neglected the Boltzmann factor for lattice corodinates. It is easily taken into account by modifying Eq. (15) to read

$$\partial\langle\mathcal{H}_d\rangle/\partial t = (\langle\mathcal{H}_d\rangle_l-\langle\mathcal{H}_d\rangle)/T_d . \tag{17}$$

Equations (12)–(17) are the basic ones to interpret our experiments. They can be applied both in the laboratory and in the rotating frame, and to a wide variety of motions.

We now wish to include the cross-relaxation between the dipolar and Zeeman systems, and the relaxation of the Zeeman system. We therefore distinguish between the dipolar and Zeeman temperatures θ_d and θ_z.

We can express these results most simply by saying that both the dipolar energy $\langle\mathcal{H}_d\rangle$ and the Zeeman energy $\langle\mathcal{H}_z\rangle$ obey simple relaxation equations.

$$\begin{aligned}\frac{\partial\langle\mathcal{H}_d\rangle}{\partial t} &= \frac{\langle\mathcal{H}_d\rangle_l-\langle\mathcal{H}_d\rangle}{T_d}+F(\theta_d-\theta_z) ,\\ \frac{\partial\langle\mathcal{H}_z\rangle}{\partial t} &= \frac{\langle\mathcal{H}_z\rangle_l-\langle\mathcal{H}_z\rangle}{T_z}-F(\theta_d-\theta_z) ,\end{aligned} \tag{18}$$

where $F(\theta_d-\theta_z)$ is some function expressing cross-relaxation between the dipolar and Zeeman systems which vanishes when the dipolar temperature θ_d is equal to the Zeeman temperature θ_z. The quantities $\langle\mathcal{H}_d\rangle_l$ and $\langle\mathcal{H}_z\rangle_l$ are simply values of $\langle\mathcal{H}_d\rangle$ and $\langle\mathcal{H}_z\rangle$ when θ_d and θ_z equal θ_l, the lattice temperature.

$$\begin{aligned}\langle\mathcal{H}_d\rangle_l &= -CH_L'^2/\theta_l ,\\ \langle\mathcal{H}_z\rangle_l &= -CH_0^2/\theta_l .\end{aligned} \tag{19}$$

Of course, if there are mechanisms other than atomic motion which cause relaxation of $\langle\mathcal{H}_d\rangle$, T_d will not be given simply by Eq. (16). Using Eq. (18), we then get an expression for the rate of change of the total energy $\langle\mathcal{H}\rangle$,

$$\frac{\partial\langle\mathcal{H}\rangle}{\partial t} = \frac{\partial}{\partial t}\langle\mathcal{H}_z+\mathcal{H}_d\rangle$$

$$= \frac{\langle\mathcal{H}_d\rangle_l}{T_d}+\frac{\langle\mathcal{H}_z\rangle_l}{T_z}-\frac{\langle\mathcal{H}_d\rangle}{T_d}-\frac{\langle\mathcal{H}_z\rangle}{T_z} . \tag{20}$$

Assuming $\theta_d=\theta_z=\theta$, and writing $\langle M_z\rangle_{\mathrm{av}}=(CH_0/\theta)$, we obtain from Eq. (20)

$$\begin{aligned}\frac{d\langle M_z\rangle_{\mathrm{av}}}{dt} &= \frac{1}{H_0^2+H_L'^2}\left(\frac{H_0^2}{T_z}+\frac{H_L'^2}{T_d}\right)(M_0-\langle M_z\rangle_{\mathrm{av}}) ,\\ \frac{d}{dt}\left(\frac{1}{\theta}\right) &= \frac{1}{H_0^2+H_L'^2}\left(\frac{H_0^2}{T_z}+\frac{H_L'^2}{T_d}\right)\left(\frac{1}{\theta_l}-\frac{1}{\theta}\right) ,\end{aligned} \tag{21}$$

where M_0 is the thermal equilibrium magnetization.

The magnetization and $(1/\theta)$ thus relax exponentially to M_0 and $(1/\theta_l)$ with a relaxation time T given by

$$\frac{1}{T}=\left(\frac{1}{H_0^2+H_L'^2}\right)\left(\frac{H_0^2}{T_z}+\frac{H_L'^2}{T_d}\right). \tag{22}$$

If, for the moment, we consider a metal with a *rigid* lattice (i.e., *no* jumping) and take the relaxation to be due to conduction electrons, the relaxation time in strong field H_0 is seen to be T_z. If the electrons flip the nuclei independently, $T_d=\frac{1}{2}T_z$ since the dipolar energy is relaxed if *either* of the pair flips.[3,8,9] More generally there are correlation effects in the interactions of an electron with several nuclei, giving

$$T_d=(1/\alpha)T_z \tag{23}$$

and

$$\frac{1}{T}=\frac{1}{T_z}\left(\frac{H_0^2+\alpha H_L'^2}{H_0^2+H_L'^2}\right). \tag{24}$$

The most thorough experimental study of this expression is that of Anderson and Redfield.[8]

To obtain the diffusion contribution to T_d, we need to evaluate the expressions of Eq. (16). A rough idea of the size predicted is obtained as follows. If we assumed the local field after a jump to be completely random with respect to its value before a jump, the dipolar energy of a spin immediately after it jumped would be zero. Therefore, the average rate at which $\langle\mathcal{H}_d\rangle$ changes is given by

$$\partial\langle\mathcal{H}_d\rangle/\partial t=(\langle\mathcal{H}_d\rangle_l-\langle\mathcal{H}_d\rangle)/\tfrac{1}{2}\tau, \tag{25}$$

where we have used $\frac{1}{2}\tau$ since the dipolar interaction involves *pairs* of spins, and changes therefore if *either* one jumps. Actually, the final local field is *not* completely random, so we introduce a quantity p such that

$$\partial\langle\mathcal{H}_d\rangle/\partial t=(1-p)(2/\tau)[\langle\mathcal{H}_d\rangle_l-\langle\mathcal{H}_d\rangle]. \tag{26}$$

p can be calculated from Eqs. (12)–(14), and we, in fact, evaluate it and thereby justify Eq. (26) for a number of cases later in this paper. From Eq. (26) we get

$$1/T_d=(1-p)2/\tau. \tag{27}$$

Actually, if there is a vacancy involved in the motion, the atom which jumps has a missing neighbor. Its average dipolar energy before the jump is not that of a *typical* nucleus, which is not near a vacancy. We can, however, include this effect formally by properly defining p.

For nuclear relaxation in a metal in weak field, we should then have

$$\frac{1}{T}=\frac{1}{T_z}\left(\frac{H_0^2+\alpha H_L'^2}{H_0^2+H_L'^2}\right)+\frac{2(1-p)}{\tau}\left(\frac{H_L'^2}{H_0^2+H_L'^2}\right). \tag{28}$$

It is of interest to compare this result with that of Torrey,[6] using the BPP formalism. In that theory, one divides the dipolar interaction into two parts, one of which commutes with the Zeeman energy, the other of which does not. Both parts fluctuate in time as a result of atomic motion. The time variation of the noncommuting part induces transitions of the Zeeman system among its energy levels. In the limit of slow motion and rigid lattices, we can express Torrey's answer for the contribution of diffusion as

$$1/T=[2(1-p)/\tau](H_L'^2/H_0^2)A, \tag{29}$$

where A is a dimensionless function of the orientation of the static magnetic field with respect to the crystal axes.

Utilizing the fact that[3]

$$H_L'^2=\gamma^2\hbar^2I(I+1)\sum_j\frac{1}{r_{jk}^6}, \tag{30}$$

one can identify A from Torrey's equations. To compare Eq. (29) with the dipolar contribution to Eq. (28), it is most convenient to average A over all orientations of field. "A" then becomes

$$A=\langle\mathrm{Tr}(\mathcal{H}_d{}^n)^2\rangle/\mathrm{Tr}\mathcal{H}_d{}^2=\tfrac{4}{5}, \tag{31}$$

where $\mathcal{H}_d{}^n$ is that part of the dipolar energy which does not commute with the Zeeman energy (the "nonsecular" part[12]), and where the brackets indicate an angular average.

Thus

$$\frac{1}{T}=\frac{2(1-p)}{\tau}\frac{H_L'^2}{H_0^2}\frac{4}{5}. \tag{32}$$

We note two differences with our result

$$\frac{1}{T}=\frac{2(1-p)}{\tau}\frac{H_L'^2}{H_0^2+H_L'^2}. \tag{33}$$

The first is that ours predicts a rate which does *not* go to infinity as H_0 goes to zero. This clearly expresses the fact that as H_0 goes to zero, individual nuclei still experience a field due to the neighbors. We should therefore expect that the H_0 in Torrey's expression should be replaced by $H_0^2+BH_L'^2$, where B is a constant of order unity. (Our theory enables us to calculate B.)

The second difference is the coefficient $\frac{4}{5}$ which multiplies Torrey's result. We have assumed that the changes in dipolar temperature are communicated to the Zeeman system. This is true in low H_0, where cross-relaxation between the dipolar and Zeeman systems proceeds rapidly. Once $H_0\gg H_L'$, however, the energy levels of the two systems no longer match, and a change in the dipolar temperature can no longer be communicated. Since atomic motion changes the dipolar energy, but not the Zeeman energy, the Zeeman system is sluggish in following the dipolar relaxation. On this basis we would be inclined to suppose that the atomic motion

[12] See, for example, C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, Publishers, New York, 1963), Chap. 3.

would need a time equal to the cross-relaxation time to communicate the dipolar temperature. Actually, for $H_0 \gg H_L'$, this time becomes exceedingly long—infinite for all practical purposes.

This view is only partially correct. To discuss the cross-relaxation, we must first define two systems. Let us take the Zeeman energy $\mathcal{H}_z$ as one and $\mathcal{H}_d^0$, that part of the dipolar Hamiltonian which commutes with $\mathcal{H}_z$, as the other. These two systems alone would be perfectly isolated from one another since they have commuting Hamiltonians. We still have a further part, $\mathcal{H}_d^n$, the rest of the dipolar Hamiltonian. When $H_0 \gg H_L'$, $\mathcal{H}_d^n$ has only a minor effect on the energy levels of the system. It does, however, bring about cross-relaxation between the Zeeman and dipolar systems.[13] When the dipolar and Zeeman energy level spacings are quite different, as when $H_L' \ll H_0$, this transfer of energy is very slow.

When there is motion, both $\mathcal{H}_d^0$ and $\mathcal{H}_d^n$ change in time. The energy changes of $\langle \mathcal{H}_d^0 \rangle$ are well isolated from the Zeeman system, requiring cross-relaxation. The process of a jump *also* brings about a momentary change in $\langle \mathcal{H}_d^n \rangle$. This energy, however, is rapidly (within about a T_2) transferred to the Zeeman system, since $\mathcal{H}_d^n$ and $\mathcal{H}_z$ do not commute. Therefore, jumping brings about a change in $\langle \mathcal{H}_z \rangle$. Customarily we say that $\mathcal{H}_d^n$ becomes time-dependent, and is thus able to induce transitions among the Zeeman levels,[1] the energy transfer being then between the lattice and the Zeeman system. But this transfer may actually be thought of as a momentary fluctuation of $\langle \mathcal{H}_d^n \rangle$. It is only the changes in $\langle \mathcal{H}_d^n \rangle$ and not in $\langle \mathcal{H}_d^0 \rangle$ which are able to produce relaxation when $H_0 \gg H_L'$, so the relaxation is reduced by the factor 4/5.

An analogous situation arises when one asks what happens to the magnetization when a magnetic field H_0 is suddenly applied to an unmagnetized sample sitting in zero field. We can analyze this problem by defining three quantities H_L', H_{L0}', and H_{Ln}' as follows:

$$\begin{aligned} CH_L'^2 &= [1/k(2I+1)^N] \operatorname{Tr}(\mathcal{H}_d)^2, \\ C(H_{L0}')^2 &= [1/k(2I+1)^N] \operatorname{Tr}(\mathcal{H}_d^0)^2, \\ C(H_{Ln}')^2 &= [1/k(2+1)^N] \operatorname{Tr}(\mathcal{H}_d^n)^2. \end{aligned} \tag{34a}$$

They satisfy the equation

$$H_L'^2 = (H_{L0}')^2 + (H_{Ln}')^2. \tag{34b}$$

The energy of the spin system E_b, before H_0 is applied, is

$$E_b = -\frac{CH_L'^2}{\theta} = -\left[\frac{C(H_{L0}')^2}{\theta} + \frac{C(H_{Ln}')^2}{\theta}\right], \tag{35}$$

where θ is the spin temperature. Since the magnetization is zero before application of H_0 (as dictated by Curie's law), the Zeeman energy immediately after H_0 is applied is zero, so the total energy is also E_b. Part of this energy resides in the secular dipolar system. It is

$$-C(H_{L0}')^2/\theta. \tag{36}$$

The rest, $-[C(H_{Ln}')^2/\theta]$, lies in the nonsecular part. This latter part is communicated to the Zeeman system within a time of the order to T_2, establishing a Zeeman temperature θ_z given approximately by

$$-(CH_0^2/\theta_z) = -[C(H_{Ln}')^2/\theta] \tag{37}$$

and a magnetization

$$M = \frac{CH_0}{\theta_z} = \frac{CH_0}{\theta}\frac{(H_{Ln}')^2}{H_0^2}. \tag{38}$$

The energy in the secular dipolar system only couples to the Zeeman system by cross-relaxation. When it eventually mixes, a new temperature of the *total* system θ_f is reached given by

$$-(CH_L'^2/\theta) = -[C(H_0^2 + H_L'^2)/\theta_f], \tag{39}$$

so that eventually we get

$$M = \frac{CH_0}{\theta}\frac{(H_L')^2}{H_0^2 + (H_L')^2}. \tag{40}$$

The change in Zeeman energy, $-MH_0$, in the first process is

$$-(CH_0^2/\theta)(H_{Ln}'^2/H_0^2), \tag{41}$$

whereas in the second case it is

$$-(CH_0^2/\theta)[H_L'^2/H_0^2 + (H_L')^2]. \tag{42}$$

If one averages $(H_{Ln}')^2$ for a powder, it is exactly $\frac{4}{5}$ of $(H_L')^2$. We note that this change is of exactly the same sort as we encounter due to relaxation by sudden changes in the dipolar energy. It is in fact just the distinction between $(H_L')^2$ and $(H_{Ln}')^2$ which distinguishes the low field relaxation from the BPP case, giving rise to the extra $\frac{4}{5}$ found in Eq. (32) but not in Eq. (33). We see, therefore, that our zero-field calculation goes over to the BPP result in a natural way. Of course, their calculation looks quite different at first sight since they consider $\mathcal{H}_d^n$ as being a time-dependent perturbation which induces transitions between the Zeeman levels. That is, they divide the Hamiltonian into a time-independent part which has a set of energy levels, and a time-dependent part which induces transitions among these levels. The difficulty when H_0 is zero is that the entire Hamiltonian is time-dependent. We can no longer make such a division. However, the "sudden approximation" viewpoint is valid for both strong and weak collisions, and the spin-temperature concept applies as long as there is no motional narrowing. Thus we can apply these ideas in either low fields (by considering the cross-relaxation time between the dipolar and Zeeman systems to be zero) or high fields

[13] N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959); P. S. Pershan, *ibid.* **117**, 109 (1960).

(by considering the cross-relaxation time between Zeeman and the secular dipolar systems to be finite). We could presumably even treat the intermediate field region if we included corrections for the cross-relaxation by writing a set of coupled equations for both Zeeman and secular dipolar temperatures.

IV. MOTIONAL EFFECTS IN THE ROTATING FRAME

In the previous sections we have shown how the effect of motion can be introduced into relaxation at low applied fields. Now we turn to a similar discussion in the rotating reference frame. The discussion is based on the original idea of Redfield[3,14] that in the presence of an alternating field sufficiently strong to produce saturation, the spin system can be described by a temperature in a reference system rotating in the sense of the precession at the angular frequency ω of the alternating field.

The rotating coordinate transformation is quite standard. Using it, Redfield shows that in the rotating frame we have an effective Hamiltonian $\mathcal{H}$

$$\mathcal{H}=\mathcal{H}_z+\mathcal{H}_d{}^0, \tag{43}$$

where

$$\mathcal{H}_z=-\gamma\hbar[(H_0-(\omega/\gamma))I_z+H_1I_x], \tag{44}$$

where

$$I_z=\sum_j I_{zj} \tag{45}$$

is the total z component of magnetization. I_z is similarly defined. $\mathcal{H}_d{}^0$ is that part of the dipolar Hamiltonian which commutes with I_z. Frequently $\mathcal{H}_d{}^0$ is called the secular part of the dipolar energy.

Redfield's spin temperature idea means that there is a density matrix ρ, given as

$$\rho=\exp(-\mathcal{H}/k\theta)/Z, \tag{46}$$

where

$$Z=\mathrm{Tr}e^{-\mathcal{H}/k\theta}, \tag{47}$$

and where θ is the spin temperature in the rotating frame.

One can again calculate the magnetization $\langle\mathbf{M}\rangle_{\mathrm{av}}$, energy $\bar{E}$, and entropy σ as

$$\begin{aligned}\langle\mathbf{M}\rangle_{\mathrm{av}}&=C\mathbf{H}_{\mathrm{eff}}/\theta,\\ \sigma&=Nk\ln(2I+1)-[C(H_{\mathrm{eff}}{}^2+H_L{}^2)/2\theta^2],\\ \bar{E}&=-[C(H_{\mathrm{eff}}{}^2+H_L{}^2)/\theta],\end{aligned} \tag{48}$$

where C is the Curie constant

$$\begin{aligned}\mathbf{H}_{\mathrm{eff}}&=\mathbf{k}[H_0-(\omega/\gamma)]+\mathbf{i}H_1\\ &\equiv\mathbf{k}h_0+\mathbf{i}H_1,\end{aligned} \tag{49}$$

and

$$CH_L{}^2=\frac{1}{k}\frac{\mathrm{Tr}(\mathcal{H}_d{}^0)^2}{(2I+1)^N}. \tag{50}$$

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

The relaxation in the rotating frame was first discussed by Redfield.[14] Solomon and Ezratty[15] have re-expressed Redfield's results.

We consider that the energy, $\bar{E}$, is given as

$$\begin{aligned}\bar{E}&=\langle\mathcal{H}_z\rangle+\langle\mathcal{H}_d{}^0\rangle\\ &=-h_0\langle M_z\rangle-H_1\langle M_x\rangle+\langle\mathcal{H}_d{}^0\rangle.\end{aligned} \tag{51}$$

We assume that at all times there is rapid transfer of energy between the parts of the spin system. We postulate certain elemental relaxation processes, however, which change $\langle M_z\rangle$, $\langle M_x\rangle$, and $\langle\mathcal{H}_d{}^0\rangle$. They obey the equations

$$\partial\langle M_z\rangle/\partial t=(M_0-\langle M_z\rangle)/T_a, \tag{52a}$$

$$\partial\langle M_x\rangle/\partial t=-\langle M_x\rangle/T_b, \tag{52b}$$

and

$$\partial\langle\mathcal{H}_d{}^0\rangle/\partial t=(\langle\mathcal{H}_d{}^0\rangle_l-\langle\mathcal{H}_d{}^0\rangle)/T_c, \tag{52c}$$

where

$$\begin{aligned}M_0&=CH_0/\theta_l\\ \langle\mathcal{H}_d{}^0\rangle_l&=-CH_L{}^2/\theta_l,\end{aligned} \tag{53}$$

where θ_l is the lattice temperature. Consider Eq. (52a). This gives the rate of change of $\langle M_z\rangle$ due to an elemental relaxation process with the lattice. There will be *additional* contributions due to the fact that M_z does not commute with either the Zeeman or the dipolar parts of the Hamiltonian. These latter effects are what is responsible for the exchange of energy between the dipolar and Zeeman reservoirs in the process of bringing about a uniform spin temperature in the rotating frame. We may say that Eq. (52a) is analogous to one of the terms in the Boltzmann equation in which we write the rate of change of the distribution function due to one type of collision. Equations (52b) and (52c) have similar meanings.

Then, using Eqs. (48), (51), and (52) and neglecting $\langle\mathcal{H}_d{}^0\rangle_l$, one can show that M, the magnitude of the magnetization, relaxes exponentially towards the equilibrium value M_{eq} given as

$$M_{\mathrm{eq}}=\frac{M_0H_{\mathrm{eff}}[h_0/T_a]}{(h_0{}^2/T_a)+(H_1{}^2/T_b)+(H_L{}^2/T_c)}, \tag{54}$$

with a time constant T given by

$$\frac{1}{T}=\frac{1}{h_0{}^2+H_1{}^2+H_L{}^2}\left[\frac{h_0{}^2}{T_a}+\frac{H_1{}^2}{T_b}+\frac{H_L{}^2}{T_c}\right]. \tag{55}$$

We will describe an experimental technique for measuring T in a later paper.[2] Exactly at resonance, $M_{\mathrm{eq}}=0$ and

$$\frac{1}{T}=\frac{1}{H_1{}^2+H_L{}^2}\left[\frac{H_1{}^2}{T_b}+\frac{H_L{}^2}{T_c}\right]. \tag{56}$$

This result was obtained by Redfield and by Solomon and Ezratty who point out that for a metal the con-

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

duction electron contributions to T_a and T_b are equal. T_a is in this instance the spin-lattice relaxation time, T_1. They remark that

$$1/T_c=\alpha/T_1, \tag{57}$$

where $\alpha=2$ when nuclei are flipped independently by electrons. Thus the conduction electrons contribute

$$\frac{1}{T}=\frac{1}{T_1}\frac{H_1^2+\alpha H_L^2}{H_1^2+H_L^2}. \tag{58}$$

We are interested in the phenomenon of atomic motion. Following the argument of the previous section, we can assume that before a jump the dipolar energy of a typical spin is proportional to $\langle\mathcal{H}_d\rangle$, whereas after the jump it is zero if the final local field is random. If the final local field is not random, then we assume (and prove below) that the *change* in energy is proportional to $\langle\mathcal{H}_d\rangle$. Since the jumping is proportional to $(1/\tau)$, we get

$$\partial\langle\mathcal{H}_d\rangle/\partial t=-\beta\langle\mathcal{H}_d\rangle/\tau, \tag{59}$$

where β is a constant of order unity, and where we have neglected the term $\langle\mathcal{H}_d\rangle_l$ on the right. We get therefore

$$1/T_c=\beta/\tau. \tag{60}$$

In the later sections we compute β in several cases.

Introducing β, then we find exactly at resonance that

$$\frac{1}{T}=\frac{1}{H_1^2+H_L^2}\left[\frac{H_1^2}{T_b}+\frac{H_L^2}{T_c'}+\frac{\beta H_L^2}{\tau}\right], \tag{61}$$

where T_c' is the contribution to T_c due to all mechanisms other than atomic motion. Often $T_b\cong T_c'\cong T_1$. Equation (61) shows us that measurement of T can tell us about atomic motion when $\tau<T_1$.

V. DIFFUSION EFFECTS IN THE ROTATING FRAME

In this section we apply the general considerations of the previous sections to discuss the effects of self-diffusion in the rotating reference system.

We shall assume the diffusion goes by a vacancy mechanism, and that a given vacancy can jump into any of G distinct positions in an elemental jump with equal probability. The positions are ordinarily crystallographically equivalent.

Let us consider that there are N_v vacancies, and that the mean time a vacancy sits between jumps is τ_v.

The dipolar Hamiltonian[12] $\mathcal{H}_d^0$ is

$$\mathcal{H}_d^0=\frac{\gamma^2\hbar^2}{4}\sum_{i,k}\frac{(1-3\cos^2\theta_{ik})}{r_{ik}^3}(3I_{zi}I_{zk}-\mathbf{I}_i\cdot\mathbf{I}_k)$$
$$\equiv\tfrac{1}{2}\sum_{i,k}A_{ik}(3I_{zi}I_{zk}-\mathbf{I}_i\cdot\mathbf{I}_k), \tag{62}$$

where θ_{ik} is the angle between the applied field and the internuclear vector $\mathbf{r}_{ik}$.

We can consider two limiting cases. In the first case, τ_v is much longer than the rigid lattice T_2. (Actually, it is the cross-relaxation time between the dipolar and Zeeman systems which must be compared with τ_v. However, as long as H_1 is comparable to H_L, this is nearly T_2.) In this case, the spin system has time to come to thermal equilibrium between vacancy jumps. It is then appropriate to say that just before each jump the system is described by a spin temperature. Moreover, the system has lost all memory of how the vacancy has arrived at its position, so that we do not need to ask whether subsequent jumps return it to an earlier position.

In the second case, we require only that τ, the mean time between nuclear jumps, be less than the rigid lattice T_2. The number of nuclei N is much greater than the number of vacancies N_v. However, each time a vacancy jumps an atom also jumps. Thus

$$N/\tau=N_v/\tau_v. \tag{63}$$

We have then the chance that $\tau_v\ll T_2$. In this case, the spin system is not able to arrive at a spin temperature between vacancy jumps. We can think then of a trail of hot spins left behind by the vacancy. It is probably an excellent approximation to neglect this effect, however, and to say that *most* of the atoms near a vacancy have spin orientations characteristic of the average temperature of the sample. In this connection the following theorem is useful.

Consider a nonuniform distribution of spin temperature. Then the spin temperature θ becomes a function of position $\theta(\mathbf{r})$. The total energy of the spins and the total magnetization (for simplicity we assume we are exactly at resonance) are

$$\bar{E}=-\int\frac{C(H_1^2+H_L^2)}{\theta(\mathbf{r})}d^3r$$
$$=-C(H_1^2+H_L^2)\int\frac{1}{\theta(\mathbf{r})}d^3r, \tag{64}$$

$$M=-\int\frac{CH_1d^3r}{\theta(\mathbf{r})}=CH_1\int\frac{1}{\theta(\mathbf{r})}d^3r=\frac{H_1\bar{E}}{H_1^2+H_L^2}.$$

Therefore, in any redistribution of θ which keeps $\bar{E}$ constant, as would be involved in the equilibration of the spin temperature following a diffusion jump, the total magnetization M also remains constant.

The trail of hot spins left behind a vacancy will therefore diffuse the hot temperature throughout the sample, but in the process will not affect M.

We then make the assumption that when a vacancy jumps, the nuclei near to it are at the average spin temperature of the sample. Since typically one near neighbor just took part in a jump, it is "hot," and we should not include it in computing energy changes. Since

$\tau_v \ll T_2$, however, a vacancy may jump back into a previous position. The correlations are complicated to follow. If we are considering the ith jump of a vacancy, we wish to be sure that it does not simply undo jump $(i-1)$, and furthermore that jump $(i+1)$ does not undo jump i. Since a fraction $1/G$ of all jumps undo a previous one, we have that the jumping rate of distinct jumps is $(G-2)/(G\tau_v)$ instead of $(1/\tau_v)$. The trail of hot spins further reduces the relaxation rate by a fraction $1/G$. We have not attempted to give a more rigorous discussion of the case $\tau_v \ll T_2$ since in practice corrections of this magnitude (typically to 20 to 30%) are rather unimportant since τ_v varies over many orders of magnitude in typical experiments, and there is little meaning to such corrections.[16]

We shall therefore work out the analysis of the basis that $\tau_v > T_2$, keeping in mind that we can approximate the case $\tau_v < T_2$ by replacing τ_v by $\tau_v G/(G-3)$.

Our problem is now to calculate T_c, the rate at which the dipolar energy changes. Of course, we use the general theory developed in Sec. III. In any given jump, we can say that the dipolar Hamiltonian changes since the relative coordinates of the nuclei change. However, the spin factors do not change. Thus, characterizing the quantum states of the total Hamiltonian by n and calling $\mathcal{H}_d{}^0$ the dipolar Hamiltonian before the jump, and $\mathcal{H}_{dq}{}^0$ the Hamiltonian after the jump, we have in the high-temperature approximation:

$$\bar{E}_{\text{after}}-\bar{E}_{\text{before}} = \frac{1}{k\theta(2I+1)^N}[\mathrm{Tr}(\mathcal{H}_d{}^0)^2-\mathrm{Tr}(\mathcal{H}_d{}^0\mathcal{H}_{dq}{}^0)]. \quad (65)$$

We note first that in the jump only one nucleus, which we label the rth, makes a jump. Therefore, the only A_{ij}'s which change are those in which either i or $j=r$. Using the definition of $H_L{}^2$, we can write

$$\frac{\mathrm{Tr}(\mathcal{H}_d{}^0)^2}{k\theta(2I+1)^N} = U\sum_{i,j}{}'(A_{ij})^2 = \frac{CH_L{}^2}{\theta}, \quad (66)$$

where the prime indicates that only occupied lattice sites are included and U is a factor given by the trace over spin variables. Removing the restriction on the lattice sites, we get

$$CH_L{}^2 = U\left(\frac{N}{N+N_v}\right)^2\sum_{i,j}(A_{ij})^2 \cong NU\sum_i(A_{ij})^2, \quad (67)$$

where the sum over i and j includes *all* lattice sites (even those occupied by vacancies), and where we have used the approximation that $N_v \ll N$. Then

$$\mathrm{Tr}\frac{(\mathcal{H}_d{}^0\mathcal{H}_{dq}{}^0)}{k\theta(2I+1)^N} = U\sum_{ij}{}' A_{ij}A_{ijq}, \quad (68)$$

where A_{ijq} is the value of A_{ij} after the jump. Subtracting, we get

$$\bar{E}_{\text{after}}-\bar{E}_{\text{before}} = U\sum_{ij}{}'(A_{ij}{}^2-A_{ij}A_{ijq}) = 2U\sum_i{}'(A_{ir}{}^2-A_{ir}A_{irq}), \quad (69)$$

where we have used the fact that only the rth nucleus jumps, that either i or j can be r, and that $A_{ij}=A_{ji}$. Now in sums of Eq. (69), nucleus r has a vacancy next to it, so that the sums do not include all lattice sites. If we let q stand for the label of the vacant lattice site into which the rth nucleus jumps, we can write Eq. (57) as

$$\bar{E}_{\text{after}}-\bar{E}_{\text{before}} = 2U[\sum_i(A_{ir}{}^2-A_{ir}A_{iq})-A_{qr}{}^2], \quad (70)$$

where now the sum i goes over all other lattice sites. (We here neglect N_v compared to N and use the fact that $A_{ii}=0$ for all i.) If we now define p_q as

$$p_q = (A_{qr}{}^2+\sum_i A_{ir}A_{iq})/\sum_i A_{ir}{}^2 \quad (71)$$

and make use of Eq. (67) we can say that

$$\bar{E}_{\text{after}}-\bar{E}_{\text{before}} = \frac{2(1-p_q)}{N}\frac{CH_L{}^2}{\theta} = -\frac{2(1-p_q)}{N}\langle\mathcal{H}_d{}^0\rangle. \quad (72)$$

This is the change in energy for a jump from site r to q. There are in fact G distinct values of q for a given r as we have remarked, so that the average energy change per jump is

$$\bar{E}_{\text{after}}-\bar{E}_{\text{before}} = -\frac{2}{N}\left(1-\frac{1}{G}\sum_q p_q\right)\langle\mathcal{H}_d{}^0\rangle = -\frac{2}{N}(1-p)\langle\mathcal{H}_d{}^0\rangle, \quad (73)$$

where q ranges over the G possible values. This equation defines the quantity p.

$$p = \frac{1}{G}\sum_q[A_{qr}{}^2+\sum_i A_{ir}A_{iq}]/\sum_i A_{ir}{}^2. \quad (74)$$

Equation (73) gives the average energy change in a single vacancy jump. Since there are N_v vacancies each

[16] We have neglected electric quadrupole effects when the vacancy is close to an atom. For the case of $\delta\omega_Q\tau_v \ll 1$, where $\delta\omega_Q$ is the quadrupole splitting frequency, this will introduce weak collisions which can be included in T_a, T_b, and T_c. However, this will be a small effect compared to the dipole effect which represents, as we have seen, a "strong" collision.

jumping at a rate $1/\tau_v$, the total rate of change of dipolar energy due to jumping is

$$\frac{\partial\langle\mathcal{H}_d{}^0\rangle}{\partial t}=-\frac{N_v}{\tau_v}\frac{2}{N}(1-p)\langle\mathcal{H}_d{}^0\rangle$$

$$=-\frac{2}{\tau}(1-p)\langle\mathcal{H}_d{}^0\rangle, \tag{75}$$

where we have used Eq. (63). Therefore

$$1/T_c=(2/\tau)(1-p). \tag{76}$$

As a numerical example, we have computed p for the case of vacancy diffusion by jumps to nearest-neighbor sites for a body-centered cubic lattice. The result, averaged for a powder, is $p=0.266$.[17]

The analysis we have given treats the effect of diffusion for the rotating frame. A completely analogous procedure gives one the expression for the effect of diffusion on T_d in the laboratory frame. It turns out that the same expression for p arises in both our case and Torrey's. Actually, he does not make explicit mention of the fact that a particular lattice site is vacant when a jump occurs, but it is implicit in his equations.[18]

The calculation we have made applies to the case in which $H_L\sim H_1$, so that the dipolar and Zeeman energies can rapidly exchange. In terms of Eq. (61) we get a diffusion contribution to the relaxation time T of

$$\frac{1}{T}=\frac{2}{\tau}(1-p)\frac{H_L{}^2}{H_1{}^2+H_L{}^2}. \tag{77}$$

It is of interest to consider the expression for the case of $H_1\gg H_L$, for which the spin temperature approximation is not valid, but for which a calculation analogous to Torrey's should apply. We then have to consider transitions in the Zeeman energy produced by the time variation of $\mathcal{H}_d{}^0$. Actually, when H_1 is so strong that the spins become quantized along H_1 in the rotating frame, we are concerned only with that part of $\mathcal{H}_d{}^0$ which does not commute with I_x, since quantization is along the x direction. This nonsecular term $\mathcal{H}_d{}^{0n}$ is, if we are exactly at resonance,

$$\mathcal{H}_d{}^{0n}=\tfrac{3}{4}\sum_{i,j}A_{ij}(I_{iz}I_{jz}-I_{iy}I_{jy})$$

$$=\tfrac{3}{8}\sum_{i,j}A_{ij}(I_i{}^+I_j{}^++I_i{}^-I_j{}^-), \tag{78}$$

where the $I_i{}^\pm$ are the raising and lowering operators relative to the x axis. It is then a simple matter to use the expression of Eq. (78) in which the A_{ij}'s are time-dependent functions and to take over Torrey's calculated correlation functions to get

$$\frac{1}{T}=\frac{2(1-p)}{\tau}\frac{H_L{}^2}{H_1{}^2}\frac{3}{4}. \tag{79}$$

That is, for $H_1{}^2>H_L{}^2$, the relaxation rate is 3/4 of the value predicted by Eq. (77). Of course, Eq. (79) is most seriously in error if we try to extrapolate it to low values of H_1, since it predicts that T goes to zero as H_1 goes to zero.

Lowe, who has independently realized that motional effects can be observed in the rotating frame, has made a calculation along the lines of Eq. (79). We demonstrate the fact that Eq. (77) correctly describes the results for self-diffusion in lithium metal in the limit $H_1\sim H_L$ in a following paper.[2]

VI. PAIR ROTATIONS

In the previous section we outlined the effect of atomic diffusion on the relaxation time T_c. Another important class of atomic motion is that of molecular rotation. In this instance there are certain nuclei which can be thought of as being imbedded in a rigid framework which reorients. The internuclear distances within the framework then do not change, though the angles θ_{ij} do. However, there is a simultaneous change of both distance and angle if the nuclei i and j are in different molecules. One can envisage situations in which only one molecule turns at a time, or situations in which correlated motions arise. For diffusion there is the possibility that $\tau_v\ll T_2$ even though $\tau\gg T_2$. That situation led to the possibility that the nuclei which actually jump are not in a region properly characterized by a spin temperature. For the case of rotation it is probably safe to say that rotation typically occurs with little spatial correlation to previous rotations. Therefore, as long as $\tau\gg T_2$, we can be confident that a typical nucleus finds itself in surroundings described by the average temperature.

It is perhaps most useful to work out a concrete example. We shall do so first for a system consisting of pairs of nuclei which can jump between various positions. For the purpose of this example we neglect interactions between one pair and another. Thus, if we had protons in H_2O, we consider the H-H coupling solely within a given water molecule. It is in fact quite straightforward to add the contribution of the H-H coupling between different water molecules. This we do at the end of this section, but to obtain anything more than a completely general formula would require a specific assumption about crystal structure, just as would be the case for the intermolecular contributions to the second moment.

---

[17] We have discovered an algebraic error in our calculation of p mentioned in Ref. 2. The value given there was $p=0.52$. The new value of p improves the agreement between our experimental data and the value predicted by extrapolating the data of Holcomb and Norberg.

[18] A. G. Redfield and M. Eisenstadt have discussed correlation effects in Phys. Rev. **132**, 635 (1963).

A. The Intramolecular Contribution

Let us turn now to the intramolecular contribution. We consider pair couplings only. However, if one had more than pairs, as in a CH_3 group, the relaxation time is expressible as a sum of pairwise couplings. Therefore, our calculations of T_c for jumping about a threefold axis actually give the answer for CH_3, although we work out the case of one pair only.

Let us, therefore, consider a pair of nuclei with relative positions $\mathbf{r}_{ij}$. Let us define a set of axes x, y, z (see Fig. 1). We take the z axis along the axis of rotation of the pair. We choose the x axis so that the static field H_0 lies in the x–z plane, making angle θ_H with the rotation axis. We denote the polar angles of $\mathbf{r}_{ij}$ as θ_r and φ_r. Then, the angle θ, between $\mathbf{r}_{ij}$ and $\mathbf{H}_0$ is given by the equation

$$\cos\theta=\cos\theta_H\cos\theta_r+\sin\theta_H\sin\theta_r\cos\varphi_r. \tag{80}$$

We assume that there are G possible positions for the vector $\mathbf{r}_{ij}$. Thus, for a twofold rotation axis, $G=2$. We denote each position by a symbol q, where $q=1, 2, \cdots, G$. Then, we can write the dipolar energy as

$$\langle\mathcal{H}_d{}^0\rangle=-\frac{U}{G}\sum_q A_{ijq}{}^2, \tag{81}$$

where U is a constant for various q's. When q jumps to a new position s, we have a change in dipolar energy of

$$\langle\mathcal{H}_d{}^0\rangle_{\text{final}}-\langle\mathcal{H}_d{}^0\rangle_{\text{initial}}=U(A_{ijq}{}^2-A_{ijs}), \tag{82}$$

where we include just those values of s into which a jump is possible. (For example, with a fourfold axis we might assume only rotations of $\pm\pi/2$ to be possible and would, therefore, exclude values of s corresponding to a rotation of π.)

The average change in dipolar energy, $\langle\Delta E\rangle_{\text{av}}$, is obtained by averaging Eq. (82) over the G possible values of q and G' possible values of s for a given q.

$$\begin{aligned}\langle\Delta E\rangle_{\text{av}}&=\frac{1}{GG'}U\sum_{q,s}[A_{ijq}{}^2-A_{ijq}A_{ijs}]\\&=-(1-p)\langle\mathcal{H}_d{}^0\rangle,\end{aligned} \tag{83}$$

defining p. We have then

$$p=\sum_{q,s}A_{ijq}A_{ijs}/\sum_{q,s}(A_{ijq})^2, \tag{84}$$

where the summation over s in the denominator means that we repeat the value for q for each value of s. [A similar comment applies to the first term on the right of the top line of Eq. (83).] The relaxation time T_c is then

$$1/T_c=(1-p)/\tau, \tag{85}$$

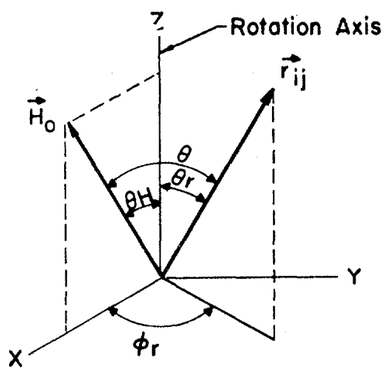

FIG. 1. The relationship between the axis of molecular rotation, z, the internuclear vector, $\mathbf{r}_{ij}$, and the static field, $\mathbf{H}_0$, defining the angles θ_H, θ_r, and φ_r.

where τ is the mean time between rotational jumps. Using the fact that

$$A_{ij}\propto(1-3\cos^2\theta_{ij}), \tag{86}$$

we get

$$p=\sum_{q,s}[(1-3\cos^2\theta_{ijq})(1-3\cos^2\theta_{ijs})/\sum_{q,s}(1-3\cos^2\theta_{ijq})^2], \tag{87}$$

defining

$$\begin{aligned}A&=1-3\cos^2\theta_H\cos^2\theta_r,\\B&=-6\sin\theta_H\cos\theta_H\sin\theta_r\cos\theta_r,\\C&=-3\sin^2\theta_H\sin^2\theta_r.\end{aligned} \tag{88}$$

We find readily that

$$p=\sum_{q,s}\frac{(A+B\cos\varphi_q+C\cos^2\varphi_q)(A+B\cos\varphi_s+C\cos^2\varphi_s)}{\sum_{q,s}(A+B\cos\varphi_q+C\cos^2\varphi_q)^2}, \tag{89}$$

where it is still to be understood that s takes on the values allowed in Eq. (82).

We can easily work out values for p for different cases. We shall take three cases, the 2-, 3-, and 4-fold rotation axes, *all with the internuclear axis perpendicular to the rotation axis* ($\theta_r=\pi/2$). A simple check on all our formulas is provided by the fact that they must give $p=1$ if $\theta_H=0$, since in this case θ_{ij} is not changed by a jump.

Case I: *2-fold rotation axis*. $p=1$ (the dipolar energy is unchanged by the rotation, since it keeps $\cos\theta_{ij}$ the same). Then $T_c=\infty$.

Case II: *3-fold rotation axis*. Then, we let $\varphi_r=\varphi_0$, $\varphi_0+120°$, $\varphi_0-120°$.

$$p=\frac{16-48\sin^2\theta_H+27\sin^4\theta_H}{16-48\sin^2\theta_H+54\sin^4\theta_H}. \tag{90}$$

If, for example, $\theta_H=\pi/2$, $p=-5/22$.

Case III: *4-fold rotation axis (jumps of* $\pm\pi/2$). $\varphi_r=\varphi_0$, $\varphi_0+\pi/2$, $\varphi_0+\pi$, $\varphi_0-\pi/2$.

$$p=\frac{2[1-3\sin^2\theta_H+9\sin^4\theta_H\sin^2\varphi_0\cos^2\varphi_0]}{2-6\sin^2\theta_H+9\sin^4\theta_H(\cos^4\varphi_0+\sin^4\varphi_0)}. \tag{91}$$

If $\varphi_0=0$, $\theta_H=\pi/2$, $p=-\frac{4}{5}$.

We see that in general studies of the angular dependence of the relaxation times as one varies the

orientation of H_0 with respect to the molecular axes (θ_H) can tell us the type of motion involved. This sort of information is quite analogous to the line-narrowing studies of molecular rotation done in conventional resonance.

B. Intermolecular Contributions

It is a straightforward matter to generalize Eq. (87) to take into account the intermolecular contribution. The labels i and j then refer to atoms not necessarily in the same molecule. We get a particularly simple form when the molecules can only jump about a 2-fold axis perpendicular to the internuclear line within the molecule, as when the protons of a water molecule exchange positions. Let us use the labels i, q, and r to label the *positions* of the nuclei which will be involved in the dipole sum. We let q and r stand for the two sites within a molecule whose nuclei exchange positions. We assume the other nuclei i do not move when nuclei at q and r interchange. Then we get

$$\frac{1}{T_c}=\frac{2}{\tau}\sum_i(A_{iq}-A_{ir})^2/\sum_i(A_{iq}+A_{ir}^2)\,, \tag{92}$$

where

$$A_{iq}=(1/r_{iq}^3)(3\cos^2\theta_{iq}-1)\,. \tag{93}$$

It is important to realize that Eq. (92) holds true as long as the various dipolar and Zeeman terms can exchange energy in the rotating reference frame. To the extent that this holds true, Eq. (92) automatically takes care of splittings of the resonance into several components, as when one has a Pake doublet in a water molecule.

ACKNOWLEDGMENTS

We wish to thank our colleagues Dr. P. Mansfield, Dr. P. R. Moran, Mrs. Judith Franz, and Professor Leo Kadanoff for stimulating conversations on a variety of the theoretical questions related to this work.

PHYSICAL REVIEW VOLUME 135, NUMBER 4A 17 AUGUST 1964

Electronic Structure of Magnesium Silicide and Magnesium Germanide*

PETER M. LEE
Institute for the Study of Metals and Department of Physics, University of Chicago, Chicago, Illinois
(Received 30 March 1964)

Pseudopotentials previously calculated for metallic magnesium and semiconductors silicon and germanium are used to calculate the electronic energy-band spectra of magnesium silicide and magnesium germanide. Results are obtained for the energy gap and the positions of the valence-band maximum and conduction-band minimum which are in agreement with what is known experimentally about these substances. The use of the energy levels determined is discussed in interpreting ultraviolet reflectance spectra of these compounds. Finally, on the basis of the present calculations, some speculations are made about the nature of the electron and hole energy surfaces in the semimetallic region of the alloy system $Mg_2\,(Sn)_x\,(Pb)_{1-x}$.

I. INTRODUCTION

THE series of compounds Mg_2Si, Mg_2Ge, Mg_2Sn, and Mg_2Pb have the interesting property that while the first three members of the series are semiconductors, Mg_2Pb has electrical properties which are definitely of a metallic nature. The transition appears to be smooth and occurs somewhere in the alloy system $Mg_2(Sn)_x(Pb)_{1-x}$. The present work reports results of band-structure calculations on the first two members of the series. These have been carried out using pseudopotentials which were originally evaluated for the elements separately. Although there has been some discussion of the usefulness of these pseudopotentials, the present calculation is, as far as the author knows, the first one for a compound which takes over the pseudopotentials determined separately for the various constituent elements, one metallic and one insulating. The approximations involved in doing this are discussed in the text.

Experimental measurements of the electrical properties have been made on polycrystalline samples of all members of the series by Busch and Winkler[1,2] and of the resistivity and Hall effect on single crystals of magnesium silicide and germanide by Danielson and co-workers.[3–5] Piezoresistance measurements of magnesium silicide[6] have been made and the position of the bottom of the conduction band determined from

* Work supported by the National Science Foundation and also by a general grant to the Institute for the Study of Metals by the Advanced Research Projects Agency.

[1] G. Busch and U. Winkler, Physica **20**, 1067 (1958).
[2] U. Winkler, Helv. Phys. Acta **28**, 633 (1955).
[3] R. G. Morris, R. D. Redin, and G. C. Danielson, Phys. Rev. **109**, 1909 (1958).
[4] R. D. Redin, R. G. Morris, and G. C. Danielson, Phys. Rev. **109**, 1916 (1958).
[5] M. W. Heller and G. C. Danielson, in *Proceedings of the International Conference on Semiconductor Physics*, (Czechoslovakian Academy of Sciences, Prague, 1961), p. 881.
[6] W. B. Whitten and G. C. Danielson (to be published).