PHYSICAL REVIEW VOLUME 113, NUMBER 6 MARCH 15, 1959

Nuclear Spin Relaxation in Normal and Superconducting Aluminum*

L. C. HEBEL†‡ AND C. P. SLICHTER§
University of Illinois, Urbana, Illinois

(Received October 22, 1958)

Nuclear spin-lattice relaxation times have been measured in normal and superconducting Al from 0.94°K to 4.2°K, and as a function of static field in the normal state. In the normal state the relaxation rate is proportional to temperature as predicted by Redfield and others. The field dependence is somewhat greater than predicted. Relaxation in the superconductor was studied by a field cycling method which allowed the measurements to be made in the normal state but relaxation to occur in the superconductor. The results disagree with a simple two-fluid model, but are explained by the theory of Bardeen, Cooper, and Schrieffer. The contrast between the temperature dependence of nuclear relaxation and ultrasonic absorption confirms the central feature of the Bardeen-Cooper-Schrieffer theory that electrons of opposite spin and momentum are correlated.

I. INTRODUCTION

CONDUCTION electrons strongly influence the nuclear magnetic resonance in a normal metal through the interaction of their magnetic moments with those of the nuclei. Two effects are important. First, the electrons alter the static magnetic field seen by the nuclei from the value of the applied magnetic field; the shift in the value of external field at which the nuclear resonance occurs in the metal, compared to a salt, is the so-called "Knight shift."[1] Secondly, energy exchanges with conduction electrons at the top of the Fermi distribution usually provide the quickest means for the nuclear spins to come into thermal equilibrium with their surroundings—the process characterized by the "nuclear spin-lattice relaxation time," T_1.[2]

Several years ago Bardeen and Fröhlich published preliminary theories of superconductivity which showed that in all likelihood the wave functions and energies of electrons near the Fermi energy are drastically modified when a metal makes the transition into the superconducting phase. Since these are the very electrons which are important in both the Knight shift and in nuclear relaxation, it was clear that measurements of the Knight shift and T_1 in both normal and superconducting phases of a metal should provide a test of any theory of superconductivity. These expectations have been borne out. In this paper we report experiments on nuclear relaxation in normal and superconducting aluminum and their theoretical interpretation using various theories including the recent one of Bardeen, Cooper, and Schrieffer[3] (hereafter referred to as BCS).

The Meissner effect[4] makes it difficult to do conventional nuclear magnetic resonance experiments in superconductors; that is, superconductors exclude the magnetic fields necessary for magnetic resonance except in a small skin region approximately 10^{-5} cm to 10^{-6} cm thick. By using colloidal particles whose mean diameters were smaller than this field penetration depth, Reif[5] and Knight[6] recently were able to measure the Knight shift in normal and superconducting mercury.

As reported in a preliminary communication,[7] our experiments on relaxation times avoid the impasse posed by the Meissner effect by utilizing another property of superconductors: superconductivity can be destroyed by application of a sufficiently strong magnetic field. The critical field which will destroy superconductivity[4] depends on temperature and is conventionally described by a two-dimensional phase diagram of critical field *versus* temperature. The boundary line between the superconducting and normal phases, the critical field *vs* temperature curve,[4] is approximated fairly closely by the equation

$$H_c(\theta)=H_c(0)[1-(\theta/\theta_c)^2], \qquad (1)$$

where $H_c(\theta)$ and $H_c(0)$ are the critical fields at the temperature θ and absolute 0, respectively, and θ_c is the critical temperature above which superconductivity cannot exist even in zero field. For aluminum, $H_c(0)=98.4$ gauss and $\theta_c=1.172$°K.[8] In a magnetic field greater than the critical field for any given temperature, the metal is normal and the magnetic fields necessary for magnetic resonance experiments can penetrate into the metal in the usual manner.

To obtain the T_1 characteristic of the superconducting phase, the resonance was observed in the normal state but the nuclei allowed to relax in the superconducting

---

* This research supported in part by the Office of Naval Research and in part by a grant from The Alfred P. Sloan Foundation.

† General Electric Predoctoral Fellow. This work is part of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

‡ Now at the Bell Telephone Laboratories, Murray Hill, New Jersey.

§ Alfred P. Sloan Fellow.

[1] Townes, Herring, and Knight, Phys. Rev. **77**, 852 (1950).

[2] See, for example, D. F. Holcomb and R. E. Norberg, Phys. Rev. **98**, 1074 (1955).

[3] Bardeen, Cooper, and Schrieffer, Phys. Rev. **106**, 162 (1957); Phys. Rev. **108**, 1175 (1957).

[4] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952).

[5] F. Reif, Phys. Rev. **102**, 1417 (1956); Phys. Rev. **106**, 208 (1957).

[6] W. Knight, Phys. Rev. **104**, 852 (1956).

[7] L. C. Hebel and C. P. Slichter, Phys. Rev. **107**, 901 (1957).

[8] Cochran, Mapother, and Mould, Phys. Rev. **103**, 1657 (1956).

state. The following cycle was followed: First, the nuclear spins were allowed to come to thermal equilibrium with the lattice in a static magnetic field strong enough so that the metal was in the normal phase. (Approximately 450–500 gauss was used.) The magnetic field was then quickly turned to zero, the metal becoming superconducting; nuclear spin relaxation took place during the time, *t*, that the field was off. Next the field was turned on quickly, the metal returning to the normal phase, and the nuclear resonance signal was observed "on the run" as the magnetic field passed through the resonance value (360 gauss). The nuclear spin-lattice relaxation time characteristic of the superconducting phase could then be obtained by studying the height of the resonance signals so obtained *versus* "*t*," since the height of the resonance signal was a direct measure of the amount of nuclear magnetization left after relaxation.

The technique described in the foregoing is similar to that of Sachs and Turner,[9] Pound and Ramsey,[10] and Abragam and Proctor[11]; it was suggested independently for the superconductivity problem by Redfield, who has recently reported measurements in both normal and superconducting aluminum[12] as well as in lithium and sodium.[13] Throughout our work we have been in close touch with Redfield and have benefited greatly from the exchange of data and ideas.

Because of the Meissner effect, nuclear spin relaxation in the superconducting phase occurs at zero external field. To compare results with the normal metal, it was necessary to measure in the normal state the zero-field relaxation time as a function of temperature. To further test the theory for the normal state, measurements as a function of field were also made in the normal phase.

A detailed analysis of our procedure and a discussion of zero-field relaxation appear in parts II and III of this paper; the experimental details of the measurements in aluminum between 0.94°K and 4.2°K follow in part IV. The results and analysis of T_1 measurements in the normal phase are given in part V. In part VI, the results of measurements of T_1 in the superconducting phase are presented and discussed in terms of several theories of superconductivity; the simple "two-fluid" theory; the one-electron, energy-gap theory; and the new microscopic theory of Bardeen, Cooper, and Schrieffer. Special details and conclusions follow in parts VII and VIII.

II. NUCLEAR SPIN-LATTICE RELAXATION IN STRONG AND WEAK MAGNETIC FIELDS

The nuclear spin-lattice relaxation process in a strong external magnetic field is usually treated in terms of the nuclear magnetization, M. In thermal equilibrium, M is given by Curie's law.

$$M_0 = CH/\theta_L, \tag{2}$$

where M_0 is the thermal equilibrium nuclear magnetization, H is the applied static magnetic field, θ_L is the lattice temperature, and C is the nuclear Curie constant. When the nuclear magnetization is not in thermal equilibrium with the lattice, energy is exchanged between the spin system and the lattice, the magnetization relaxing toward M_0, following the equation

$$dM/dt = (M_0 - M)/T_1. \tag{3}$$

The time constant, T_1, is the nuclear spin-lattice relaxation time—the characteristic time for energy transfer between the nuclear spin system and the lattice.

From an experimental standpoint the nuclear magnetization is especially convenient for characterizing the nuclear spin-lattice relaxation process, because, all other things being equal, the height of a nuclear magnetic resonance signal is directly proportional to the nuclear magnetization present; nuclear resonance techniques, then, provide ways of following the relaxation process with time.

An alternative way of treating the spin-lattice relaxation process is in terms of the nuclear spin temperature. At thermal equilibrium with the lattice, the nuclear spin system has the lattice temperature; that is, the energy levels of the nuclear spin system are populated according to Boltzmann statistics characterized by the lattice temperature.

$$p_n^0/p_m^0 = \exp[(E_m - E_n)/k\theta_L], \tag{4}$$

where p_n^0 and p_m^0 are the thermal equilibrium probability of occupation of the nth and mth nuclear energy levels with energies E_n and E_m, respectively. (E_n and E_m are the exact energies of the total nuclear system.)

When not at thermal equilibrium with the lattice, the nuclear spin system is still often characterized by a temperature, in this case unequal to that of the lattice. That is,

$$p_n/p_m = \exp[(E_m - E_n)/k\theta_s], \tag{5}$$

where θ_s is the spin temperature. When a magnetic field, H, is present an alternative definition of θ_s can often be given in terms of Curie's law; that is,

$$\theta_s = CH/M. \tag{6}$$

Equation (6) can be derived from Eq. (5), but the reverse is not true. Comparing Eqs. (3) and (6), we see that in the presence of a magnetic field

$$\frac{d}{dt}\left(\frac{1}{\theta_s}\right) = \left(\frac{1}{\theta_L} - \frac{1}{\theta_s}\right)\frac{1}{T_1}. \tag{7}$$

---

[9] E. Turner, thesis, Harvard University, 1949 (unpublished).

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

[11] A. Abragam and W. G. Proctor, Phys. Rev. **106**, 160 (1957); Phys. Rev. **109**, 1441 (1958).

[12] A. G. Redfield (private communication).

[13] A. Anderson and A. G. Redfield, *Proceedings of the Fifth International Conference on Low-Temperature Physics, Madison, Wisconsin, August, 1957*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958).

Thus, instead of characterizing nuclear spin-lattice relaxation in terms of growth or decay of magnetization, one may think of the energy exchanged with the lattice as causing the nuclear spin system to warm up or cool off as its spin temperature approaches that of the lattice. From Eqs. (3) and (7), we see that the same T_1 characterizes either treatment of spin-lattice relaxation.

We are concerned with relaxation in *zero* field. If the nuclear system is characterized by a spin temperature (not low enough for nuclear ferromagnetism) Curie's law tells us that in zero field the magnetization is *zero* independent of θ_s. In zero field, relaxation cannot then be characterized by changes in magnetization. As will be shown explicitly in Sec. III, it may still be discussed in terms of spin temperature using Eq. (7). The concept of spin temperature is therefore particularly useful for discussing our experiment.

Further insight into zero-field relaxation is given by a detailed picture of the nuclear orientations. In a strong magnetic field the nuclear temperature measures the extent to which nuclear moments line up along rather than opposed to the external field. In zero external field, the nuclei experience solely the fields due to their neighbors. A nucleus may line up along or opposed to the local field it experiences. The spin temperature in zero external field characterizes the degree of alignment of nuclei in their individual local fields. The fact that the local fields at various parts in the sample have basically random orientations causes the *bulk* nuclear magnetization to be zero.

It is easy to have a spin system at zero field whose spin temperature differs from θ_L. The situation could be obtained, for example, as the result of adiabatic demagnetization from a strong field to zero field carried out in a time short compared to T_1. (Such a demagnetization is part of our field cycling procedure for measuring T_1 as mentioned in part I.) Energy transfer between spin system and lattice would, of course, take place as the spin system came into thermal equilibrium with the lattice; that such is the case is illustrated in paramagnetic salts by the cooling of the lattice after an adiabatic demagnetization of the electron spins.

A full description of relaxation at zero external field requires as its starting point a solution of the energy levels and wave functions of the nuclei which are coupled together by their magnetic dipole fields. The solution has never been obtained. As we will see, the use of a spin temperature enables us to formulate the relaxation time calculation in terms of diagonal sums, whose evaluation does *not* require solution of the exact energy levels. We are thus able to calculate the relaxation time completely. We therefore have two compelling reasons for assuming a spin temperature: (1) the relaxation in zero field is most easily pictured in terms of temperature changes, and (2) the theory of the relaxation time can be carried through.

The arbitrariness of the spin temperature assumption is somewhat mollified by its success in describing similar situations. It has been very fruitful in discussing cooling done by adiabatic demagnetization on paramagnetic salts; spin temperature gives a description of many types of spin situations as discussed by Purcell and Pound.[14] It has proven especially useful in analyzing recent "spin calorimetry" experiments[11] of Abragam and Proctor performed in weak field and recently extended by Schumacher.[15] As discussed more completely in parts III and V, assumption of a spin temperature results in a one-parameter spin-lattice relaxation process even at zero field; (i.e., the approach to equilibrium involves only one exponential). Our experiments, discussed in parts V and VI, indicate that the relaxation at zero field is indeed describable by a one-parameter process in both the normal and superconducting phases.

III. ANALYSES OF PROCEDURE TO MEASURE T_1

In this section the concept of spin temperature will be used to derive the relationship between T_1 and the magnetization measured immediately after the cycle of measurement described in the introduction. Since nuclear spin level splittings in common laboratory magnetic fields are much less than $k\theta$ down to exceedingly low temperatures, the nuclear spins obey Curie's law and have a simple spin specific heat expression in the temperature range of interest in this paper. That means that thermodynamic relations can be used to calculate what happened to both θ_s and M during the cycle of measurement.

If the nuclear spin Hamiltonian, $\mathcal{H}$, is taken to consist of the nuclear Zeeman interaction, $\mathcal{H}_Z$, and the nuclear dipole-dipole interaction, $\mathcal{H}_{dd}$, the spin-lattice interaction being treated as a perturbation, then the expressions for the magnetization, M, and the specific heat at constant field, C, become[16]

$$M=CH/\theta_s;\quad C_H=(b+CH^2)/\theta_s^2, \tag{8}$$

where the nuclear Curie constant, $C=\mathrm{tr}\mathcal{H}_Z^2/kH^2\,\mathrm{tr}1$ and $b=\mathrm{tr}\mathcal{H}_{dd}^2/k\,\mathrm{tr}1$. For the purposes of this section, $(b/C)^{\frac{1}{2}}$ will be defined as H_{loc} since it is of the order of the local magnetic fields at the nuclear site due to the presence of neighboring nuclei. With this notation, we have

$$M=CH/\theta_s;\quad C_H=C(H_{\mathrm{loc}}^2+H^2)/\theta_s^2. \tag{9}$$

At the beginning of the cycle of measurement the nuclear spins are characterized by the lattice temperature, θ_L, since they were allowed to sit for several spin-lattice relaxation times in the magnetic field. When the field is switched to zero, the nuclear spin system is adiabatically demagnetized. From thermo-

---

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

[15] R. T. Schumacher, Phys. Rev. **112**, 837 (1958).

[16] C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Inc., New York, 1947).

dynamics, for an adiabatic process,

$$dQ=C_H d\theta+\theta(\partial M/\partial\theta)_H dH=0. \tag{10}$$

Integrating this equation between the limits H_i and H_f, we obtain

$$\theta_s(H_f)=\theta_s(H_i)[1+(H_f/H_{\mathrm{loc}})^2]^{\frac{1}{2}}/[1+(H_i/H_{\mathrm{loc}})^2]^{\frac{1}{2}}, \tag{11}$$

$$M(H_f)=M(H_i)H_f[1+(H_i/H_{\mathrm{loc}})^2]^{\frac{1}{2}}/H_i[1+(H_f/H_{\mathrm{loc}})^2]^{\frac{1}{2}}, \tag{12}$$

where Eq. (9) has been used. For the case of adiabatic demagnetization from an external field H and the lattice temperature θ_L, to zero field and a spin temperature θ_{s1}, we have

$$\theta_{s1}=\theta_L[1+(H/H_{\mathrm{loc}})^2]^{\frac{1}{2}}\cong\theta_L H_{\mathrm{loc}}/H, \tag{13}$$

$$M_f=\lim_{H_f\to 0}\{M_0H_f[1+(H/H_{\mathrm{loc}})^2]^{\frac{1}{2}}/H[1+(H_f/H_{\mathrm{loc}})^2]^{\frac{1}{2}}\}=0. \tag{14}$$

From Curie's law the magnetization must go to zero at zero field, as in Eq. (14). Upon reaching the low value given by Eq. (13), the spin temperature begins to rise towards the lattice temperature as relaxation takes place. The temperature reached at the end of the relaxation period, θ_{s2}, is obtained by integrating Eq. (4) in terms of the time, t, during which the field is off. For T_1 we use the nuclear spin relaxation time in the superconducting phase, T_{1s}.

$$\frac{1}{\theta_{s2}}=\frac{1}{\theta_L}+\left(\frac{1}{\theta_{s1}}-\frac{1}{\theta_L}\right)\exp(-t/T_{1s}). \tag{15}$$

Next, the field is turned back on to its original value; the spin system is adiabatically remagnetized from θ_{s2}, following Eq. (11), to a temperature θ_s':

$$\theta_s'=\theta_{s2}[1+(H/H_{\mathrm{loc}})^2]^{\frac{1}{2}};\quad M'=CH/\theta_s'. \tag{16}$$

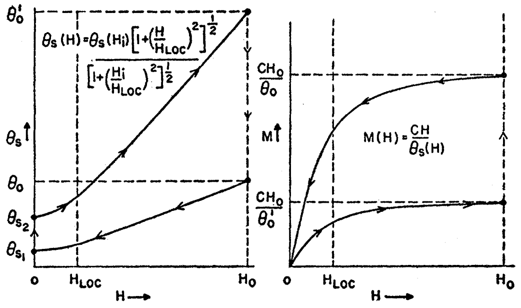
As a result of the spin-lattice relaxation, $\theta_s'>\theta_L$ and $M'<M$. A plot of M *versus* H and θ_s *versus* H for the cycle is shown in Fig. 1 for $H_{\mathrm{loc}}/H=5$. Combining Eqs. (13), (15), and (16), and using Curie's law, the final result for the magnetization after the cycle, M', becomes

$$M'=\frac{C_H}{\theta_L}\left[\frac{\theta_{s1}}{\theta_L}+\left(1-\frac{\theta_{s1}}{\theta_L}\right)\exp(-t/T_{1s})\right], \tag{17}$$

or

$$M'=A+B\exp(-t/T_{1s}).$$

In general, $A\ll B$. Equation (17) is the desired relation between M' measured using nuclear magnetic resonance in the normal phase, and the T_1 characteristic of the superconducting phase. The same type of cycle was used to determine both T_1 *versus* magnetic field and T_1 (at zero field) *versus* temperature above the critical temperature. Experimentally, $\log(M'-A)$ *versus* t gave a straight line in agreement with Eq. (17). This is a good indication that spin temperature is an appropriate variable with which to treat the nuclear spin system in the presence of the nuclear dipole-dipole interaction.



(a) (b)

FIG. 1. (a) A cycle of the spin temperature, θ_s, *versus* magnetic field starting at temperature θ_0 in a field $H_0=5H_{\mathrm{loc}}$, going to zero field adiabatically, relaxing, and returning adiabatically to a temperature θ_0' in the field H_0. (b) Magnetization, M, *versus* magnetic field for the cycle of Fig. 1(a).

Implied in this discussion is the assumption that the demagnetization and remagnetization be adiabatic and reversible. This means, first of all, that the time constant for the change of field must be much shorter than the spin-lattice relaxation time so that T_1 effects can be neglected during the demagnetization and remagnetization. Also it is essential that the field be varied slowly enough compared to the characteristic spin-spin interaction time, T_2, that the nuclear spin system quasi-statically follow the external field and act as a thermodynamic whole. Let us amplify these remarks.

Suppose we start with a nuclear system in thermal equilibrium with the lattice in a strong field and turn the field to zero instantaneously. We may analyze what happens in terms of the sudden approximation: since the wave function immediately after turning the field to zero is the same as it was immediately before, the magnetization is initially unchanged. However, the nuclei now precess about their *local* fields which are randomly oriented. In one or two precession periods (of order of the strong-field T_2), the nuclei will be randomly oriented spatially and the magnetization will be zero. If we then turn the field on again suddenly, we trap the magnetization at zero in the strong field. No resonance will be seen because the magnetization cannot be established in the strong field without spin-lattice relaxation. Thus we lose the resonance completely and have certainly not performed a reversible process.

It is essential to our experiment that we avoid the situation of *sudden* switching just described. We must turn the field off and on sufficiently slowly for the magnetization to decrease or grow in step with H. Neglecting spin-lattice relaxation, a crude way of describing what we want to happen is as follows: consider a nucleus which is initially lined up along the strong field. As we turn H to zero, the total field seen by the nucleus is the vector sum of H and H_{local}. If we change H sufficiently slowly compared to the precession rate in the total field, the nucleus will remain lined up along the total field. By the time H reaches zero, the nucleus is pointing parallel to H_{local}. Although the spatial orientation of the nuclear moment may have changed, it will still be lined up along the total field it experiences. *The degree of alignment is thus maintained.* If H is turned back on slowly, the nucleus will continue lined up along the total field so that when we reach the initial value of H, the nucleus will only again have its original strong-field spatial orientation. The original bulk magnetization will thus be recovered; *the process is reversible.* Since the degree of nuclear alignment is maintained at all times, we can easily estimate the temperature reached by equating $\mu H/k\theta_L$ to $\mu H_{\text{loc}}/k\theta_s$. The result agrees with Eq. (13).

Of course the local field varies in time, but we may hope that the essential features of our description are maintained. We may say that the most critical region of switching is when H is comparable to H_{local} (since it is at this condition that the total field is changing direction from that of H to that of H_{local}). Under these circumstances the precession period in the total field is comparable to the high-field T_2. Therefore, we must turn the field off slowly compared to T_2. To avoid spin-lattice relaxation effects while the field is being switched, we must turn it off or on faster than T_1. The switching time, τ, must therefore satisfy the relation $T_1 > \tau > T_2$.

In measurements in the normal state the requirement on τ is easily satisfied. Since $T_2 = 35$ microseconds and the normal state relaxation time T_{1n} is about 0.2 to one second in the temperature range of interest, τ can be in the millisecond region. However, the measurement of T_{1s} poses a problem. At the boundary between the normal and superconducting phases, the magnetic field drops from the critical field value to zero in a distance, λ, of about 10^{-5} cm. As the transition between phases is made, this boundary wall sweeps through the sample at a velocity determined either by the size of the particle and the external field time constant, in the case of a powered sample such as was used in this experiment, or by factors beyond one's control when appreciable supercooling is present. Assuming a smooth wall motion with no granular intermediate state in the powdered particles of radius r, this means that $\tau \gtrsim T_2 r/\lambda \cong 3.5$ milliseconds for our sample. A precipitous switching, of course, shows up experimentally as a loss in signal as described above.

IV. EXPERIMENTAL DETAIL

The resonance was observed with a bridgeless system similar to that used by Schumacher.[17] A 400-kc oscillator of the Pound-Watkins type[18] fed the rf through a high impedance to the sample coil, which was directly connected to the grid of an rf amplifier. As used, the apparatus was sensitive only to changes in χ'', the imaginary part of the complex nuclear susceptibility. The amplified signal was then detected, and after further audio amplification it was displayed both on an oscilloscope and on a gated detector; the latter was used to improve the signal-to-noise ratio.

A special laminated magnet was constructed out of 0.014-in. thick sheets of silicon steel, so that it could be pulsed rapidly. Adjustable laminated sections were provided near the gap as shims to obtain favorable homogeneity of magnetic field over the aluminum sample. The current through the magnet was switched using Western Electric mercury relays.

In order to work at the critical temperature and below in aluminum ($\theta_c = 1.172$°K), a 3-Dewar system was used—an outer liquid nitrogen Dewar enclosed a Dewar containing liquid helium at 4.2°K and an inner Dewar containing liquid helium which was pumped over by an oil booster pump backed up with a mechanical pump. The inner Dewar contained the sample which sat in the helium bath which was sealed beneath two one-millimeter constrictions placed for the purpose of cutting down the flow of Rollin film.[19] The lowest temperature attained was 0.94°K. The sample coil and leads sat in the middle Dewar at 4.2°K separated from the sample by a vacuum jacket.

Our sample was "atomized" particles of 99.9% purity obtained from Alcoa and sieved through a 325-mesh sieve. The mean particle size determined by a microscope was about 10 microns. The sample was annealed after many measurements were made, and several of the measurements were repeated to look for effects of strains; Debye-Scherrer x-ray photographs were taken of the annealed and unannealed samples to look for the presence of dislocations. No difference in the two photographs could be detected.

Since the transition between normal and superconducting phases at finite critical fields is a first-order transition, heat must be transferred between the helium bath and the powdered sample to keep the sample at the bath temperature. The characteristic time for thermal contact between particles and bath was measured by the following method. When the field is turned off, the sample is heated to a temperature higher than that of the bath. The sample then cools. When H is turned on again, the transition occurs at a field which corresponds to the sample temperature at turn-on time. By means of an oscilloscope across the sample coil, we could observe when the sample was in the superconducting state, and therefore at what critical field it returned to the normal state. We observed no dependence of the turn-on critical field on the time, t, which elapsed after the sample went superconducting. Therefore, the thermal contact be-

---

[17] R. T. Schumacher and C. P. Slichter, Phys. Rev. **101**, 58 (1956).

[18] G. D. Watkins and R. V. Pound, Phys. Rev. **82**, 343 (1951).

[19] W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., New York, 1942).

TABLE I. Zero-field relaxation in aluminum.

Temperature (°K)	$T_1\theta$ (seconds °K)
1.185	0.45±0.05
2.30	0.45±0.05
3.70	0.46±0.05
4.20	0.52±0.05

tween bath and powdered sample was much faster than any times important to this experiment.

Sample temperatures below the critical temperature were determined by measuring the critical field and using the curve of critical field *versus* temperature determined by Cochran, Mapother, and Mould.[8] This curve was checked for our powdered aluminum sample by use of a carbon resistor thermometer. Temperatures just above the critical temperature were determined using a thermocouple vacuum gauge calibrated for temperatures just below the critical temperature by means of the critical field curve. Temperatures between 4.2°K and 2.2°K were determined by using helium vapor pressure curves.

V. EXPERIMENT AND THEORY IN THE NORMAL PHASE

A. Experimental Results

The discussion to follow will be given in terms of the relaxation rate, R, the reciprocal of the relaxation time T_1. At high magnetic field the relaxation rate in the normal phase, $R_n(\infty)$, is found to be directly proportional to the absolute temperature in many metals[2,13]; this in agreement with the one-electron theories of Korringa[20] and of Overhauser.[21] A sample of our results in aluminum for the relaxation rate at zero external field, $R_n(0)$, are given in Table I; the field dependence of R_n is summarized in Fig. 2. $R_n(0)$ for pure aluminum samples was found to be directly proportional to the absolute temperature in agreement with recent measurements by Redfield and Anderson.[13] We find $R_n(0)/R_n(\infty)=3.35\pm0.35$.

B. Theory of Nuclear Spin-Lattice Relaxation

Korringa,[20] Overhauser,[21] Heitler and Teller,[22] and others have developed theories of the nuclear relaxation in metals for the strong field case. Redfield[23] has developed a general theory of relaxation which enables him to calculate the zero-field relaxation.

We have developed an alternative derivation which we give in order to point out the main features which determine the external field and the temperature dependences of the nuclear spin relaxation by conduction electrons. Our basic equation [Eq. (24)] is a slight generalization of one previously obtained by Gorter.[16] The expression to be derived will also be used in part VI to discuss nuclear relaxation in the superconducting phase. To our knowledge, the first use of the general methods we present was by Van Vleck[24] in his paper on paramagnetic relaxation in Ti and Cr alums. He used the spin temperature concept to get an expression for the relaxation in the form of a diagonal sum, thereby avoiding the necessity of solving a complicated spin Hamiltonian involving combined crystalline and Zeeman splittings.

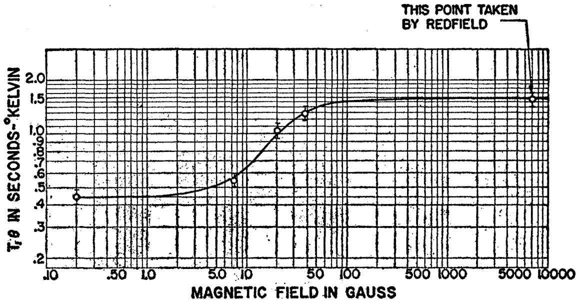


FIG. 2. Magnetic field dependence of $T_1\theta$ for normal aluminum.

As previously mentioned, the exact nuclear spin energy levels and wave functions in the presence of both the nuclear Zeeman interaction and the nuclear dipole-dipole interaction have never been obtained. Nevertheless, the theory below will be formulated in terms of these exact levels and their probability of occupation; the assumption of spin temperature will enable us to put the end result in the form of a diagonal sum, which we can evaluate without obtaining the true level energies.

The time derivative of the total nuclear spin energy of the system relaxing at zero field may be written:

$$\frac{d}{dt}\bar{E}=\frac{d}{dt}\sum_n p_nE_n=\sum_n\frac{dp_n}{dt}E_n=\frac{d}{dt}\bar{E}(\theta_s)=\frac{\partial\bar{E}}{\partial\theta_s}\frac{d\theta_s}{dt}, \tag{18}$$

where p_n and E_n are the probability of occupation and the energy of the exact nuclear spin states. [If we regard Eq. (18) as the first law of thermodynamics applied to the nuclear spins relaxing at zero field, $\partial\bar{E}/\partial\theta_s$ is just the spin specific heat at constant field.]

The interaction between the nuclear spin and the electron spin causes transitions between the various nuclear states n and m. In terms of W_{nm}, the probability per unit time of a transition from the nth to the mth state, we have a family of rate equations,

$$dp_n/dt=\sum_n(p_mW_{mn}-p_nW_{nm}). \tag{19}$$

If we could solve the rate equations, we could substitute the resultant dp_n/dt's back into Eq. (18) to determine how the spin temperature relaxes. We are unable to carry through such a solution. Accordingly,

---

[20] J. Korringa, Physica **16**, 601 (1950).

[21] A. W. Overhauser, Phys. Rev. **89**, 689 (1953).

[22] W. Heitler and E. Teller, Proc. Roy. Soc. (London) **A155**, 629 (1936).

[23] A. G. Redfield, IBM J. Research and Develop. **1**, 19 (1957).

[24] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

we assume that the solution of Eq. (19) is consistent with there always being a spin temperature. Now, the spin temperature assumption means that

$$p_n/p_m=\exp[(E_m-E_n)/k\theta_s]\cong 1-(E_n-E_m)/k\theta_s. \tag{20a}$$

Also, since $\mathrm{tr}\mathcal{H}=0$, we have

$$\sum_n e^{-E_n/k\theta_s}=\sum_n\left(1-\frac{E_n}{k\theta_s}+\cdots\right)=\sum_n \delta_{nn}. \tag{20b}$$

To guarantee equilibrium when $\theta_s=\theta_L$, the principle of detail balance requires

$$\frac{W_{nm}}{W_{mn}}=\exp[(E_n-E_m)/k\theta_L]\cong 1-\frac{(E_m-E_n)}{k\theta_L}. \tag{21}$$

Thus, omitting various algebraic steps,

$$\sum_n E_n\frac{dp_n}{dt}\cong\left(\frac{1}{\theta_s}-\frac{1}{\theta_L}\right)\Big[\sum_{n,m}(E_n-E_m)^2W_{nm}\Big]/2\sum_n\delta_{nn}. \tag{22}$$

Also,

$$\frac{\partial E}{\partial\theta_s}=\frac{\partial}{\partial\theta_s}\left(\frac{\sum_n E_n e^{-E_n/k\theta_s}}{\sum_n e^{-E_n/k\theta_s}}\right)\cong\frac{1}{k\theta_s^2}\frac{\sum_n E_n^2}{\sum_n\delta_{nn}}. \tag{23}$$

Substituting Eqs. (22) and (23) in Eq. (18), we obtain the simple relaxation form of Eq. (5), with

$$R=\frac{1}{T_1}=\tfrac{1}{2}\Big[\sum_{n,m}(E_n-E_m)^2W_{nm}\Big]/\sum_n E_n^2. \tag{24}$$

The relaxation described by Eqs. (18) and (19) is equivalent to a normal-modes problem with real coefficients. It would be characterized by many relaxation times were it not for the simplification introduced by the spin temperature assumption which leads to the simple form of Eq. (24), characterized by a single relaxation rate.

One should note that the lattice temperature appears only in W_{nm}; this fact will make it easy to draw conclusions about the dependence of R on lattice temperature (at any given external field), since the nuclear spin levels n and m are not temperature dependent. Equation (24) also shows us that R should depend on external magnetic field since the energy level spacing and arrangement at any given temperature will be dependent upon the relative strengths of the Zeeman and dipole-dipole interactions.

To calculate the temperature and field dependences explicitly, we evaluate W_{nm} using perturbation theory. The interaction, $\mathcal{H}_{SL}$, between the nuclear moments and those of the conduction electron may be written

$$\mathcal{H}_{SL}=\sum_{i,j}(8\pi/3)\gamma_e\gamma_n\hbar^2\mathbf{I}_i\cdot\mathbf{S}_j\delta(\mathbf{r}_j-\mathbf{R}_i), \tag{25}$$

where i labels the nucleus at $\mathbf{R}_i$ with spin operator $\mathbf{I}_i$ and gyromagnetic ratio γ_n, and j labels the electron at $\mathbf{r}_j$ with spin operator $\mathbf{S}_j$ and gyromagnetic ratio γ_e. $\delta(\mathbf{r}_j-\mathbf{R}_i)$ is a Dirac delta function. We are using in Eq. (25) the interaction appropriate to s states since it is generally much more effective in producing relaxation than the usual dipole-dipole term.

A Bloch function will be used for the electron wave function in the metal: $\psi=\chi_{\mathbf{k}}\eta_j\exp(-i\mathbf{k}\cdot\mathbf{r}_j)$, where η_j is the spin function and $\mathbf{k}$ is the wave vector. We use first-order perturbation theory to calculate the transition probability between two discrete states of the combined system of nuclei plus electrons. We sum over all electrons, taking into account Fermi statistics, to obtain W_{nm}, the transition probability between two *nuclear* states. Labeling nuclear states again by n and m, electron states by $\mathbf{k}$ and s (for spin), the transition probability per unit time between two states of the combined system may be written

$$P_{m\mathbf{k}'s';n\mathbf{k}s}=(2\pi/\hbar)\,|(n\mathbf{k}s|\mathcal{H}_{SL}|m\mathbf{k}'s')|^2\times\delta(E_f-E_i-\hbar\omega), \tag{26}$$

where E_i and E_f are initial and final electron energies and $\hbar\omega$ is the difference in nuclear energies. So far we have taken account of one electron in a given initial state going to a given final state. We must now add the contributions of all electrons (sum over $\mathbf{k}$ and s) and over all final states (sum over $\mathbf{k}'$ and s') taking into account the exclusion principle. Since the probability that a state of initial energy, E_i, be occupied is the Fermi function $f(E_i)$, and the probability of an empty final state is $1-f(E_f)$, we have

$$\begin{aligned}W_{nm}&=\sum_{\mathbf{k},\mathbf{k}',s,s'}P_{m\mathbf{k}'s';n\mathbf{k}s}f(E_i)[1-f(E_f)]\\&=\sum_{s,s'}\int\int dE_idE_fP_{m\mathbf{k}'s';n\mathbf{k}s}f(E_i)\\&\qquad\times[1-f(E_f)]\rho(E_i)\rho(E_f),\end{aligned} \tag{27}$$

where $\rho(E)$ is the density of electron states in energy. Equation (27) is evaluated in detail in Appendix I. The result is

$$W_{nm}=\sum_{i,j,\alpha}a_{ij}(n|I_{i\alpha}|m)(m|I_{j\alpha}|n), \tag{28}$$

where $\alpha=x$, y, or z and where a_{ij} are given by

$$\begin{aligned}a_{ij}=\frac{64\pi^3}{9}\hbar^3\gamma_e^2\gamma_n^2|\chi(0)|^4\frac{\sin^2k_FR_{ij}}{(k_FR_{ij})^2}\int\rho(E_i)\rho(E_f)\\\times f(E_i)[1-f(E_f)]dE_i.\end{aligned} \tag{29a}$$

In this expression, k_F is the magnitude of the wave vector at the Fermi surface, and R_{ij} the distance between nuclei i and j. If we normalize our wave functions to a volume V, we have for the free-electron case $\rho = Vmk/2\pi^2\hbar^2$, so that

$$a_{ij} = \frac{16}{9\pi}\frac{m^2V^2k_F{}^2}{\hbar}\gamma_e{}^2\gamma_n{}^2|\chi(0)|^4\frac{\sin^2 k_FR_{ij}}{(k_FR_{ij})^2}\int f(E_i) \times[1-f(E_f)]dE_i. \quad (29b)$$

As we have remarked, $f(E_i)$ appears in Eq. (29a) because it takes an electron to flip a nucleus and $[1-f(E_f)]$ appears because there must be a hole available for the electron after having flipped the nucleus. $E_f - E_i$ is the difference in Zeeman energy of the initial and final electron states; the electron changes its kinetic energy slightly to conserve total energy for nucleus plus electron. Since $E_f - E_i \ll k\theta_L$, the difference between E_f and E_i can be ignored in the normal phase. The factor $\sin^2 k_FR_{ij}/k_F{}^2R_{ij}{}^2$ reflects the correlation in the relaxation of two nuclei arising because the electron wave function spreads over many nuclei. The correlation vanishes if the electron wave function has zero wavelength. When Eq. (28) is substituted in Eq. (24), and the commutator $[\mathcal{H}, I_{i\alpha}]$ introduced, then

$$R = \frac{1}{T_1} = (-1)\Big(\sum_{i,j,\alpha} a_{ij}\,\mathrm{tr}\{[\mathcal{H},I_{i\alpha}][\mathcal{H},I_{j\alpha}]\}/2\,\mathrm{tr}\mathcal{H}^2. \quad (30)$$

For our case $\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{dd}$, the Zeeman and dipolar portions, respectively; that is,

$$\mathcal{H}_Z = -\gamma_n\hbar H_0 \textstyle\sum_i I_{iz}. \quad (31)$$

Also

$$\mathcal{H}_{dd} = \tfrac{1}{2}\sum_{i,j}\frac{\gamma_n{}^2\hbar^2}{R_{ij}{}^3}\left[\mathbf{I}_i\cdot\mathbf{I}_j - 3\frac{(\mathbf{I}_i\cdot\mathbf{R}_{ij})(\mathbf{I}_j\cdot\mathbf{R}_{ij})}{R_{ij}{}^2}\right]$$

$$= \tfrac{1}{2}\sum_{i,j,\alpha,\beta}\frac{\gamma_n{}^2\hbar^2}{R_{ij}{}^3} f_{\alpha\beta}{}^{ij} I_{i\alpha} I_{j\beta}, \quad (32)$$

where $f_{\alpha\beta}{}^{ij}$ are angular factors involving the direction cosines of $\mathbf{I}_i$ and $\mathbf{I}_j$ with $\mathbf{R}_{ij}$. Evaluation of the terms in Eq. (30) for $i=j$ (according to Appendix I) shows that

$$\sum_{i,\alpha} a_{ii}\,\mathrm{tr}[\mathcal{H},I_{i\alpha}]^2 = a_{00}\sum_{i,\alpha}\mathrm{tr}[\mathcal{H}_Z,I_{k\alpha}]^2 + \mathrm{tr}[\mathcal{H}_{dd},I_{i\alpha}]^2. \quad (33)$$

Also

$$\mathrm{tr}\mathcal{H}^2 = \mathrm{tr}\mathcal{H}_Z{}^2 + \mathrm{tr}\mathcal{H}_{dd}{}^2. \quad (34)$$

There are additional terms involving a_{ij} for $i\neq j$. These terms are smaller than the terms for $i=j$ (shown above) by at least the factor $\sin^2 k_FR_{ij}/k_F{}^2R_{ij}{}^2$ which is much less than one. Consequently, these terms are dropped here.

Substitution of Eqs. (33) and (34) into the relaxation expression, Eq. (24), gives the final result:

$$R = \frac{1}{T_1} = a_{00}\frac{\mathrm{tr}\mathcal{H}_Z{}^2 + 2\,\mathrm{tr}\mathcal{H}_{dd}{}^2}{\mathrm{tr}\mathcal{H}_Z{}^2 + \mathrm{tr}\mathcal{H}_{dd}{}^2}, \quad (35)$$

where

$$\mathrm{tr}\mathcal{H}_Z{}^2 = N\gamma_n{}^2\hbar^2H_0{}^2(2I+1)^N I(I+1)/3, \quad (36)$$

$$\mathrm{tr}\mathcal{H}_{dd}{}^2 = \tfrac{1}{2}\gamma_n{}^4\hbar^4\left[\frac{I(I+1)}{3}\right]^2(2I+1)^N \times\sum_{i,j,\alpha,\beta}\frac{1}{R_{ij}{}^6}(f_{\alpha\beta}{}^{ij})^2. \quad (37)$$

C. Temperature Dependence of R_n

The entire temperature dependence of R_n appears in a_{00}, Eqs. (29a) and (29b). In fact, it is contained in the expression

$$\int \rho(E_i)\rho(E_f)f(E_i)[1-f(E_f)]dE_i. \quad (38)$$

In our case $E_f - E_i \ll kT \ll E_F$, where E_F is the Fermi energy; since $f(E)[1-f(E)]$ is large only within about $k\theta$ of E_F, we obtain

$$R \propto \int \rho^2(E)f(E)[1-f(E)]dE = \rho^2(E_F)k\theta \quad (39)$$

at any given field. Consequently, the entire temperature dependence of R_n at any external field comes from Fermi statistics and is a linear dependence. The complete expression for R_n for strong external field, shown in Appendix I, agrees with previous one-electron calculations by Korringa[20] and by Overhauser.[21] As pointed out in Sec. A, the prediction of linear temperature dependence agrees well with experiment both in strong and weak fields in aluminum and other metals.

D. Field Dependence of R_n

From Eq. (34) we have at any given temperature,

$$R(H)/R(\infty) = (H^2+2A)/(H^2+A), \quad (40)$$

where H is the external field and $A = H^2\,\mathrm{tr}\mathcal{H}_{dd}{}^2/\mathrm{tr}\mathcal{H}_Z{}^2$ which is independent of H. Equation (40) agrees with a previous calculation by Redfield.[23] It predicts $R_n(0)/R_n(\infty) = 2$, whereas 3.35 ± 0.35 is found in aluminum. However, a form similar to Eq. (40), $R(H)/R(\infty) = (H^2+A')/(H^2+A)$ shown as the solid line in Fig. 2, fits the data very well. Measurements in aluminum by Anderson and Redfield[25] agree well with ours. A discrepancy of this size is much too large to explain by taking into account the terms of Eqs. (32) and (33) for $i\neq j$. Calculations of the effects of p and higher angular momentum components in the conduction electron wave function give a very small correction in the wrong direction. The disagreement is not understood at present.

Recent data in lithium and sodium by Anderson and Redfield[13] show that $R_n(0)/R_n(\infty)$ is very close to the theoretical value of 2 in these metals. This suggests

---

[25] A. Anderson and A. G. Redfield (private communication).

that the difficulty is not with the fundamentals of the present theory of the field dependence, but rather with its application to aluminum.

VI. EXPERIMENT AND THEORY IN THE SUPERCONDUCTING PHASE

A. Experimental Results

The data for the relaxation rate in the superconducting phase, R_s, are shown in Table II. For purposes of comparison, we have extrapolated the values of the normal relaxation rate in zero field, $R_n(0)$ below the critical temperature, and have plotted $R_s/R_n(0)$ *versus* T in Fig. 3. A point obtained by Reif[5] (using saturation technique in colloidal mercury) is included in Fig. 3. Recently Anderson and Redfield[25] have extended the data in aluminum by using adiabatic demagnetization of a paramagnetic salt to cool their sample. In this manner they reach $\theta/\theta_c=0.35$. Their data agree with the general form of the points in Fig. 3—a sharp rise in $R_s/R_n(0)\cong 2$ just below the critical temperature followed by a slow falling off for lower temperatures. By $\theta/\theta_c\cong 0.5$, $R_s/R_n(0)\cong 1$. From these data one would conclude that, for temperatures just below the critical temperature, R_s is considerably greater than $R_n(0)$, whereas for temperatures near absolute zero, R_s is much less than $R_n(0)$.

B. Two-Fluid Model Theory of R_s

Of the various theories of superconductivity that have been proposed, the simplest theory that has had any degree of success is the "two-fluid" theory.[4] It supposes there to be two different kinds of electrons, i.e., normal and superconducting ones. Reasonable assumptions for a two-fluid model would make the relaxation rate always slower in the superconductor (or in any event *either* always slower or always faster), so that nuclear spin relaxation does not seem capable of interpretation in terms of this theory.

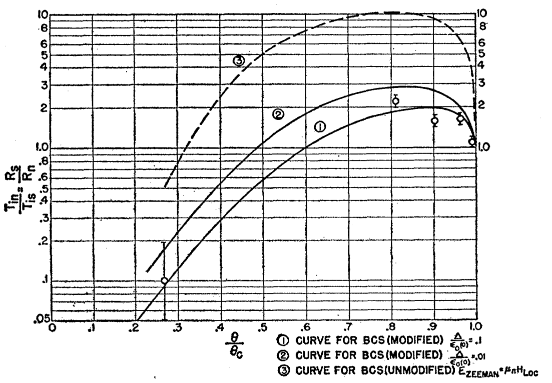


FIG. 3. Relaxation rate in a superconductor, R_s, relative to the zero-field value extrapolated from the normal state, $R_n(0)$, *versus* reduced temperature θ/θ_c. The three theoretical curves using BCS theory are described in the text.

TABLE II. Temperature dependence of the superconducting relaxation rate.

Temperature (°K)	θ/θ_c	R_s/R_n
1.16	0.99	1.1 ±0.2
1.127	0.963	1.6 ±0.2
1.06	0.906	1.55±0.2
0.945	0.81	2.2 ±0.3
1.2[a]	0.28	0.05 to 0.15

[a] Data on Hg by F. Reif, Phys. Rev. 102, 1417 (1956).

C. Bardeen-Cooper-Schrieffer Theory of R_s

Recently, Bardeen, Cooper, and Schrieffer developed a theory of superconductivity[3] based on the attractive interaction between electrons which results from virtual exchange of phonons if the phonon energy, $\hbar\omega$, is greater than the difference in energy of the electrons involved. When this attractive interaction is stronger than the screened Coulomb repulsion, it is energetically favorable to form the superconducting state. We shall not attempt to review their theory, which is quite clearly set forth elsewhere,[3] but we shall mention the key points essential to calculation of nuclear relaxation.

For our calculations we need to know the electron wave function of the superconductor, the energy of the wave function, and the appropriate statistical factors which describe thermal excitation. BCS describe the ground state of the superconductor at absolute zero as a linear combination of Bloch states in which the momenta and spins of pairs of electrons are correlated; that is, labeling states by wave vector $\mathbf{k}$, and spin quantum number s ($s=\pm\frac{1}{2}$), BCS consider cases in which the states $\mathbf{k}$, s, and $-\mathbf{k}$, $-s$ are either both occupied or both vacant. Now for a normal metal at absolute zero, states lying above the Fermi energy, E_F, are unoccupied, those below occupied. In a superconductor the BCS ground state contains fractional occupation of pair states above the Fermi energy, and correspondingly vacant pair states below. It is convenient to express the wave function in terms of the electron creation and destruction operators, $c_{\mathbf{k},s}{}^*$ and $c_{\mathbf{k},s}$; the pair creation operators are then $b_{\mathbf{k}}{}^*=c_{\mathbf{k}\uparrow}{}^*c_{-\mathbf{k}\downarrow}{}^*$.

Denoting the vacuum by Φ_0, BCS find that the wave function, ψ_0, at absolute zero is given by

$$\psi_0=\prod_{\mathbf{k}}[(1-h_{\mathbf{k}})^{\frac{1}{2}}+h_{\mathbf{k}}{}^{\frac{1}{2}}b_{\mathbf{k}}{}^*]\Phi_0, \qquad (41)$$

where $h_{\mathbf{k}}$ is a function of $\mathbf{k}$ given by BCS.

The term $(1-h_{\mathbf{k}})^{\frac{1}{2}}\Phi_0$ corresponds to pair state $\mathbf{k}$ being unoccupied, whereas $(h_{\mathbf{k}})^{\frac{1}{2}}b_{\mathbf{k}}{}^*\Phi_0$ corresponds to occupation. In a *normal* metal, $h_{\mathbf{k}}=1$ for a state below E_F, and $h_{\mathbf{k}}=0$ for a state above. BCS determine $h_{\mathbf{k}}$ for the superconducting ground state by minimizing the total energy of the conduction electrons, using Eq. (41) taking into account the electron-phonon and screened Coulomb interactions mentioned above. It should be emphasized that the excited pairs which form the superconducting ground state do *not* result from *thermal* excitation but rather from choosing a linear combination of Bloch states to obtain a lower energy; BCS have introduced the terminology "virtual pair" to emphasize this fact.

Excited states corresponding to temperatures above zero are obtained by allowing a fraction of the electrons to be thermally excited, the remainder being formed into virtual pairs as in the ground state. Two types of thermal excitation are possible. First, there may be an electron in state **k**, s while state $-\mathbf{k}$, $-s$ is unoccupied —so-called "singles." Second, there may be thermally excited pairs (occupation of both **k**, s and $-\mathbf{k}$, $-s$). BCS have called these "real" pairs to emphasize their thermal origin. The function which specifies a real pair in state k must be orthogonal to one specifying a virtual pair in the state. Accordingly, BCS choose the function

$$[(1-h_{\mathbf{k}})^{\frac{1}{2}}b_{\mathbf{k}}^{*}-h_{\mathbf{k}}^{\frac{1}{2}}]\Phi_0 \tag{42}$$

to specify real pair occupation of state **k**.

The most general wave function which is orthogonal to the ground state (and thus which corresponds to excitation) is taken as

$$\psi_{\mathrm{exc}}=\{\prod_{\mathbf{k}}[(1-h_{\mathbf{k}})^{\frac{1}{2}}+h_{\mathbf{k}}^{\frac{1}{2}}b_{\mathbf{k}}^{*}]\prod_{\mathbf{k}'}[(1-h_{\mathbf{k}'})^{\frac{1}{2}}b_{\mathbf{k}'}^{*}-h_{\mathbf{k}'}^{\frac{1}{2}}]\prod_{\mathbf{k}''}c_{\mathbf{k}''}^{*}\}\Phi_0, \tag{43}$$

where **k**$''$, **k**$'$, and **k** specify the states occupied by singles, real pairs, and virtual pairs, respectively. (Phase space is exhausted by the three types.) Using Eq. (45), BCS minimize the *free* energy $(E-TS)$ to determine the equilibrium values of the probabilities of occupation by singles, real pairs, and virtual pairs $s(\theta)$, $p(\theta)$, $g(\theta)$, and of the quantity $h_{\mathbf{k}}(\theta)$ at a given temperature.

To calculate the nuclear relaxation time, R_s, one must know W_{nm}, the transition probability per unit time between two nuclear states, n and m. (See part V.) To calculate W_{nm} for the superconducting phase, one must calculate the matrix elements of $\mathcal{H}_{SL}$, the nuclear spin-electron spin interaction, using the electron wave function, Eq. (43). The matrix elements must be squared, multiplied by the appropriate statistical factors (s, p, and/or g) and summed over all electron coordinates, taking into account conservation of energy. In as much as the entire temperature dependence of R_s or R_n occurs in W_{nm}, the ratio of R_s to R_n at zero field, $R_s/R_n(0)$, *versus* temperature can be obtained from W_{nm} directly. A detailed calculation is made in Appendix II using second quantization to treat the electrons.

When one performs the multi-electron calculation of W_{nm} for the superconducting state, W_{nm}^{S}, outlined above and derived in detail in Appendix II, one obtains an expression of almost the same one-electron form as that for the normal state W_{nm}^{N}. From Eqs. (28) and (29) (part V), one should note that the entire temperature dependence of W_{nm}^{N} occurs in an integral involving the density of electron states and Fermi functions:

$$W_{nm}^{N}\propto\int_0^\infty \rho(E_i)\rho(E_f)f(E_i,\theta)[1-f(E_f,\theta)]dE_i. \tag{44}$$

E_f and E_i are conveniently measured relative to the Fermi energy, E_F, and differ by a nuclear Zeeman energy, as discussed in part V.

The expression for W_{nm}^{S} is the same as that for W_{nm}^{N} except that the integral in Eq. (44) is replaced by

$$W_{nm}^{S}\propto\int_0^\infty \rho_s(E_i)\rho_s(E_f)C(E_i,E_f,\theta)f(E_i,\theta)\times[1-f(E_f,\theta)]dE_i, \tag{45}$$

where

$$\begin{aligned}\rho_s(E)&=0 \quad \text{for} \quad |E|<\epsilon_0(\theta)\\ &=\rho(E)\{E^2/[E^2-\epsilon_0^2(\theta)]\}^{\frac{1}{2}} \quad \text{for} \quad |E|>\epsilon_0(\theta),\end{aligned} \tag{46}$$

and

$$C(E_i,E_f,\theta)=1+[\epsilon_0^2(\theta)/E_iE_f]. \tag{47}$$

Again, E is measured from E_F. The parameter ϵ_0, having dimensions of energy, is a temperature-dependent quantity characteristic of the superconducting phase. ϵ_0 *versus* temperature is shown in Fig. 4. $\epsilon_0(0)=1.75k\theta_c$ and $\epsilon_0(\theta)\rightarrow 0$ as $\theta\rightarrow\theta_c$. BCS show that $2\epsilon_0(\theta)$ plays the role of an energy gap associated with excitations. Accordingly, the density of states in Eq. (45), ρ_s, has a gap centered about E_F, of width $2\epsilon_0(\theta)$, and is highly peaked near the gap edge.

The factor $C(E_i,E_f,\theta)$, which spoils the complete one-electron appearance of W_{nm}^{S}, is a two-electron correlation factor that has its origin in the virtual pairing in the superconducting state wave function; a given initial and final state may be connected by $\mathcal{H}_{SL}$ in two ways depending on whether the electron in $\mathbf{k}\uparrow$ or that in $-\mathbf{k}\downarrow$ is being scattered (see Appendix II). Thus the matrix elements, when squared, will have interference terms which become $C(E_i,E_f,\theta)$ when the sum over electrons is carried out.

The factor C goes from about 2 for E_i and E_f near the edge of the gap to 1 far from the gap. BCS point out that a similar expression comes when one is computing other rate processes involving electron scattering except that the factor C may be either $1+(\epsilon_0^2/E_iE_f)$

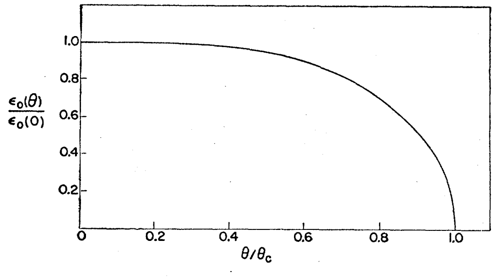


FIG. 4. BCS energy gap parameter, ϵ_0, *versus* reduced temperature θ/θ_c.

or $1-(\epsilon_0^2/E_iE_f)$, the + or − sign being appropriate to the particular process. Thus for ultrasonic absorption the *minus* sign is appropriate. In this case, C goes to zero for E_i and E_f near the gap. The result is that ultrasonic absorption[26] should and does experimentally drop rapidly as one goes down in temperature from the critical temperature, whereas the nuclear relaxation rate should and does go up and then down. *No one-electron theory can simultaneously explain both results. Consequently the comparison of the nuclear relaxation (or for that matter infrared absorption[27]) data with data on ultrasonic absorption provides direct verification of the basic feature of spin-momentum correlation (through virtual pairing) of the BCS theory.*

Even without evaluating R_s by Eq. (45), one can see that $R_s/R_n(0)$ given by the BCS theory will have qualitatively the correct temperature dependence [$R_s>R_n(0)$ just below θ_c, $R_s<R_n(0)$ near absolute zero]. The factor $f(1-f)$ peaks about the Fermi energy and roughly speaking cuts off the integral a distance $k\theta$ above and below E_F. When the gap is small, the total number of states within the energy interval $\pm k\theta$ is nearly the same in superconducting and normal states:

$$\int_{-k\theta}^{+k\theta}\rho_s dE\cong\int_{-k\theta}^{+k\theta}\rho_n dE. \tag{48}$$

However, ρ_s is peaked where as ρ_n is flat. Therefore

$$\int_{-k\theta}^{+k\theta}\rho_s^2 dE>\int_{-k\theta}^{+k\theta}\rho_n^2 dE \quad\text{and}\quad R_s>R_n(0), \tag{49}$$

and the superconductor has faster relaxation.

When $\theta\cong 0$, ρ_s is much smaller than ρ_n in the interval $\pm k\theta$, and $R_s<R_n(0)$. In fact, the exponential tails of the function $f(1-f)$ make $R_s/R_n(0)$ approach zero exponentially with $1/\theta$ as θ goes to zero.

If the difference between electron energies E_i and E_f is ignored in evaluating R_s, as is legitimate in evaluating the relaxation in the normal state, the BCS result for $R_s/R_n(0)$ diverges logarithmically. Of course, the Zeeman energy, $\mu_n H_{\mathrm{loc}}$, prevents this catastrophe, but the fact that $\mu_n H_{\mathrm{loc}}\ll\epsilon_0$ results in the BCS value of $R_s/R_n(0)$ being quite a bit larger than the experimental values. The dotted curve in Fig. 3 is that calculated using $E_f-E_i=\mu_n H_{\mathrm{loc}}$. Indeed, $\mu_n H_{\mathrm{loc}}$ is much less than the expected energy breadth, δE, of the electron spin energy levels. Since the BCS theory does not include such an energy level breadth, the calculation of R_s must be modified when $\mu_n H_{\mathrm{loc}}\ll\delta E$. A breadth such that $\mu_n H_{\mathrm{loc}}\ll\delta E\ll\epsilon_0(\theta)$ would limit the peaking in ρ_s, so that the larger the breadth, the lower the calculated value of $R_s/R_n(0)$.

To correctly put such a breadth into the BCS theory, one would have to allow for electron scattering effects in the construction of their theory. However, a fairly natural way of including electron state lifetime effects is to modify the usual expression for the transition probability per unit time between two states to take into account such a level breadth. The usual expression for W_{ij} is derived from

$$W_{ij}=4|V_{ij}|^2\int\rho(E_j)dE_j\frac{\sin^2[(E_j-E_i\pm\hbar\omega)t/2\hbar]}{\hbar^2 t(E_j-E_i\pm\hbar\omega)^2}. \tag{50}$$

Instead of regarding $\rho(E_j)$ as slowly varying and taking it outside the integral to obtain the usual expression for W_{ij}, one can introduce normalized breadth functions, $\Delta(E)$, centered about E_i and E_f and having a width δE; the usual calculation for the relaxation rate using W_{ij} would then be carried out using Eq. (50) along with $\Delta(E-E_i)$ and $\Delta(E-E_f)$. However, the result of the procedure is the same as if one kept using the usual transition probability expression for W_{ij} and applied the breadth functions instead to the density of states, ρ_s, which appear in the relaxation rate expression $R_s/R_n(0)$, Eq. (45).

Then $\rho_s(E,\theta)$ would be replaced by a new function $\rho_s'(E,\theta)$ given by

$$\rho_s'(E,\theta)=\int\rho_s(E',\theta)\Delta(E'-E)dE',$$
$$\int\Delta(E'-E)dE'=1, \tag{51}$$

for both E_i and E_f. The simplest breadth function for calculational purposes is a rectangular function of total width $2\delta E$ and height $1/2\delta E$, centered about E_i or E_f. One would expect $\mu_n H_{\mathrm{loc}}\ll\delta E\ll\epsilon_0(\theta=0)$, so that in the modified relaxation expression (with ρ_s'), E_f could be set equal to E_i. Under these circumstances, the ratio of relaxation times is given by

$$\frac{R_s}{R_n(0)}=2\int_0^\infty[\rho_s'(x,\eta,\delta)]^2\left(1+\frac{\eta}{x^2}\right)f(x)[1-f(x)]dx, \tag{52}$$

where $x=E/k\theta$, $\delta=\delta E/k\theta$ and $\eta=\epsilon_0/k\theta$. We use

$$\begin{aligned}\rho_s'&=0, \quad 0\leqslant x\leqslant\eta-\delta\\ &=(1/2\delta)[(x+\delta)^2-\eta^2]^{\frac{1}{2}}, \quad \eta-\delta\leqslant x\leqslant\eta+\delta\\ &=(1/2\delta)\{[(x+\delta)^2-\eta^2]^{\frac{1}{2}}-[(x-\delta)^2-\eta^2]^{\frac{1}{2}}\},\\ &\qquad\qquad x\geqslant\eta+\delta.\end{aligned} \tag{53}$$

Equation (53) was split into integrals over four regions: $0\leqslant x\leqslant\eta-\delta$, $\eta-\delta\leqslant x\leqslant\eta+\delta$, $\eta+\delta\leqslant x\leqslant 1.1\eta$, and $1.1\eta\leqslant x\leqslant\infty$. The first three were evaluated by pulling $f(x)[1-f(x)]$ outside, giving it the value $f(\eta)[1-f(\eta)]$. The last integral, for $1.1\eta\leqslant x\leqslant\infty$, was evaluated numerically by using ρ_s rather than ρ_s', as it was expected that the δ needed would be less than 0.1η to get agreement with experiment.

---

[26] R. W. Morse and H. V. Bohm, Phys. Rev. **108**, 1094 (1957).

[27] R. E. Glover and M. Tinkham, Phys. Rev. **104**, 844 (1956); **108**, 243 (1957).

The result for $R_s/R_n(0)$ using Eqs. (52) and (53), for two values of $\delta E/\epsilon_0(\theta=0)$, are shown in Fig. 3 as the solid curves. The theoretical curves all have the correct qualitative features but peak at a temperature somewhat high by comparison with the present experimental points. Two comments should be made. First, the manner in which the level width was introduced is reasonable but somewhat artificial; it is not clear what would be the result of a more correct theory, containing electron lifetime effects in its formation. However, since the result for R_s depends only logarithmically on the width, one would not expect significant change in curve shape to result from the correct theory. Second, the appropiate breadth might well be temperature dependent. This would mean that one should move from one of the curves on Fig. 3 to another as temperature changes, presumably using a smaller value of $\delta E/\epsilon_0(\theta=0)$ as the temperature decreases. A curve featuring such a $\delta E/\epsilon_0(\theta=0)$ would fit the data for θ just below θ_c somewhat better than the curves shown.

One possible estimate of the level breadth could be made in terms of the time needed to cross the 10-micron particles. This gives a value of about unity for $\delta E/\epsilon_0(\theta=0)$. A better fit is found with a value between 0.1 and 0.01. Perhaps the smaller numbers express the idea that an elastic scattering may be removed by a redefinition of the eigenstates. Thus, even for particles of dimension b for which $\hbar b/v_0 \gg k\theta_c$ (where v_0 is the velocity of electrons at the Fermi surface), the critical temperature is unchanged.

VII. DISCUSSION OF SPECIAL DETAILS

Most of the data were taken with an unannealed sample. The signal observed after the field-switching cycle obeyed the exponential decay law very well. However, some loss of signal was observed which was independent of the relaxation process when the sample became superconducting during the cycle. The powdered sample also had a slight tendency to supercool. (H_c for passage from normal to superconducting phase was less than H_c for the reverse passage.) The spurious loss of magnetization was attributed to nonadiabatic phase transitions for some of the nuclei during the very rapid phase changes in the supercooled portions of the sample; that is, the nuclear spins in some regions of the sample could not follow the rapidly changing magnetic field and were "dephased" relative to the spins in the rest of the sample. Spin diffusion from these dephased spins would undoubtedly affect additional spins near the dephased ones, but only within a distance of about 10^{-6} cm in the times important for our experiment. All such spins would be lost in contributing to signal. That supercooling was the cause of the spurious magnetization was made clear by annealing the sample. This resulted in pronounced supercooling (up to 50% change in H_c), and almost all of the magnetization was lost.

In this experiment considerable trouble would be caused by flux trapped within the aluminum particles after transition from normal to superconducting phase has been made. The nuclei in the regions of trapped flux would be in the normal state, so that they would have a relaxation time different from that of the nuclei in the superconducting regions of the samples. Since for our points (just below the critical temperature) R_s is greater than R_n, this effect would give rise to a long tail in the plot of M' *versus* t. No such tail could be found in any of the data, indicating that the amount of trapped flux, if any, was small. The effect of a *small* contribution of trapped flux would be to lower slightly the value of R_s interpreted from the data; however, the change would be less than the present experimental error. In addition, the detuning of the sample coil upon transition from normal to superconducting phase was about what it should be according to the Q of the coil and the sample-filling factor, again indicating a small amount of trapped flux, if any. It is reassuring that Cochran, Mapother, and Mould[8] found no evidence of trapped flux in pure single crystals of aluminum.

VIII. CONCLUSIONS

In the normal phase nuclear spin-lattice relaxation in a given field is characterized by a single relaxation time (to within an experimental uncertainty of about 5%). This means that as a result of adiabatic demagnetization to a low field from thermal equilibrium in a high field, the nuclear spins relax as if their density matrix were diagonal at the low field and characterized by a spin temperature.

The ratio of low-field to high-field relaxation rates in aluminum disagrees with the theoretical result in aluminum. Recent data in lithium and sodium by Anderson and Redfield show that the external field dependence of relaxation rate is very close to the theoretical result in the alkali metals. This suggests that the difficulty with aluminum is not with the fundamentals of the present theory based on the spin temperature assumption but rather with the application of it to aluminum. In contrast, the temperature dependence of the relaxation rate at a given field seems to obey the predicted linear temperature dependence very well in aluminum.

In the superconducting phase the nuclear relaxation is characterized by a single relaxation rate. R_s is greater than $R_n(0)$ for temperatures just below the critical temperature; for temperatures near zero, the reverse is true. The data are in semiquantitative agreement with the predictions of the theory of Bardeen, Cooper, and Schrieffer as modified to take into account broadening of the electron levels. Their result is similar to that of a one-electron, energy-gap model of superconductivity *except* for a factor that expresses the effect of the correlation of electron pairs of opposite spin and momentum. The nuclear relaxation, when contrasted with data on ultrasonic absorption, confirms the essential idea of pair correlation which is central to the BCS theory.

Further experiments are being undertaken by one of us (LCH) in aluminum, tin, and some alloys to obtain a better quantitative check of the BCS theory and to obtain a quantitative estimate of the appropriate energy breadth of the BCS states for this type of experiment.

ACKNOWLEDGMENTS

We are pleased to acknowledge the great help of several of our colleagues: Professor Dillon Mapother, Professor John Wheatley, and Mr. Frank Witt for extensive aid and advice in the design and construction of the cryogenic apparatus; Dr. John Spokas for his assistance in the actual performance of the experiments; Mr. K. T. Rogers for aid in construction of equipment. The generous instruction given us by Professor John Bardeen, Dr. Leon Cooper, and Dr. J. R. Schrieffer in their theory during the course of its development provided the basis for the interpretation of the data on superconductors. The free and cordial exchange of information with Dr. Alfred Redfield and Dr. Arthur Anderson has been of great aid throughout the course of the experiment. Lastly, we wish to acknowledge the fellowships provided by the General Electric Company (to LCH) and the Alfred P. Sloan Foundation (to CPS).

APPENDIX I. CALCULATION OF R_n

We first wish to calculate W_{nm}, the transition probability per unit time of a nuclear spin transition between two nuclear spin states n and m, induced by the nuclear spin-electron spin interaction. This interaction may be written

$$\mathcal{H}_{SL}=\sum_{i,j}(8\pi/3)\gamma_e\gamma_n\hbar^2\mathbf{I}_i\cdot\mathbf{S}_j\delta(\mathbf{r}_j-\mathbf{R}_i), \tag{54}$$

which is Eq. (25) of part V. The nuclear states are eigenfunctions of $\mathcal{H}=\mathcal{H}_Z+\mathcal{H}_{dd}$, the Zeeman and nuclear dipolar portions, respectively. A Bloch function will be used for the electron wave function: $\chi=\chi_{\mathbf{k}}\eta_j e^{-i\mathbf{k}\cdot\mathbf{r}_j}$ where $\mathbf{k}$ is the wave vector and η_j is the spin function. Using $\mathbf{k}$ and s to represent the electron states, the matrix elements of Eq. (54) may be written

$$V_{if}=\sum_{i,j}(8\pi/3)\gamma_e\gamma_n\hbar^2(n|\mathbf{I}_i|m)\cdot(s|\mathbf{S}_j|s')\times\chi_{\mathbf{k}'}(\mathbf{R}_i)\chi_{\mathbf{k}}(\mathbf{R}_i)e^{-i(\mathbf{k}_j-\mathbf{k}_j')\cdot\mathbf{R}_i}. \tag{55}$$

Now $\chi_{\mathbf{k}}(\mathbf{R}_i)$ is independent of $\mathbf{R}_i$. It will also be regarded as independent of $\mathbf{k}$, since $\chi\mathbf{k}(\mathbf{R}_i)$ is a slowly varying function of $\mathbf{k}$, and the only wave vectors involved will be those close to k_F, the wave vector corresponding to the Fermi energy. Hence

$$V_{if}=(8\pi/3)\gamma_e\gamma_n\hbar^2\chi(0)^2\sum_{i,j}(n|\mathbf{I}_i|m)\cdot(s|\mathbf{S}_j|s')e^{-i(\mathbf{k}_j-\mathbf{k}_j')\cdot\mathbf{R}_i}. \tag{56}$$

Using perturbation theory, we have

$$W_{nm}=\sum_{k,k',s,s'}(2\pi/\hbar)|V_{if}|^2\delta(E_i-E_f-\hbar\omega), \tag{57}$$

where E_i and E_f are electron energies and $\hbar\omega$ is a Zeeman energy.

Calling the density of electron states in energy $\rho(E)$, and introducing $\mathbf{R}_{ij}=\mathbf{R}_i-\mathbf{R}_j$, and the angle θ between $\mathbf{k}$ and $\mathbf{R}_{ij}$, θ' between $\mathbf{k}'$ and $\mathbf{R}_{ij}$, substitution of Eq. (55) in (57) gives

$$\begin{aligned}W_{nm}=&\left(\frac{2\pi}{\hbar}\right)\frac{64\pi^2}{9}\gamma_e^2\gamma_n^2\hbar^4|\chi(0)|^4\\&\times\sum_{i,j,s,s'}\Bigg\{\int\frac{\sin\theta d\theta}{2}\frac{\sin\theta' d\theta'}{2}dEdE'\rho(E)\rho(E')f(E)\\&\times[1-f(E')](n|\mathbf{I}_i|m)\cdot(s|\mathbf{S}|s')(s'|\mathbf{S}|s)\cdot(m|\mathbf{I}_j|n)\\&\times e^{-ikR_{ij}\cos\theta}e^{ik'R_{ij}\cos\theta'}\delta(E-E'\pm\hbar\omega)\Bigg\},\end{aligned} \tag{58}$$

where $f(E)$ and $[1-f(E')]$ are the probabilities that the initial electron state is occupied and the final state is vacant, respectively. Using

$$\begin{aligned}\sum_{s,s'}(s|s_\alpha|s')(s'|s_{\alpha'}|s)&=\mathrm{tr}s_\alpha s_{\alpha'}\\&=\tfrac{1}{3}\delta_{\alpha\alpha'}(2s+1)s(s+1)=\tfrac{1}{2}\delta_{\alpha\alpha'},\end{aligned} \tag{59}$$

and performing the integrations over θ and θ', there results

$$\begin{aligned}W_{nm}=&\frac{64\pi^3\hbar^3}{9}\gamma_e^2\gamma_n^2|\chi(0)|^4\sum_{i,j}(n|I_{i\alpha}|m)(m|I_{j\alpha}|n)\\&\times\frac{\sin^2 k_FR_{ij}}{(k_FR_{ij})^2}\int\rho(E_i)\rho(E_f)f(E_i)[1-f(E_f)]dE_i,\end{aligned} \tag{60}$$

where $E_i-E_f=\hbar\omega$ is a Zeeman energy difference, Equation (60) may be written as

$$W_{nm}=\sum_{i,j,\alpha}a_{ij}(n|I_{i\alpha}|m)(m|I_{j\alpha}|n) \tag{61}$$

[which is Eq. (28) of part V]. As remarked in part V. $a_{ij}=[\sin^2k_FR_{ij}/(k_FR_{ij})^2]a_{ii}\ll a_{ii}$, so that the terms in Eq. (61) for $i\neq j$ are dropped here. Now

$$R_n=\left[\sum_{n,m}W_{nm}(E_n-E_m)^2\right]/2\sum_n E_n^2 \tag{62}$$

[which is Eq. (24) of part V]. Here

$$\begin{aligned}\sum_{nm}W_{nm}(E_n-E_m)^2&=\sum_{nmij\alpha}a_{ij}(n|I_{j\alpha}|m)(m|I_{j\alpha}|m)(E_n-E_m)^2\\&=-\sum_{nmij\alpha}a_{ij}(n|[\mathcal{H},I_{i\alpha}]|m)(m|[\mathcal{H},I_{j\alpha}]|n)\\&=-\sum_{ij\alpha}a_{ij}\,\mathrm{tr}[\mathcal{H},I_{i\alpha}][\mathcal{H},I_{j\alpha}],\end{aligned} \tag{63}$$

where $\mathcal{H}=\mathcal{H}_Z+\mathcal{H}_{dd}$. We evaluate only the terms for $i=j$. Now

$$-\sum_{i\alpha}\operatorname{tr}[\mathcal{H},I_{i\alpha}]^2=-\sum_{i\alpha}\{\operatorname{tr}[\mathcal{H}_Z,I_{i\alpha}]^2+\operatorname{tr}[\mathcal{H}_{dd},I_{i\alpha}]^2+2\operatorname{tr}[\mathcal{H}_Z,I_{i\alpha}][\mathcal{H}_{dd},I_{i\alpha}]\},\tag{64}$$

where

$$\mathcal{H}_Z=-\gamma_n\hbar H_0\textstyle\sum_j I_{jz}$$

and

$$\mathcal{H}_{dd}=\frac{1}{2}\sum_{j,k,\alpha,\beta}\frac{\gamma_n{}^2\hbar^2}{R_{jk}{}^3}f_{\alpha\beta}{}^{jk}I_{j\alpha}I_{k\beta},$$

as in Eqs. (31) and (32) of part V. Consequently, the third term in Eq. (64) has an odd number of spin operators, so that $\operatorname{tr}[\mathcal{H}_Z,I_\alpha][\mathcal{H}_{dd},I_{i\alpha}]=0$. Using the commutation laws of the $I_{i\alpha}$, one can show that

$$-\operatorname{tr}[\mathcal{H}_Z,I_{i\alpha}]^2=2\gamma_n{}^2\hbar^2H^2N(2I+1)^NI(I+1)/3=2\operatorname{tr}\mathcal{H}_Z{}^2,$$

and

$$-\operatorname{tr}[\mathcal{H}_{dd},I_{i\alpha}]^2=2\gamma_n{}^4\hbar^4(2I+1)^N\left[\frac{I(I+1)}{3}\right]^2\times\sum_{i,j,\alpha,\beta}\frac{(f_{\alpha\beta}{}^{ij})^2}{R_{ij}{}^6}=4\operatorname{tr}\mathcal{H}_{dd}{}^2.$$

Thus, substituting in Eq. (63), we obtain the numerator of Eq. (62):

$$\sum_{n,m}W_{nm}(E_n-E_m)^2=a_{ii}2\operatorname{tr}\mathcal{H}_Z{}^2+4\operatorname{tr}\mathcal{H}_{dd}{}^2.\tag{65}$$

Now

$$\textstyle\sum_n E_n{}^2=\operatorname{tr}(\mathcal{H}_Z+\mathcal{H}_{dd})^2=\operatorname{tr}\mathcal{H}_Z{}^2+\operatorname{tr}\mathcal{H}_{dd}{}^2.\tag{66}$$

Substituting Eqs. (65) and (66) in Eq. (62) gives the final result [Eq. (35) in part V],

$$R_n=a_{ii}\frac{\operatorname{tr}\mathcal{H}_Z{}^2+2\operatorname{tr}\mathcal{H}_{dd}{}^2}{\operatorname{tr}\mathcal{H}_Z{}^2+\operatorname{tr}\mathcal{H}_{dd}{}^2}.$$

For the free-electron case, from Eqs. (60) and (61),

$$a_{ii}=\frac{16}{9\pi}\frac{m^2V^2k_F{}^2}{\hbar}\gamma_e{}^2\gamma_n{}^2|\chi(0)|^4\int f(E)[1-f(E)]dE.$$

Since $\operatorname{tr}\mathcal{H}_Z{}^2\sim H^2$, $\lim_{H\to\infty}R_n=a_{ii}$. Thus we obtain the high-field $R_n=(16/9\pi)(m^2k_F{}^2\gamma_e{}^2\gamma_n{}^2/\hbar^2)V^2|\chi(0)|^4k\theta$, in agreement with Overhauser[21] and Korringa.[20]

APPENDIX II. CALCULATION OF NUCLEAR SPIN RELAXATION USING SECOND QUANTIZATION

When the conduction electrons are treated using second quantization, but the nuclei are treated using ordinary quantization, the nuclear spin–electron spin interaction has the form

$$\mathcal{H}_{SL}=(8\pi/3)\gamma_e\gamma_n\hbar^2\textstyle\sum_i\mathbf{I}_i\cdot(\psi,\mathbf{S}\delta(\mathbf{r}_j-\mathbf{R}_i)\psi),\tag{1'}$$

where $\mathbf{S}$ is a spin operator for one electron and ψ is regarded as an operator, expressed in terms of the complete set of Bloch states for one electron with annihilation operators as coefficients. That is,

$$\psi=\sum_{\mathbf{k},s}c_{\mathbf{k},s}u_{\mathbf{k},s}(\mathbf{r}),\tag{2'}$$

where the $u_{\mathbf{k},s}(\mathbf{r})$ are one-electron Bloch functions for wave vector $\mathbf{k}$ and spin s, and the $c_{\mathbf{k},s}$ are the annihilation operators for the Bloch state labeled by $\mathbf{k}$ and s. The complex conjugate, $c_{\mathbf{k},s}{}^*$, is the creation operator for the Bloch state $\mathbf{k}$, s; both operators obey the usual anticommutation relations. Substituting Eq. (2′) in Eq. (1′) gives

$$\mathcal{H}_{SL}=\frac{8\pi}{3}\gamma_e\gamma_n\hbar^2\sum_i\mathbf{I}_i\cdot\sum_{\mathbf{k},\mathbf{k}',s,s'}\int c_{\mathbf{k}'s}{}^*u_{\mathbf{k}'s'}{}^*(r)\mathbf{S}\times\delta(\mathbf{R}_i-\mathbf{r}_i)c_{\mathbf{k},s}u_{\mathbf{k},s}(r)d\mathbf{r}.\tag{3'}$$

Since $\mathbf{I}\cdot\mathbf{S}=I_zS_z+\frac{1}{2}[I_+S_-+I_-S_+]$, where $I_\pm=I_x\pm iI_y$ and $S_\pm=S_x\pm{}_iS_y$, $\mathcal{H}_{SL}$ will consist of three parts, $\mathcal{H}_{SLz}$, $\mathcal{H}_{SL+}$, and $\mathcal{H}_{SL-}$. The spatial integration for each operator yields $|u(0)|^2$ with the assumptions of part V that $u_k(0)$ is a slowly varying function of $\mathbf{k}$ near $\mathbf{k}_F$ and $\sin^2k_FR_{ij}/(k_FR_{ij})^2\cong0$ for $i\neq j$. Finally, using $(m_s|S_z|m_s)=m_s$ and $(m_s+1|S_+|m_s)=(m_s|S_-|m_s+1)=[S(S+1)-m(m+1)]^{\frac{1}{2}}=1$ for $S=\frac{1}{2}$, we obtain

$$\mathcal{H}_{SLz}=(8\pi/3)\gamma_e{}^2\gamma_n{}^2\hbar^2|u(0)|^2\sum_{j,\mathbf{k},\mathbf{k}'}\tfrac{1}{2}I_{zj}\times(c_{\mathbf{k}'\uparrow}{}^*c_{\mathbf{k}\uparrow}-c_{\mathbf{k}'\downarrow}{}^*c_{\mathbf{k}\downarrow}),$$

$$\mathcal{H}_{SL+}=(8\pi/3)\gamma_e{}^2\gamma_n{}^2\hbar^2|u(0)|^2\sum_{j,\mathbf{k},\mathbf{k}'}\tfrac{1}{2}I_{+j}c_{\mathbf{k}'\downarrow}{}^*c_{\mathbf{k}\uparrow},\tag{4'}$$

$$\mathcal{H}_{SL-}=(8\pi/3)\gamma_e{}^2\gamma_n{}^2\hbar^2|u(0)|^2\sum_{j,\mathbf{k},\mathbf{k}'}\tfrac{1}{2}I_{-j}c_{\mathbf{k}'\uparrow}{}^*c_{\mathbf{k}\downarrow}.$$

As discussed in part V, to calculate the nuclear spin-lattice relaxation rate it is necessary to know W_{nm}, the transition probability per unit time between two nuclear states m and n, induced by $\mathcal{H}_{SL}$. To obtain W_{nm}, one must calculate the matrix elements of $\mathcal{H}_{SL}$, $(\psi,\mathcal{H}_{SL},\psi)_{n,m,s,s',\mathbf{k},\mathbf{k}'}$, which will in general depend on both initial and final state electron quantum numbers. Each of the matrix elements must be multiplied by the statistical weights of electron states involved, and finally a sum carried out over s, s', $\mathbf{k}$, and $\mathbf{k}'$ to obtain W_{nm}. Since the BCS wave functions contain the electron states paired off in the grouping $\mathbf{k}$, $-\mathbf{k}$, we shall relabel the $\mathbf{k}$'s and $\mathbf{k}'$'s in Eq. (4′) introducing $A=(8\pi/3)\gamma_e\gamma_n\hbar^2|u(0)|^2$, to obtain

$$\mathcal{H}_{SLz}=A\sum_j\sum_{\mathbf{k}',\mathbf{k}(\text{pairs})}\tfrac{1}{2}I_{zj}(c_{\mathbf{k}'\uparrow}{}^*c_{\mathbf{k}\uparrow}-c_{-\mathbf{k}'\downarrow}{}^*c_{-\mathbf{k}\downarrow}),$$

$$\mathcal{H}_{SL+}=A\sum_j\sum_{\mathbf{k}',\mathbf{k}(\text{pairs})}\tfrac{1}{2}I_{+j}c_{\mathbf{k}'\downarrow}{}^*c_{\mathbf{k}\uparrow},\tag{5'}$$

$$\mathcal{H}_{SL-}=A\sum_j\sum_{\mathbf{k}',\mathbf{k}(\text{pairs})}\tfrac{1}{2}I_{-j}c_{\mathbf{k}'\uparrow}{}^*c_{-\mathbf{k}\downarrow}.$$

The minus sign occurring in the I_{zj} term has its physical origin in the fact that electrons of spin up and spin down produce magnetic fields at the nucleus of opposite sign. This fact is important because with a superconductor one gets interference between the two terms.

The BCS wave function is discussed in part VI; they choose

$$\Phi=\{\prod_{\mathbf{k}}[(1-h_{\mathbf{k}})^{\frac{1}{2}}+h_{\mathbf{k}}^{\frac{1}{2}}b_{\mathbf{k}}^*]\prod_{\mathbf{k}'}[(1-h_{\mathbf{k}'})^{\frac{1}{2}}b_{\mathbf{k}'}^* -h_{\mathbf{k}'}^{\frac{1}{2}}]\prod_{\mathbf{k}''} c_{\mathbf{k}''}^*\}\Phi. \tag{6'}$$

where $b_{\mathbf{k}}^*=c_{\mathbf{k}\uparrow}^*c_{-\mathbf{k}\downarrow}^*$ (the pair creation operator), and $\mathbf{k}$, $\mathbf{k}'$, and $\mathbf{k}''$ specify states occupied by virtual pairs, real pairs, and singles, respectively. BCS minimize the free energy, $E-TS$, using Eq. (6′) to determine the equilibrium values of statistical weights of singles, real pairs, and virtual pairs $s(\theta)$, $p(\theta)$, $g(\theta)$, and the coefficients $h_k(\theta)$ corresponding to a given temperature.

Their results are given most simply in terms of an electron energy $E_{\mathbf{k}}=+(\epsilon_{\mathbf{k}}^2+\epsilon_0^2)^{\frac{1}{2}}$ instead of the usual energy of the Bloch state, $\epsilon_{\mathbf{k}}$. ϵ_0 is a temperature-dependent parameter characteristic of the superconductor as evaluated by BCS.[6] $\epsilon_0(\theta)$ *versus* θ/θ_c is shown in Fig. 4. $\epsilon_0(0)=1.75k\theta_c$; $\epsilon_0(\theta)$ varies slowly near $\theta/\theta_c=0$ but $\epsilon_0(\theta)\rightarrow 0$ fairly rapidly as θ/θ_c goes to 1. BCS show that $2\epsilon_0(\theta)$ plays the role of an energy gap associated with excitations. The density of electron states in E_k, ρ_s, also displays this gap:

$$\rho_s=\frac{dn}{dE_{\mathbf{k}}}=\frac{dn}{d\epsilon_{\mathbf{k}}}\frac{d\epsilon_{\mathbf{k}}}{dE_{\mathbf{k}}}=\rho_n\left(\frac{E_{\mathbf{k}}^2}{E_{\mathbf{k}}^2-\epsilon_0^2}\right)^{\frac{1}{2}} \quad \text{for} \quad |E_{\mathbf{k}}|>\epsilon_0,$$

where all energies are relative to the Fermi energy.

In terms of $E_{\mathbf{k}}$, BCS find that the results for the probabilities $s(\theta)$ and $p(\theta)$ are the same as in the normal metals; defining a function $f(E_{\mathbf{k}},\theta)$ which looks like the normal metal Fermi function,

$$f(E_{\mathbf{k}},\theta)=\frac{1}{e^{E_{\mathbf{k}}/k\theta}+1}, \tag{7'}$$

BCS find that the thermal equilibrium values of $s(\theta)$ and $p(\theta)$ are

$$s(\theta)=2f(1-f), \quad p(\theta)=f^2, \tag{8'}$$

as in the normal metal. Since $g(\theta)=1-s(\theta)-p(\theta)$, one has

$$g(\theta)=(1-f)^2. \tag{9'}$$

Also BCS find that at thermal equilibrium

$$h(E_{\mathbf{k}},\theta)=\tfrac{1}{2}[1-\epsilon_{\mathbf{k}}/E_{\mathbf{k}}]. \tag{10'}$$

BCS define $E_{\mathbf{k}}$ to be positive, which means that $f(E_{\mathbf{k}})$ describes electron occupation for $k>k_F$ and hole occupation for $k<k_F$. From the form of $f(E_{\mathbf{k}})$, the single particles and excited pairs form a set of independent fermions with a dispersion law $E_{\mathbf{k}}=+(\epsilon_{\mathbf{k}}^2+\epsilon_0^2)^{\frac{1}{2}}$.

The only aspect of the calculation remaining to be discussed is the energy of wave function. The energy $E_{\mathbf{k}}$ plays an additional role here. Let us consider two excited states 1 and 2. They will differ because of the assignment of states among the three types of terms: s, p, or g. As a result the total energy, W_1, of the electrons in state 1 will differ from W_2, the total energy in state 2. BCS show that

$$W_1-W_2=\sum\nolimits_1 E_{\mathbf{k}}-\sum\nolimits_2 E_{\mathbf{k}}, \tag{11'}$$

where we include in the sum the value of $E_{\mathbf{k}}$ for *each* electron which is found in a single (s) or a real pair (p); if $\mathbf{k}$ is used for a single, $E_{\mathbf{k}}$ appears once, whereas if it is used as a real pair, $E_{\mathbf{k}}$ appears twice. Consequently, because of the Eqs. (7′) through (11′) we do not need to distinguish between real pairs or singles, but we can merely compute the probability of occupancy and energy as though any single Bloch state $\mathbf{k}$ had an energy $E_{\mathbf{k}}$ and a probability of occupation given by the Fermi function of energy $E_{\mathbf{k}}$.

In light of the above, the fact that the Zeeman energy difference between initial and final states in zero field is very much less than the gap energy, $\epsilon_0(\theta)$, means that there are only three types of matrix elements for which conservation of energy is possible:

I. Single+single ↔ real pair+virtual pair.
II. Single+real pair ↔ real pair+single.
III. Single+virtual pair ↔ virtual pair+single.

These will be called types I, II, and III, respectively. At first it looks peculiar to see a transition such as I which does not appear to conserve particles. Detailed study shows that such is not the case since each pair state is partly occupied and partly empty. We use the empty real pair with occupied virtual pair, or conversely. Since the scattering operator $c_{\mathbf{k}'s'}^*c_{\mathbf{k}s}$ conserves particles, we need never fear that we shall violate conservation of matter. Because the $\mathcal{H}_{SL}$ operators are of the form $c_{\mathbf{k}'}^*c_{\mathbf{k}}$ corresponding to an electron scattering, each of the three types can be further divided into four cases: $k>k_F$ and $k'>k_F$, $k<k_F$ and $k'>k_F$, $k>k_F$ and $k'<k_F$, $k<k_F$ and $k<k_F$. They will be referred to as "above-above," "below-above," "above-below," and "below-below." Since the BCS theory treats electrons and holes on equal footing, as does $\mathcal{H}_{SL}$, one need only calculate the "above-above" and "above-below" matrix elements for the three types, I, II, and III, to get the complete answer.

Finally, two further subdivisions arise. If the energy of a single in $\mathbf{k}$ is designated by E and in $\mathbf{k}'$ by E', there is a group of matrix elements of types I, II, and III for which the energy difference between initial and final state is $E'-E$; for the second group it is $E-E'$. The various matrix elements for each operator must be divided into these two groups to keep track of conservation of energy.

A typical matrix element will now be calculated for illustration. Only that portion of the wave functions dealing with the states $\mathbf{k}$ and $\mathbf{k}'$ will be shown. Let us consider a matrix element using $\mathcal{H}_{SLz}$. One should note that the initial state will be connected to one part of the final state by $c_{\mathbf{k}'\uparrow}{}^*c_{\mathbf{k}\uparrow}$ and to another part of the final state by $c_{-\mathbf{k}\downarrow}{}^*c_{-\mathbf{k}'\downarrow}$, so that interference will result for these two states. This result arises because either the electron in $\mathbf{k}\uparrow$ or in $-\mathbf{k}'\downarrow$ can be scattered. A sign change will take place due to the difference in sign between $c_{\mathbf{k}'\uparrow}{}^*c_{\mathbf{k}\uparrow}$ and $c_{-\mathbf{k}'\downarrow}{}^*c_{-\mathbf{k}\downarrow}$ in $\mathcal{H}_{SLz}$.

Type I.—"Above-above"—Group $E'-E$.

Initial state: $c_{\mathbf{k}\uparrow}{}^*c_{-\mathbf{k}'\downarrow}{}^*\Phi_0$.

Final state: $$[(1-h_{\mathbf{k}})^{\frac{1}{2}}+h_{\mathbf{k}}{}^{\frac{1}{2}}c_{\mathbf{k}\uparrow}{}^*c_{-\mathbf{k}\downarrow}{}^*]\times[(1-h_{\mathbf{k}})^{\frac{1}{2}}c_{\mathbf{k}'\uparrow}{}^*c_{-\mathbf{k}'\downarrow}{}^*-h_{\mathbf{k}}{}^{\frac{1}{2}}]\Phi_0.$$

The matrix elements with the parts of $\mathcal{H}_{SLz}$ are

$$\begin{aligned}(\psi_{\text{excited}}{}',\mathcal{H}_{SLz}\psi_{\text{excited}}) &= (\Phi_0,[(1-h_{\mathbf{k}'})^{\frac{1}{2}}c_{-\mathbf{k}'\downarrow}c_{\mathbf{k}'\uparrow}-h_{\mathbf{k}}{}^{\frac{1}{2}}][(1-h_{\mathbf{k}})^{\frac{1}{2}}\\ &\quad +h_{\mathbf{k}}{}^{\frac{1}{2}}c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}](c_{\mathbf{k}'\uparrow}{}^*c_{\mathbf{k}\uparrow}\text{ or }c_{-\mathbf{k}\downarrow}{}^*c_{-\mathbf{k}'\downarrow})c_{\mathbf{k}\uparrow}{}^*c_{-\mathbf{k}'\downarrow}{}^*\Phi_0).\end{aligned}$$

We make use of the anticommutation rules for the operators. The result with $c_{\mathbf{k}'\uparrow}{}^*c_{\mathbf{k}\uparrow}$ is $(1-h_{\mathbf{k}'})^{\frac{1}{2}}(1-h_{\mathbf{k}})^{\frac{1}{2}}$; that for $c_{-\mathbf{k}\downarrow}{}^*c_{-\mathbf{k}'\downarrow}$ is $(-)h_{\mathbf{k}'}{}^{\frac{1}{2}}h_{\mathbf{k}''}{}^{\frac{1}{2}}$. Thus for this matrix element,

$$(\psi_{\text{exc}}{}',\mathcal{H}_{SLz}\psi_{\text{exc}})=A\sum_j\sum_{k,\,k'\,(\text{pairs})}\tfrac{1}{2}(n|I_{zj}|m)\times[h_{\mathbf{k}'}{}^{\frac{1}{2}}h_{\mathbf{k}}{}^{\frac{1}{2}}+(1-h_{\mathbf{k}'})^{\frac{1}{2}}(1-h_{\mathbf{k}})^{\frac{1}{2}}],\qquad(12')$$

where n and m label nuclear states.

The same result as Eq. (12′) is obtained for $\mathcal{H}_{SL+}$ and $\mathcal{H}_{SL-}$ with I_{zj} replaced by I_{+j} and I_{-j}. Again the initial and final states of ψ_{exc} are connected in two different ways for both $\mathcal{H}_{SL+}$ and $\mathcal{H}_{SL-}$ since both the electron in k or that in $-k$ may be scattered. The fact that $\mathcal{H}_{SLz}$, $\mathcal{H}_{SL+}$, and $\mathcal{H}_{SL-}$ give the same result here is a reflection of the equivalence of the x, y, and z directions for spin scattering processes in zero field.

The above matrix element is typical of those which must be calculated. Each of the matrix elements, when squared, must be multiplied by the appropriate statistical factors giving the probability of occurrence of the initial state of the matrix element; the weighting factors can be written down directly in terms of s, p, and g, and substitution in terms of f can be made using Eqs. (8′) and (9′). The weighted, squared matrix elements for each operator, $\mathcal{H}_{SLz}$, $\mathcal{H}_{SL+}$, and $\mathcal{H}_{SL-}$, must then be added in two groups, one for $E_f-E_i=E-E'$ and the other for $E_f-E_i=E'-E$, as previously commented.

All the squared matrix elements have in common the term
$$[h_{\mathbf{k}}{}^{\frac{1}{2}}h_{\mathbf{k}'}{}^{\frac{1}{2}}+(1-h_{\mathbf{k}})^{\frac{1}{2}}(1-h_{\mathbf{k}'})^{\frac{1}{2}}]^2.$$

Using Eq. (10′) and the symmetry of electrons and holes, this contributes a factor $1+\epsilon_0{}^2/EE'$.

The nuclear matrix elements previously obtained (in part V) were in terms of I_x, I_y, and I_z rather that I_+, I_-, and I_z which were more natural in the second quantized calculation; a change back to I_x, I_y, and I_z will now be made to facilitate comparison with previous results. When all the additions are performed, one obtains for $W_{nm}{}^S$

$$W_{nm}{}^S=\frac{2\pi}{\hbar}A^2\sum_{i,j}\sum_{\mathbf{k},\,\mathbf{k}'\,(\text{unrestricted})}\frac{(n|\mathbf{I}_i|m)\cdot(m|\mathbf{I}_j|n)}{2}\times f(1-f')\left(1+\frac{\epsilon_0{}^2}{EE'}\right)\delta(E'-E+\hbar\omega).\qquad(13')$$

Changing now from sums over $\mathbf{k}$ and $\mathbf{k}'$ to integrals over E and E' and introducing $dn_{\mathbf{k}}=\rho_s(E)dE$ and $dn_{\mathbf{k}'}=\rho_s(E')dE'$, one obtains the final results, Eq. (45) of part VI for $W_{nm}{}^S$:

$$W_{nm}{}^S=\frac{2\pi}{\hbar}A^2\sum_{i,\,j}\frac{(n|\mathbf{I}_i|m)\cdot(m|\mathbf{I}_j|n)}{2}\int\rho_s(E_i)\rho_s(E_f)\times\left(1+\frac{\epsilon_0{}^2}{E_iE_f}\right)f(E_i)[1-(E_f)]dE_i,\qquad(14')$$

where $E_f-E_i=\mu_nH_{\text{loc}}$ and ρ_s is given in Eq. (46) of part VI.