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Nuclear Spin-Lattice Relaxation in Metals*

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The nuclear spin-lattice relaxation time, T_1, has been measured in the range of 1.1°K to 4.2°K for the metals lithium, sodium, aluminum, and copper. A combination of nuclear magnetic resonance at fixed frequency and adiabatic variation of the magnetic field was used to measure T_1 as a function of field between zero and one thousand gauss. At fields of between one hundred and one thousand gauss T_1 is independent of magnetic field and inversely proportional to temperature in agreement with theory. The experimental values of the relaxation time multiplied by absolute temperature in sec °K are 44 ± 2.0 for Li^7; 5.1 ± 0.3 for Na^{23}; 1.80 ± 0.05 for Al^{27}; 1.27 ± 0.07 for Cu^{63}. These values are in good agreement with previous experimental data at room temperature and above. At fields comparable with the nuclear magnetic dipole-dipole fields, T_1 is a function of applied field. The theory of relaxation in low fields is presented in an elementary form. Qualitative agreement with theory is obtained for Al^{27} and Cu^{63}; detailed agreement is obtained for Li^7 and Na^{23}.

INTRODUCTION

THIS paper reports the results of an experimental investigation of the nuclear spin-lattice relaxation time in several metals. The discussion will include relaxation at high external fields which are large in comparison with the nuclear magnetic dipole-dipole fields in the metal, and also relaxation at fields of a few gauss or less which are comparable with the dipole-dipole fields.

Korringa[1] has calculated the single-spin relaxation time in a metal in terms of the nuclear spin-conduction electron interaction and has shown that the spin-lattice relaxation time, T_1, should be inversely proportional to temperature, independent of magnetic field, and simply related to the Knight shift. Pines[2] has extended this work by including electron correlation effects. At the time this work was initiated, high-field T_1 measurements had been made at various temperatures and fields[3,4] which were in reasonable agreement with theory. We have extended these measurements to lower fields and temperatures, in order to check the theoretical predictions with greater certainty, and to resolve discrepancies in the earliest data.[5,6]

Korringa's theory is applicable to a collection of interacting spins only if the applied field is large. When the external field is comparable with the magnetic dipole-dipole fields between nuclear spins, the Korringa theory must be modified to take account of the fact that the energy of the spin system with respect to the external field (Zeeman energy) is no longer large compared with the energy which pairs of spins have with respect to each other (dipole-dipole energy). The necessary modifications of the theory have been considered by one of us,[7] and also by Hebel and Slichter[8] who used an equivalent but simpler method. This theory predicts a relaxation time at zero field which is approximately half the relaxation time at high field and a transition from the low to the high-field relaxation time at a field determined by the Van Vleck second moment[9] of the nuclear magnetic resonance line. The theory is based solely on the spin temperature approximation,[10] and is presented below in a simplified version. By testing this theory we hoped to get information on the validity of the spin temperature approximation, on the existence of spatial correlation of the motion of the conduction electrons, and on the interpretation of nuclear relaxation measurements in superconductors.[8,11] Hebel and Slichter[8] have reported qualitative agreement with the theory for aluminum, while we report here some experimental results for lithium, sodium, aluminum, and copper.

The experimental setup consisted of a nuclear resonance spectrometer capable of measuring the intensity of the resonance, and thus the nuclear spin magnetization, very rapidly at 1000 gauss, and a magnet which could be automatically varied to produce fields of from 0 to 1000 gauss. The relaxation time at 1000 gauss is measured simply by turning on the field and sweeping through the resonance at a later, variable time to monitor the rate of rise of magnetization. At lower fields the relaxation time is measured by first letting the spins polarize for a long time at 1000 gauss, then lowering the field to the field value at which the measurement is to be made and leaving it there for a variable time, τ, and finally increasing the field to 1000 gauss again and immediately sweeping through resonance to observe the decrease of magnetization caused by relaxation at the low field. Using the spin temperature approximation, in the low-field method the nuclear spin system is initially in equilibrium at a spin temperature, T_S, equal to the

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

[2] D. Pines, *Solid State Physics*, edited by F. Seitz and D. Tumbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 367.

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

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

[5] N. J. Poulis, Physica **16**, 373 (1950).

[6] N. Bloembergen, Physica **15**, 588 (1949).

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

[8] L. C. Hebel and C. P. Slichter, Phys. Rev. **107**, 901 (1957); **113**, 1504 (1959).

[9] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

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

[11] A. G. Redfield, Phys. Rev. Letters **3**, 85 (1959).

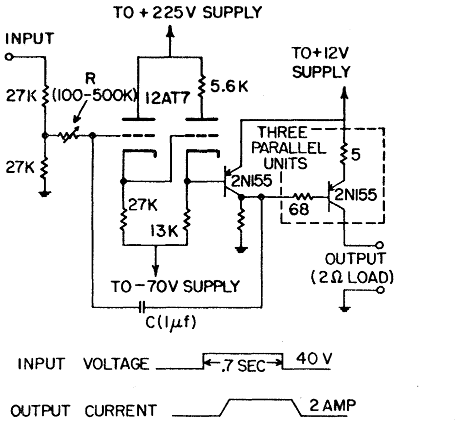

FIG. 1. Transistor linear sweep drive. Maximum current output is approximately 2 amperes. The slope of rise and fall is determined by R and C.

lattice temperature, T_L; the spin system is then adiabatically demagnetized and cools to a temperature $T_S<T_L$ with gradual warming by contact with the lattice through the conduction electron—nuclear spin interaction during the τ time interval. A subsequent adiabatic remagnetization finds $T_S>T_L$ and this difference is measured on the pass through resonance. The method is discussed in greater detail by Hebel and Slichter.[8] These techniques were first used by Bloembergen, Purcell, and Pound[12] and by Sachs and Turner[13] some time ago; they are easy in metals only at low temperatures where the relaxation times are long and the signals large.

EXPERIMENTAL DETAILS

The metal to be studied was made in the form of a powder or fine dispersion, and was placed in a radiofrequency head which could be inserted into a conventional glass helium Dewar. The tail of the Dewar was surrounded by a magnet, which was a concentric copper coil cooled in liquid nitrogen, powered by a 12-volt storage battery, and controlled by heavy-duty relays. The operation of these relays, and the various other operations to be described later, were controlled electronically using a commercially built interval timer, pulse generators, and auxiliary amplifiers and relays.

The rf head was a simple miniature crossed coil bridge which was adjusted for perpendicularity (minimum leakage signal) at room temperature, before being placed in the Dewar. It was surrounded by a rigid brass shield to reduce microphonic noise. Unbalance which occurred when the head was cooled was cancelled by additional signals fed to the receiver input from an rf phase shifter and attenuator, driven by the transmitter.

The transmitter was conventional and was normally run so that the peak rf field was about 2 gauss ($H_1=1$ gauss). It could be turned on and off with a relay and contained a slow acting level regulator, similar to the automatic volume control used in most commercial receivers. Because of the sluggishness of this circuit it took about 0.1 second for the transmitter to come on when its relay was actuated; this reduced the switching transients which appeared in the detection system. The receiver was a conventional two-stage tuned radiofrequency amplifier followed by a diode detector. The frequency used (1170 kc/sec) was chosen to be as far as possible from local broadcast frequencies.

The sweep fields used to observe the resonance were provided by a small coil wound on the outside of the helium Dewar. This coil was driven by the circuit shown in Fig. 1, which produces a trapezoidal current pulse when driven by a pulse of sufficient length and amplitude on the input. Normally, the total sweep thus produced was about 120 gauss and the rise time was about 0.2 second. By observing the resonance "on the fly" it is possible to avoid troubles due to instability of the main magnet or its storage battery power supply. Instabilities as large as $\frac{1}{2}\%$ in the main field produce only an insignificant delay in the time at which resonance is observed. This degree of stability could be achieved by manual adjustment of the magnet dropping resistor, provided the battery was connected (by relays) to a dummy load whenever the magnet was turned off. The stability was also enhanced by the use of large dropping resistors and by the nitrogen cooling of the magnet.

The rf leakage fed into the receiver circuit was such that the dispersion mode was observed; this is favorable since the microphonic noise is in the absorption mode. We originally planned to observe the adiabatic rapid passage signal directly, as one of us had done previ-

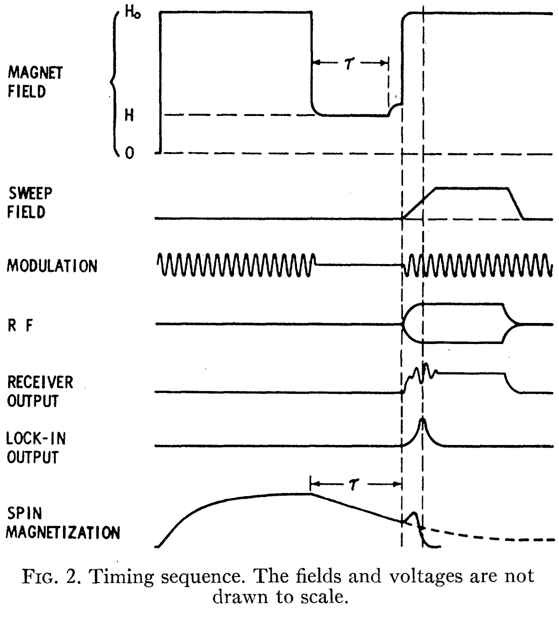

FIG. 2. Timing sequence. The fields and voltages are not drawn to scale.

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

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

ously.[14] However, at this low field, an unexpected difficulty appeared. The bridge balance, and thus the leakage signal, depended on the dc field. In other words, when the dc field was swept, an additional voltage appeared on the receiver coil of the bridge, proportional to the sweep field. This voltage was in the absorption mode phase,[15] and may have been caused by Hall effect in the metal. Attempts to reduce interference from this source by increasing the dispersion-mode leakage merely increased noise originating in the transmitter to a prohibitive level. Therefore, we finally resorted to the more conventional method of audio modulating the field (at 280 or 1000 cycles per second) and detecting the resulting audio output of the receiver with a "lock-in" detector which had an unusually wide band width and short time constant (about 0.05 sec).

The complete timing sequence used for measurements below 250 gauss is shown in Fig. 2. The magnet field is initially left on for at least ten high-field relaxation times. The interval timer is then started manually, and it turns the field from H_0 down to the field H at which the relaxation time is to be measured. When the field is turned on again, it is first given a slow initial rise to avoid shocking the spins when H is near zero. The necessity for this slow initial rise, and the consequences of a rapid rise, are discussed in detail by Hebel and Slichter[8] in their Sec. III. The field may be varied arbitrarily rapidly when it is greater than the local field of a few gauss.

When the field is at H, the sweep, modulation and rf fields are removed to avoid possible spurious effects.[16] Shortly after the magnet field is reapplied, the sweep is automatically initiated, and the modulation and rf fields are turned on. When resonance is reached a bell-shaped signal appears on the output of the lock-in, as shown in Fig. 3. This is not the shape of the adiabatic rapid passage signal which might be expected here. The modulation and sweep fields are varying too rapidly to be adiabatic; however, this mode of operation gives the largest signal. The magnetization is destroyed by the act of measurement, but this is not important since it is completely restored by relaxation before repeating the sequence with a different time τ. Adiabatic rapid passage signals having the correct S shape have been observed at lower modulation levels, but with considerable sacrifice in signal amplitude.

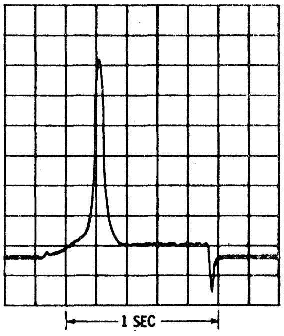

FIG. 3. Resonance signal observed in Al^{27} at 1.1°K. The transient at beginning and end of the trace is that due to turning on and off the rf field. The step upon which the signal is superimposed is due to a change of rf bridge balance with application of the dc field sweep.

TABLE I. Analysis (before filing) and suppliers of samples.

Sample	Maximum probable impurities	Supplier
Li >99.8%	Fe 0.001%; Na 0.05%; K 0.01%; N, Ca 0.02%	Lithium Corporation of America
Na >99.99%		U. S. Industrial Chemical Company
Cu >99.999%		A. D. McKay Company (New York, New York)
Al I >99.99%		A. D. McKay Company
Al II >99.995%	Fe 0.0005%; Si 0.002%; Cu 0.0005%	Johnson, Mathey
Al III >99.9999%		Bell Telephone Laboratories[a]

[a] Supplied through the kindness of Dr. J. H. Wernick.

A measurement of T_1 at any particular value of H and temperature T consists of a series of measurements as in Fig. 2, with varying τ (but keeping all other delays, rates, and other variables the same). The lock-in signal amplitude is always proportional to a constant plus $\exp[-\tau/T_1(H)]$, within experimental error, and the value of $T_1(H)$ is taken to be that which best fits the data. By taking data at several values of τ we eliminate several sources of systematic error.

The relaxation time at 1000 gauss is measured by initially leaving the magnet field *off* for several relaxation times, and turning it on at the *beginning* of the interval τ. The other fields are applied at the end of τ as before, and again the best time constant to fit the data is taken to be T_1.

The metals which could be investigated were limited by the magnetic field switching times, of the order of milliseconds, set by the use of an air core coil and relay circuitry. Fortunately, lithium, sodium, aluminum, and copper have relatively long relaxation times at temperatures in the helium range with T_1 varying from tenths of seconds to tens of seconds.

Samples of aluminum and copper were obtained by filing, sieving, and annealing in vacuum at temperatures of 350–400°C. Lithium and sodium samples were obtained in the form of dispersions in oil. It was feared that in freezing, the oil in these dispersions would set up strains, and thus induce quadrupole effects. The data near zero field, and other evidence[16] indicate that such effects are negligible.

The probable impurities in the samples are listed in Table I. These estimates do not include impurities in the Al and Cu which were introduced in the process of filing and annealing. In the case of aluminum sample III, which was zone refined, an effort was made to avoid such contamination by etching the sample with HCl after filing, to remove iron picked up from the file, before vacuum annealing.

In all cases, particle sizes were kept to dimensions of a few thousandths of a centimeter in order to minimize rf skin effect problems. In previous work, an apparent lack

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[14] A. G. Redfield, Phys. Rev. **101**, 67 (1956).

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

[16] A. G. Anderson, Phys. Rev. **115**, 863 (1959).

of skin depth effects was observed in copper and aluminum particles at 6 megacycles per second in the range of 2°K to 4.2°K. In the present work, using aluminum, we found that changing from a particle size distribution with a smallest dimension of ten to twenty-five microns to a distribution of twenty-five to fifty microns produced no change in signal amplitude. It was also found that the retuning of the receiver coil necessary on going from room temperature to helium temperatures was such that an inductance change of less than five percent was indicated with the 10–25 micron distribution, although the coil filling factor was 50%. Both of these experiments indicated that the rf field was penetrating the sample volume. Although the particles were larger than the classical skin depth, the anomalous skin depth effects due to large mean free path of the conduction electrons are apparently important here.

Temperatures in the range of 1°K to 4.2°K were determined by resistive thermometers[17] which had been calibrated with the vapor pressure-temperature scale of liquid helium.

HIGH-FIELD RELAXATION

The theory of relaxation at high fields in metals has been adequately discussed by various authors.[1–3,18] In summary, the relaxation time produced by the conduction electron-nuclear spin metallic hyperfine interaction is calculated by considering the interaction as a perturbation on a nuclear spin system consisting of noninteracting nuclear spins in a dc magnetic field; first order time dependent perturbation theory then shows[1] that the relaxation *rate* is proportional to the square of the interaction multiplied by the number of electrons allowed to enter into the process by Fermi statistics, i.e., approximately kT/E_f where E_f is the energy of an electron at the Fermi surface. The fractional line shift[19–21] (Knight shift) associated with the interaction is determined by the spin susceptibility of the electron gas multiplied by the normalized probability density at the nucleus; the shift is proportional to the first power of the interaction and independent of temperature at constant volume. Both processes are independent of dc field in this analysis. Pines[2] has recently discussed the effects of electron correlation on this problem and has derived the modified "Korringa relation"

$$T_1T\left(\frac{\Delta H}{H}\right)^2=\frac{\hbar}{4\pi k}\left(\frac{\gamma_e}{\gamma_n}\right)^2\left[\frac{N_0(E_f)}{N(E_f)}\right]\left[\frac{\chi_S}{\chi_{S0}}\right]^2, \qquad (1)$$

where $(\Delta H/H)$ is the Knight shift, k is Boltzmann's constant, γ_e and γ_n are electron and nuclear gyromagnetic ratios, $N_0(E_f)$ and $N(E_f)$ are the densities of states at the Fermi surface in an ideal Fermi gas and in the real metal, respectively, and χ_{S0} and χ_S are the corresponding spin susceptibilities. It is assumed that the predominant relaxation is that due to S-state interaction. A rough calculation by us and calculations by Masuda[22] indicate that relaxation by p-state dipolar interaction is less than two percent in the metals used here. This contribution is estimated by considering the interaction between orbital moment or spin moment of the electron and the nuclear moment for the appropriate percentage of p wave contribution to the electron wave function; the square of this interaction is compared with the square of the metallic S-state hyperfine interaction to provide an estimate of their relative importance.[1]

Our measurements of relaxation time for applied magnetic fields of greater than one hundred gauss are shown in Table II. The value of field given is that at which greatest experimental accuracy was obtained, but we found no significant variation in relaxation time between 250 and 1000 gauss. Also included in Table II are earlier measurements at high temperatures, and theoretical predictions.

The first point to be noted from the experimental data is the close agreement with the T_1T dependence predicted by the theory. Previous data,[5,6,23] reporting

TABLE II. Theoretical and experimental values of the product of relaxation time and temperature at various high fields and temperatures.

Metal	Field gauss	Temperature range °K	T_1T (experiment) sec °K	T_1T (theory)[e] sec °K
Li^{7}	700	1–4.2	44±2[a]	85[f]; 33[g]
	1800	300–400	40.6[b]	
	9100	300–400	44.6[b]	
Na^{23}	1000	1–4.2	5.1±0.3[a]	7.4[h]; 4.8[g,h]
	2700	250–450	4.38[b]	6.8[f]
	7950	250–450	4.77[b]	
Al^{27}	1000	1–4.2	1.80±0.05[a]	1.9
	10 000	77–1000	1.89[c]	
Cu^{63}	250	1–4.2	1.27±0.1[a]	1.2
	1000	300	1.06±0.2[d]	

[a] Present experiment.
[b] See reference 3.
[c] See reference 31.
[d] See reference 14.
[e] From Eq. (1), using experimental spin susceptibility for Li and Na [see R. T. Schumacher and C. P. Slichter, Phys. Rev. **101**, 58 (1956)] and calculated susceptibility (reference 2) for Al and Cu, Knight shifts from reference 21, and using (except where noted) the free-electron density of states with $m^*/m=1.45$ for Li, 0.98 for Na (see reference 2), 1.0 for Al and Cu.
[f] Using 300°K Knight shift (reference 2).
[g] Using experimental densities of states from specific heat measurements (reference 25).
[h] Using 4.2°K Knight shift (reference 2).

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[17] J. R. Clement and E. H. Quinnell, Rev. Sci. Instr. **23**, 213 (1952).

[18] E. R. Andrews, *Nuclear Magnetic Resonance* (Cambridge University Press, Cambridge, 1955), Chap. 7.

[19] W. D. Knight, Phys. Rev. **76**, 1259 (1949).

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

[21] W. D. Knight, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2.

[22] Y. Masuda, J. Phys. Soc. Japan **13**, 597 (1958).

[23] A. G. Anderson and A. G. Redfield, *Proceedings of Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August 30, 1957*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958), p. 616. (A 20% variation of T_1T with temperature in lithium reported in this paper was found to be in error.)

discrepancies at low temperatures apparently suffered from impurity effects or from the method of observation. The agreement between the data obtained here at fields of 1000 gauss or less and those obtained at high temperature and fields of up to 10 000 gauss appears to rule out any large field dependence, in agreement with theory, but in disagreement with the earliest relaxation measurements in metals.[5]

Although the agreement between high- and low-temperature experimental data is good over-all, there remain puzzling points. The most obvious of these is the variation of T_1T of sodium from room temperature to 4.2°K. The interest in this point is increased because of the previously reported change[21] in the Knight shift in the same temperature interval. The experimental $T_1T(\Delta H/H)^2$ at 4.2°K using T_1T from this experiment is in agreement within experimental error with the same quantity at 300°K and 2700 oersteds. Because of the field dependence of T_1 in lithium and sodium observed by Holcomb and Norberg near 300°K, this comparison is not too significant, but the indication remains that there is either a field dependence or a temperature dependence of T_1T, in conflict with theory. A temperature dependence of the density of states would appear to partially explain relaxation data, Knight shift data and recent susceptibility data.[24] Measurements of T_1T in the interval 4.2°K to 300°K would clarify the situation as would a search for field dependence of T_1T at 4.2°K.

Lithium, with the longest relaxation time, is the worst of these metals concerning agreement with theory. It is also the metal with the largest effective mass and the largest correlation correction to spin susceptibility. Recent data[25] on specific heats has indicated that the density of states may be higher than predicted by the effective mass approximation to the free electron gas model. On the basis of Pine's[2] theory, Fletcher and Larson[26] have predicted an increased density of states at the Fermi surface. The values of T_1T calculated from Eq. (1) with these higher densities of states are in fair agreement with experiment for both lithium and sodium.

With the exception of lithium, the experimental agreement with theory and the modified Korringa relation is within about twenty percent. The agreement is obtained in aluminum by assuming one electron per atom.

The relaxation time in Cu^{65} should be shorter than the relaxation time of Cu^{63} because of its larger gyromagnetic ratio and consequently larger hyperfine interaction. Within experimental error, the relaxation time for Cu^{65} is shorter by about fifteen percent as expected.

LOW-FIELD RELAXATION

Theory

The dynamic behavior of isolated nuclear spin systems at low applied external field has been discussed in detail by Abragam and Proctor[10] and by Hebel and Slichter[8]; the latter authors have also given a particularly lucid and thorough treatment of relaxation at low fields. In order to make the problem tractable, these authors make use of the spin temperature concept introduced some years ago by Casimir and duPre.[27] The only comment we would add to their treatment is that the spin temperature concept should be regarded as an approximation, though a very good one, in the present case. We believe that if spin temperature is viewed in this way, some of the objections to the concept discussed in reference 10 can be avoided.

Consider first the measurement at zero field. As indicated by Hebel and Slichter, when the field is lowered from the initial value of 1000 gauss to zero, the spin temperature decreases from the lattice temperature to a lower temperature. The spin temperature at zero field, neglecting relaxation, can be calculated if the field is lowered sufficiently slowly and if relaxation is negligible. It is determined by the requirement that in such an adiabatic process, initial and final entropy are equal or, equivalently, the assumption that each spin finally has the same probability of polarization along its *local* field as it initially had along the large external field. Thus the ratio of initial to final spin temperatures is simply proportional to the ratio of the external to the root mean square internal spin-spin fields.

At zero field, as at high field, the spin system energy is inversely proportional to temperature and negative (for positive temperatures such as we always consider here). The spin system energy is therefore much larger in magnitude than its equilibrium value immediately after the field is removed. In zero field the expectation spin value of the energy decays according to the usual rate equation

$$\frac{d}{dt}(\langle\mathcal{H}_{SS}\rangle) = -(\langle\mathcal{H}_{SS}\rangle - \langle\mathcal{H}_{SS}\rangle_0)/T_1(0). \qquad (2)$$

Here the spin energy $\langle\mathcal{H}\rangle$ is denoted by the spin-spin energy $\langle\mathcal{H}_{SS}\rangle$, since they are identical at zero field, $\langle\mathcal{H}_{SS}\rangle_0$ is the thermal equilibrium value of $\langle\mathcal{H}_{SS}\rangle$, and $T_1(0)$ is the relaxation time which is being measured.

It is easy to estimate $T_1(0)$ if we note that $\langle\mathcal{H}_{SS}\rangle$ is equal to the sum of a large number of terms, each of which can be regarded as the energy a spin i has with respect to the local dipole field from spin j. Naively we expect that this energy can change, through relaxation, either by relaxation of spin i at a rate $1/T_{1K}$, or relaxation of spin j at a rate $1/T_{1K}$, where T_{1K} is the relaxation time of an *isolated* spin. Therefore we expect that the rate of relaxation of the interaction to go at *double* the rate $1/T_{1K}$ of a single spin, so that $T_1(0)=\frac{1}{2}T_{1K}$. For relaxation by conduction electrons, which move rapidly compared to the Larmor frequency, the relaxation time of a single spin should be field independent, so T_{1K} is the

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[24] F. T. Hedgcock, reference 23, p. 545.

[25] L. M. Roberts, Proc. Phys. Soc. (London) **B70**, 744 (1957).

[26] J. G. Fletcher and D. C. Larson, Phys. Rev. **111**, 455 (1958).

[27] H. G. B. Casimir and F. K. duPre, Physica **5**, 507 (1938).

high-field relaxation time. This simple picture can be justified theoretically, and the experimental values in Li and Na agree remarkably well.

The relaxation time measurement is completed by turning the field on adiabatically after a time τ to its original value, as a result of which the spin temperature rises to a value greater than the lattice temperature (but proportional to the spin temperature just prior to reapplying the field). The final spin temperature is then measured by doing a rapid resonance experiment. We have not described in any detail the rate at which the field must be varied, or what is meant here by the word, "adiabatic"; we refer the reader to Hebel and Slichter[6] for a thorough discussion. In general it is difficult to satisfy the requirements that the field be varied sufficiently slowly to be adiabatic but sufficiently rapidly that relaxation be negligible. However, if the rate of turning off and on of the field are reproducible and independent of τ it is not hard to show that the signal observed should still vary exponentially with τ with a time constant $T_1(0)$; the only effect of relaxation during field switching is to reduce the limits between which the signal varies as τ is varied from zero to infinity.

Returning to the relaxation in zero field, it should be noted that the spins i and j which we considered previously were assumed to relax independently; the motion of spin i due to relaxation was assumed uncorrelated with that of spin j. This assumption may not be valid, since only those pairs i and j which are a few lattice spacings apart contribute appreciably to the spin-spin energy, and the most important pairs are neighbors and next nearest neighbors. Since the electrons responsible for relaxation have wavelengths comparable to the distance between spins, it is possible that there might be some correlation in the relaxation behavior of near neighbors.

It is easy to predict the effect of correlation on the relaxation time for one special case, unlikely to be physically realized. This is for a set of nuclear spins whose interaction is mainly of the so-called exchange form:

$$\mathcal{H}_{SS}=\mathcal{H}_{\text{dip}}+\sum A_{ij}\mathbf{I}_i\cdot\mathbf{I}_j, \tag{3}$$

where $\mathcal{H}_{\text{dip}}$ is the classical dipolar interaction, which is assumed small compared to the last term. The relaxation can be regarded semiclassically as resulting from fluctuating fields due to the electrons; we denote the fluctuating field on spin i by $\mathbf{h}_i(t)$. If the electrons have very long wavelengths, as in a semiconductor, these fluctuating fields are identical for near neighbors: $\mathbf{h}_i(t)=\mathbf{h}_j(t)$. In that case, the *total* field seen by near neighbors i and j is identical, so the angle between them is constant with time and $\mathbf{I}_i\cdot\mathbf{I}_j$ is constant. Thus in this case the zero field relaxation time would become very long because only the classical dipolar part of the spin energy would be changed by relaxation.

In general, and particularly in the light metals we consider here, the first term in (3) is dominant. In that case, it is not as easy to predict the relaxation time by such simple reasoning, and we merely state the result of semiclassical[7] and quantum mechanical[8] calculations. In general,

$$d\langle\mathcal{H}_{SS}\rangle/dt=-\delta(\langle\mathcal{H}_{SS}\rangle-\langle\mathcal{H}_{SS}\rangle_0)/T_{1K}. \tag{4}$$

Previously we had $\delta=2$. In general,

$$\delta=2+(\sum_{j>k}K_{jk}r_{jk}^{-6})/\sum_{j>k}r_{jk}^{-6}; \tag{5}$$

r_{jk} is the distance between spins j and k, and K_{jk} expresses the degree of correlation between the fluctuating fields at $\mathbf{r}_j$ and $\mathbf{r}_k$ due to the conduction electrons:

$$K_{jk}=\langle\mathbf{h}_j(t)\cdot\mathbf{h}_k(t)\rangle_{\text{Av}}/\langle|\mathbf{h}_j(t)|^2\rangle_{\text{Av}}. \tag{6}$$

Here $\langle\ \rangle_{\text{Av}}$ denotes the time average. K_{jk} is unity for complete spatial correlation, and zero if the fields at $\mathbf{r}_j$ and $\mathbf{r}_k$ are statistically independent. It will be noted that the maximum value of δ is 3; i.e., $T_1(0)=[T_1(H\gg0)]/3$ if there exists complete spatial correlation.

The quantum analog of K_{jk} can also be calculated if the wave functions of the electron gas are known. For an ideal Fermi gas,

$$K_{jk}=\sin^2(k_m r_{jk})/(k_m r_{jk})^2, \tag{7}$$

where k_m is the radius of the Fermi surface. Assuming one electron per atom, this yields only a small correlation, since δ is increased only from 2 to about 2.05.

It may be that the Coulomb interaction between conduction electrons produces additional spatial correlation in the motion of the electrons which would increase δ and thus decrease $T_1(0)$ somewhat. This could probably be estimated using the theory of Bohm and Pines.[2] It might be especially important in the case of superconductors.

We now consider the field dependence of T_1. If the field is not completely removed during the time τ the spin temperature is not as low as in the zero-field case during the time τ. More important, the spin energy consists of two parts,

$$\langle\mathcal{H}\rangle=\langle\mathcal{H}_0\rangle+\langle\mathcal{H}_{SS}\rangle. \tag{8}$$

Here $\langle\mathcal{H}_0\rangle$ is the energy $-\mathbf{M}\cdot\mathbf{H}_0$ of the spins with respect to the external field $\mathbf{H}_0$.

The spin temperature approximation tells us that the ratio of $\langle\mathcal{H}_0\rangle$ to $\langle\mathcal{H}_{SS}\rangle$ is *always* the same for a given value of H:

$$\langle\mathcal{H}_{SS}\rangle=[(10/3)\langle\Delta H^2\rangle_{\text{Av}}/H^2]\langle\mathcal{H}_0\rangle, \tag{9}$$

where $\langle\Delta H^2\rangle_{\text{Av}}$ is the Van Vleck second moment[9] of the nuclear resonance absorption line, and we neglect possible exchange-type interaction.

Since $\langle\mathcal{H}_0\rangle$ is the sum of the energies of individual spins, its relaxation rate is the same as that of a single spin:

$$d\langle\mathcal{H}_0\rangle/dt=-(\langle\mathcal{H}_0\rangle-\langle\mathcal{H}_0\rangle_0)/T_{1K}, \tag{10}$$

where $\langle\mathcal{H}_0\rangle_0$ is the thermal equilibrium value of $\langle\mathcal{H}_0\rangle$, which is related to $\langle\mathcal{H}_{SS}\rangle_0$ by an equation similar to (9). Equation (10) gives *only* the contribution of *spin-lattice* relaxation to the rate of change of $\langle\mathcal{H}_0\rangle$, while (4) gives the corresponding rate for $\langle\mathcal{H}_{SS}\rangle$. These energies also change through *spin-spin* interaction, but in equal and opposite amounts since total $\langle\mathcal{H}\rangle$ is conserved by spin-spin relaxation.

Combining (4), (8), (9), and (10) we have

$$d\langle\mathcal{H}\rangle/dt=-(\langle\mathcal{H}\rangle-\langle\mathcal{H}\rangle_0)/T_1(H), \tag{11}$$

where

$$T_1(H)=T_{1K}\frac{H^2+(10/3)\langle\Delta H^2\rangle_{\text{Av}}}{H^2+\delta(10/3)\langle\Delta H^2\rangle_{\text{Av}}}, \tag{12}$$

and $\langle\mathcal{H}\rangle_0$ is the thermal equilibrium value of $\langle\mathcal{H}\rangle$.

This is the same result obtained more rigorously elsewhere.[7,8] It is worth emphasizing that though $\langle\mathcal{H}_{SS}\rangle$ relaxes at a greater rate than $\langle\mathcal{H}_0\rangle$, their relative magnitudes are always maintained as indicated by (9) at the value required by the spin temperature approximation. The relative sizes of these two terms is maintained by the spin-spin interaction, which flips single spins, reducing the magnitude of $\langle\mathcal{H}_0\rangle$ and (by energy conservation) increasing $\langle\mathcal{H}_{SS}\rangle$. Such single spin flips are allowed energetically when H is comparable to the dipole fields, as is the case here; it is correct to think of one spin flipping one way with respect to H, while another spin flips another way with respect to its local dipole field.

The reader may well be skeptical about certain points in this simplified theory without further justification; for this justification we refer in particular to Hebel and Slichter.[8] It is interesting that the relaxation by the lattice of the spin-spin energy $\langle\mathcal{H}_{SS}\rangle$ and the external energy $\langle\mathcal{H}_0\rangle$ can be expressed independently by (4) and (10). This is not obvious from what has been said here; it is a consequence of the fact that in the high-temperature approximation ($kT\gg\hbar\gamma H$) applicable here, the spins and thus the dipolar fields are very nearly random in orientation. At temperatures in the microdegree range the spins would start to be appreciably aligned and there would be cross terms between (4) and (10).

As a result of strains due to various imperfections, each spin may be subjected to an electric field gradient[28] with which the spin will interact via its quadrupole interaction. If this interaction is very large and varies rapidly over large distances, it will be impossible for energy to diffuse rapidly enough (via spin diffusion) through the spin system to ensure a uniform spin temperature. If, however, the quadrupole interaction is not too large, and varies appreciably over a distance small enough that spin diffusion can take place during a time short compared to the observed T_1, then it appears reasonable to assume that the spin system is described by a single spin temperature, as before. The relaxation can be calculated using the method of reference 7.

We omit the tedious details of this calculation and merely state the result. Following the notation of reference 28, we assume that nucleus j has a quadrupole moment eQ and is in a field gradient having a maximum value eq_j in some direction, and a departure from axial symmetry denoted by η_j, where $0\leq\eta_j\leq 1$; $\eta_j=0$ corresponds to axial symmetry.

The relaxation time is then given by

$$\frac{1}{T_1(H)}=\frac{H^2+\delta(10/3)\langle(\Delta H)^2\rangle_{\text{Av}}+\bar{H}_q{}^2(3+\frac{2}{3}\bar{\eta}^2)}{H^2+(10/3)\langle(\Delta H)^2\rangle_{\text{Av}}+\bar{H}_q{}^2(1+\frac{1}{3}\bar{\eta}^2)}, \tag{13}$$

where $\bar{H}_q{}^2$ is the square of an "equivalent" magnetic field in which the Zeeman interaction approximates the quadrupole interaction; more precisely,

$$\bar{H}_q{}^2=\frac{e^4\bar{q}^2Q^2[4I(I+1)-3]}{80(2I-1)^2I\gamma^2\hbar^2}. \tag{14}$$

$\bar{q}^2$ is the average value of $q_i{}^2$ and $\bar{\eta}^2$ is the average value of $q_j{}^2\eta_j{}^2/\bar{q}^2$.

This expression is expected to apply only if the *difference* between the quadrupole interaction of near neighbors is not too much larger than the dipolar interaction. If this is not the case, spin diffusion will be greatly inhibited. If l is the distance between imperfections (which give rise to quadrupole interactions), then it is also necessary that this distance be small enough that energy can diffuse over distance l in a time short compared to T_1: $(D_ST_1)^{\frac{1}{2}}\gg l$ where $D_S\simeq a_0{}^2/T_2$ is the spin diffusion coefficient.

Experiment and Discussion

The relaxation time at low field, as at high field, varied inversely with temperature, with the possible exception of aluminum, which showed a slight but significant departure. The field dependence of the relaxation time is shown in Figs. 4 to 7, compared with the theoretical prediction of (12). In drawing the theoretical curves we have chosen T_{1K} equal to the high field T_1 of

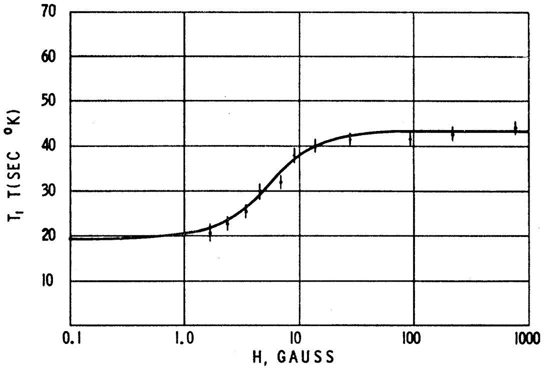

FIG. 4. Field dependence of the relaxation time of Li^7 at 1.3°K.

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[28] M. Cohen and F. Reif, *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic Press, New York, 1957), Vol. 5, p. 321.

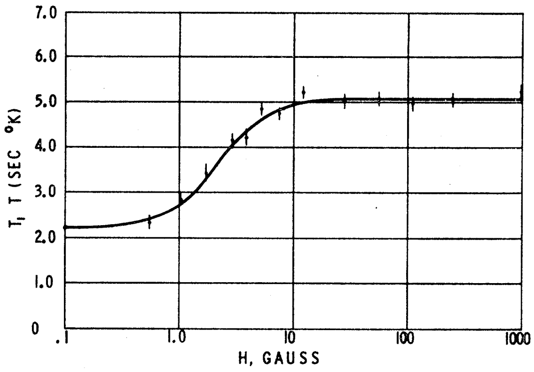

FIG. 5. Field dependence of the relaxation time of Na^{23} at 1.1°K.

Table I, and the parameter δ to make the theoretical curve agree with the zero field relaxation times. It seemed reasonable to do this because, though we expect $\delta \simeq 2$, we have seen that δ might be affected by Coulomb correlation effects. We have taken $\langle \Delta H^2 \rangle_{\mathrm{Av}}$ equal to its theoretical value[9]; the values of this quantity, and of δ, are given in Table III. We have thus neglected possible quadrupole interactions.

In lithium and sodium the experimental field dependence of T_1 is in close agreement with theory. This agreement indicates that line-broadening effects at zero field, such as the quadrupole effects produced by lattice distortion, are small. The agreement with theory for the field dependence also provides evidence that the spin temperature assumption is a good approximation in this case. It is possible to explain the values of δ obtained by assuming that there is about four to six times as much spatial correlation in the electron gas, due to Coulomb interaction, as there is in an ideal Fermi gas. This does not seem out of the question theoretically.

In the case of aluminum and copper the agreement with theory is qualitative only. In order to fit the field dependence of the experimental data for aluminum it is necessary to assume a $\langle (\Delta H)^2 \rangle_{\mathrm{Av}}$ of 25 gauss^2 which is greater than three times the theoretical value. The large value of δ found experimentally is also difficult to explain.

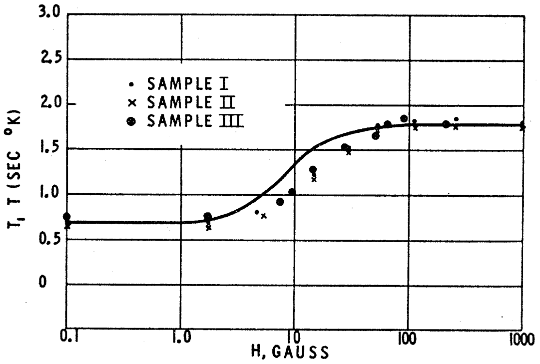

FIG. 6. Field dependence of the relaxation time of Al^{27}. Sample I at 4.2°K, Sample II at 1.3°K, Sample III at 1.4°K.

It is likely that the discrepancy in aluminum is a remanent quadrupole interaction of some kind. The experimental points can be fitted fairly well by Eq. (13), assuming $\delta = 2.2$ as in lithium and assuming a mean square quadrupole interaction such that $\bar{H}_q^2 \simeq 2.3(10/3)\langle (\Delta H)^2 \rangle_{\mathrm{Av}}$, where $\bar{H}_q^2$ is defined by Eq. (14) and where axial symmetry ($\eta = 0$) is assumed. This idea is supported by an independent experiment, reported elsewhere,[16,29] in which an audio-frequency magnetic field was applied to the sample during the time τ (Fig. 2) when the dc field was zero. It was then possible to infer the form of the "spin absorption" spectrum at zero field from the dependence of the magnetization (after again turning on the dc field) as a function of the audio-frequency. This spectrum has also been calculated[30] under the assumption of only dipole-dipole interaction; agreement with experiment is obtained for lithium and sodium, while in aluminum the experimental spectrum is too broad to be explained by dipole interaction alone. This experiment strongly indicates that the discrepancy in the present data is due to an extra unknown term in the spin Hamiltonian, rather than some unknown property of the conduction electrons or lattice.

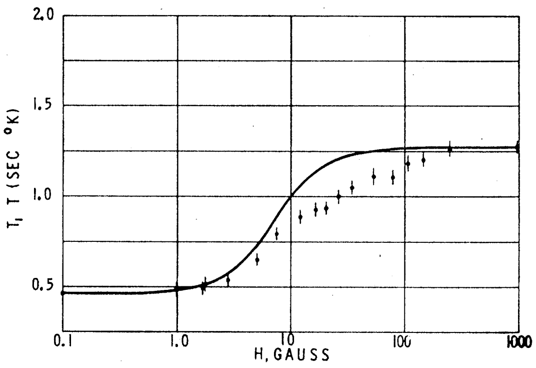

FIG. 7. Field dependence of the relaxation time of Cu^{63} at 1.1°K.

The observed existence, between 1.1 and 4.2°K of a slight (10%) temperature dependence of the zero field T_1T might also be explained by invoking quadrupole interaction. Diffusion of energy between different parts of the spin system which have different quadrupole interactions would take place at a temperature-independent (spin diffusion) rate and might tend to shorten the T_1 at the lower temperatures, as observed. There are other possible temperature-independent mechanisms (such as paramagnetic impurity relaxation via a spin diffusion bottleneck) which would explain this deviation when added to the normal conduction electron relaxation. It is noteworthy that T_1T varies only at low field; at high field it is constant.

Spokas and Slichter[31] have found a remanent inter-

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

[30] L. J. F. Broer, Physica **10**, 801 (1943).

[31] J. J. Spokas and C. P. Slichter (to be published).

action in aluminum at higher temperatures which they attribute to quadrupole effects arising from dislocations. By making crude estimates such as those made by these authors, we find that dislocation densities of the order of $10^{10}/\mathrm{cm}^2$ are required to explain the anomalous zero field line width and relaxation time in aluminum. The experimental results might also be explained by the presence of impurities; several parts per million (atomic) of typical impurities would be required.

In an effort to establish the source of the extra interaction in aluminum, measurements were made on both annealed and unannealed samples and on samples of various sizes (200 and 325 mesh) and purities. No annealing or size effects were observed, and only a questionably resolved impurity effect was found. In sample III, in particular, an attempt was made to remove surface iron picked up during filing by etching the sample in acid before annealing. However, chemical analysis on a similarly prepared sample showed of the order of 100 parts per million iron, which may be either on the surface, or in the volume of the sample as a result of diffusion. It is puzzling that the observations should be so reproducible, since any mechanism based on dislocations or impurities should vary with sample preparation. However, it is difficult to think of an alternative explanation.

TABLE III. The experimental relaxation time-temperature product, and parameters used in the theoretical curves of Figs. 4 to 7.

Sample	$T_1(0)T$[a] sec °K	Temperature range °K	δ[b]	$\langle \Delta H^2\rangle_{\mathrm{Av}}$[c] (gauss)^2
Li^7	20.5 ±2.0	1–4.2°K	2.2	4.3
Na^{23}	2.2 ±0.2	1–4.2°K	2.28	0.63
Cu^{63}	0.47±0.1	1–4.2°K	2.72	5.6
Al^{27} I	0.70±0.05	4.2°K	2.58	7.5
Al^{27} I	0.60±0.05	1.1°K		
Al^{27} III	0.84±0.05	4.2°K		
Al^{27} III	0.66±0.1	1.4°K		

[a] Present experiment.
[b] Chosen to best fit data using Eq. (12).
[c] Theoretical values from H. S. Gutowski and B. R. McGarvey, J. Chem. Phys. **20**, 1472 (1952).

It may be worth mentioning that the large quadrupole effects indicated here and in reference 31 are not necessarily inconsistent with the lack of quadrupole effects in the high-field resonance line of similarly prepared aluminum.[32] In the latter case the few percent of nuclei in a large quadrupole field are smeared out of the resonance entirely, without noticeable effect on the line; in the present experiment the few percent of nuclei contribute importantly to the spin Hamiltonian and specific heat (provided that the quadrupole interaction is not so large as to prohibit the transfer of energy from these spins to their neighbors).

The field dependence of T_1T in copper, which was similar to that of aluminum, is shown in Fig. 7. Here again the discrepancy between theory and experiment may be due to remanent quadrupole interaction. No attempt was made to establish the source of this interaction in copper. Equation (13) fits the data reasonably well, assuming $\eta=0$ and $\bar{H}_q^2=3(10/3)\langle(\Delta H)^2\rangle_{\mathrm{Av}}$.

The bump observed at about 20 gauss might have something to do with "thermal mixing" of the Cu^{63} and Cu^{65} systems. At fields of this magnitude, the difference in Zeeman energies in the two systems is comparable with the dipole-dipole energy in the systems. Unfortunately, no thermal mixing experiments were performed to locate the external fields at which mixing begins.

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[32] T. J. Rowland, Acta Met. **3**, 74 (1955).