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Effects of Electron-Electron Interactions on the Nuclear Spin-Lattice Relaxation Times in Aluminum*

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The "dipolar" spin-lattice relaxation time in aluminum has been measured for temperatures between $1.3^\circ\mathrm{K} < T < 295^\circ\mathrm{K}$. In contrast to the Zeeman spin-lattice relaxation time T_{1z}, the dipolar time does not vary linearly with $1/T$. This is interpreted in terms of cross relaxation between different groups of nuclear spins, some of which experience quadrupole interactions as a result of defects in the lattice, and others which are well removed from such defects. Both cross-relaxation and spin-lattice effects have been measured by our technique; a three-bath model of the nuclear-spin system permits a separation of these effects, with a true dipolar relaxation time T_{1dd} related to T_{1z} by $\delta = T_{1z}/T_{1dd} = 2.15 \pm 0.07$, δ being independent of temperature. This enhancement of δ over the value 2.00 and the enhancement of the Korringa relation between T_{1z} and K, the Knight shift, are discussed and compared with the predictions of the theory of Wolff in which the effects of electron-electron interactions are considered. A similar analysis in sodium is included for comparison, sodium being the metal to which the theory is best applicable.

I. INTRODUCTION

THE ratio δ in a metal of the two nuclear spin-lattice relaxation times T_{1z} (characteristic of the decay of the Zeeman component of the nuclear spin Hamiltonian) to T_{1dd} (characteristic of the decay of the dipolar component) has long been known to be sensitive to the degree of correlation between electron spin densities on adjacent nuclear sites. This was first suggested by Anderson and Redfield[1] and a theoretical treatment has been given by Wolff.[2]

The experiments of Anderson and Redfield consisted of the measurement of relaxation in various magnetic fields, including zero field where terms in the nuclear spin Hamiltonian other than Zeeman dominate, and very high field where the Zeeman term dominates. In sodium and lithium, the measured values of δ departed significantly from the value ~ 2.01 expected from a noninteracting model of the electron gas surrounding the nuclei and causing the relaxation. In aluminum and copper, the experimental results for $\epsilon = \delta - 2$ were at least an order of magnitude larger than could be predicted by the noninteracting model. The theory of Wolff[2] took into account interactions, using a δ function as a simulation of the electron-electron interactions, assuming a spherical Fermi surface with plane waves as electron wave functions, and empirically fitting the theory to the experimental determination of the enhancement of the spin susceptibility. The predicted values of ϵ in sodium and lithium of 0.03 are still much smaller than the recently measured values of Poitrenaud and Winter[3] of 0.12 ± 0.03 and 0.31 ± 0.05, respectively. The measured values of ϵ at helium temperatures in aluminum and copper, ~ 0.6 in both metals, were very much larger than are predicted by the theory, which gives $\delta \sim 0.05$.

Given these discrepancies between theory and experiment, we have undertaken an experimental program to measure the value of δ in several metals using a new experimental technique,[4] based on the use of combinations of phase-shifted pulses of rf, and permitting the measurements to be extended over a wide temperature range. The experiments reported here concern the measurements in aluminum.

The theory of Wolff also predicts a significant enhancement of the Zeeman spin-lattice relaxation rate $(T_{1z})^{-1}$ due to electron-electron interactions, this enhancement being implicitly contained in the expressions for ϵ. Moriya[5] explicitly derived this equation for the enhancement of $(T_{1z})^{-1}$ at about the same time. Since the Knight shift is also enhanced by such interactions between electrons, the experimental value of the Korringa[6] product $K^2 T_{1z} T$ provides another indication of the magnitude of electron-electron effects. To this end, therefore, a careful assessment of the Korringa enhancement in aluminum is included, and its value in relation to our measured value of δ is discussed. (An analysis of the Korringa enhancements in the alkali and noble metals has recently been published by Narath and Weaver.[7]) The theoretical and experimental Korringa and δ enhancements in sodium are included for comparison, and an assessment of the effects of a finite range for electron-electron interactions on the theoretical predictions for δ and the Korringa product in Na is given. This parallels the Narath and Weaver[7] discussion of the enhancement of the Korringa product, and we have used both screened Coulomb and Gaussian interactions as alternative representations of electron-electron effects.

The purpose of this article is to review the present state of knowledge of hyperfine effects in aluminum, to present new experimental data on dipolar relaxation

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[1] A. G. Anderson and A. G. Redfield, Phys. Rev. **116**, 583 (1959).

[2] P. A. Wolff, Phys. Rev. **129**, 84 (1963).

[3] J. Poitrenaud and J. M. Winter, Phys. Letters **17**, 199 (1965).

[4] J. Jeener and P. Broeckart, Phys. Rev. **157**, 232 (1967).

[5] T. Moriya, J. Phys. Soc. Japan **18**, 516 (1963).

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

[7] A. Narath and H. T. Weaver, Phys. Rev. **175**, 373 (1968).

times in Al, and to assess the applicability of the theory, including electron-electron interactions, of the nuclear spin-lattice relaxation times and the Knight shift in simple metals. In Sec. II, the relevant theory of the enhancement effects is reviewed. Section III is concerned with the experimental details and Sec. IV with the results and their interpretation. The data for aluminum are assembled in Sec. V, the component contributions to the Zeeman spin-lattice relaxation rate and the Knight shift are estimated, and the enhancement of the Korringa relation and the dipolar relaxation time discussed. The comparison with sodium is given in Sec. VI.

II. ELECTRON-ELECTRON ENHANCEMENT EFFECTS

We consider the case of a nuclear-spin system in an applied magnetic field B having a Hamiltonian consisting solely of Zeeman $\mathcal{H}_z$ and dipolar $\mathcal{H}_{dd}$ terms, the dominant term in fields greater than 0.01 T being $\mathcal{H}_z$. In a metal, the spin-lattice relaxation of such a spin system is via the conduction electrons (assumed in this section to be dominated by the contact part of the hyperfine interaction between the electrons and nuclei). In fields such that the Zeeman term dominates the spin Hamiltonian, then, since each nucleus is interacting independently with the magnetic field, the relaxation proceeds at a rate determined by the electron spin density at each site. This same spin density also determines the shift of the nuclear resonance, the Knight shift K_c and, therefore, leads to the simple Korringa[6] relation

$$K_c^2 T_{1z} T = A = (h/4\pi k_B)(\gamma_e/\gamma_n)^2. \tag{1}$$

The simplicity of this relation between K_c and T_{1z} permits easy comparison between theory and experiment. Equation (1) has, however, been derived neglecting interactions between electrons. When these are taken into account, the relation is modified because K_c^2 and $(T_{1z}T)^{-1}$ are not enhanced by the same amount. With the assumptions of the Wolff[2] theory, discussed in Sec. I, it is possible to express both (K_c/K_{c0}) and (T_{1z}/T_{1z0}), where K_{c0} and T_{1z0} are the values predicted by the noninteracting theory, as functions of a parameter α, characteristic of the strength of the δ-function interaction between the electrons. Thus, A in Eq. (1) becomes a function of α, and its experimental value may be used to evaluate α; an independent check on this procedure is proved in certain metals by measurement of the spin susceptibility χ_s, since (χ_s/χ_{s0}) shows the same dependence on α as (K_c/K_{c0}). The explicit expressions for these functions will not be given here, since Narath and Weaver[7] have discussed them in some detail.

Important information may also be obtained from experiments on spin systems where the dipolar Hamiltonian is the dominant term, e.g., in zero external magnetic field. After an adiabatic demagnetization or after application of the phase-shifted pair of rf pulses, the technique used by us, the dipolar subsystem is in a highly ordered state and may be described by a temperature $T \ll T_L$, where T_L is the lattice temperature. The nuclei have a high probability of being aligned along their own local fields, these being determined by the orientations of neighboring nuclei. There is, therefore, a large amount of correlation in the nuclear-spin system.

The nuclei now relaxed, with T tending towards T_L with the characteristic time T_{1dd}. With no correlation in the electron-spin system, this can be shown to proceed at a rate twice that of the Zeeman relaxation.[8] However, if there is correlation between electron spin densities at adjacent sites, then the relaxation time T_{1dd} will reflect it, and the ratio $\delta = (T_{1z}/T_{1dd})$ will deviate from the value 2.00. Since one-electron theory predicts rather small correlations in electron spin densities, Wolff[2] treated the problem, including electron-electron interactions and using a δ function as a representation of those interactions, by relating the electron-spin autocorrelation function to the nonlocal electron-spin susceptibility. His expressions may be summarized as

$$K_{ij} = \frac{1}{X_{ij}} \int_0^1 \sin(qX_{ij}) \, [1-\alpha f(q)]^{-2} dq \Bigg/ \int_0^1 q[1-\alpha f(q)]^{-2} dq, \tag{2}$$

where $q = Q/2k_F$ (Q being the amplitude of the wave vector in the susceptibility function), $X_{ij} = 2k_F R_{ij}$ (R_{ij} being the distance between the two nuclei i and j), α is the enhancement parameter proportional to the strength of the electron-electron interactions, and $f(q)$, $= \frac{1}{2}[1+(1-q^2)/2q \ln(1+q/1-q)]$, is the q-dependent factor in the real part of the susceptibility of a noninteracting electron gas. ϵ is obtained from the K_{ij}'s by a simple lattice sum

$$\epsilon = [\sum_j K_{ij}(1/R_{ij}^6)] / \sum_j (1/R_{ij}^6), \tag{3}$$

taking nucleus i as typical.

The denominator in Eq. (2) is just the prediction of the theory for the enhanced value of $(2T_{1z}T)^{-1}$ in agreement with the Moriya[5] calculation. In the limit of $\alpha \to 0$, Eq. (2) reduces to

$$K_{ij} = (\sin^2 k_F R_{ij} / k_F R_{ij})^2, \tag{4}$$

which reflects the dependence of the electron-spin correlation in the absence of interactions on the wavelength of the electrons that participate in the relaxation process.

The equations above have been derived on the basis

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

of certain assumptions that we re-emphasize here: (a) a nuclear-spin system with only Zeeman and dipolar terms; (b) plane waves, spherical Fermi surfaces, for the description of the electron states; and (c) a δ-function interaction as a simulation of electron-electron effects.

If there is the further complication of an electric quadrupole term in the nuclear-spin Hamiltonian, then its contribution to the relaxation of the non-Zeeman terms in the Hamiltonian must be carefully analyzed before the true effects of electron-spin correlation on the dipolar relaxation time T_{1dd} can be deduced. It may be shown that energy and order in a quadrupolar term relaxes towards the lattice temperature with a rate three times that of the Zeeman term,[1] unaffected by electron-spin correlations, if all the quadrupole interactions are axially symmetric. In a real sample, with impurities and strains and consisting of nuclei with $I \geqslant 1$, deviations of δ from 2.00 may, therefore, either be due to quadrupole effects or to electron-spin correlations; in general, because of cross relaxation between quadrupolar and dipolar energy baths, a mixed mode of relaxation will be observed.

III. EXPERIMENTAL

Measurements of T_{1dd} and T_{1z} have been made in two aluminum samples. Sample I was a commercial powder of nominal purity 99.99% and particle size $<75\ \mu$. Sample II was filed from a high-purity zone refined aluminum single crystal having a resistance ratio of 3650, having been used previously for Schubnikov–de Haas measurements. The resulting powder was sieved through a 300-mesh sieve, passed through a strong inhomogeneous magnetic field to rid it of magnetic particles, and annealed for half an hour at 250°C under vacuum. Second-moment measurements on the two samples gave a mean of 15.0 ± 0.4 $(\mathrm{kHz})^2$ for sample I and 12.3 ± 0.4 $(\mathrm{kHz})^2$ for sample II. The theoretical second moment is 9.2 $(\mathrm{kHz})^2$ so that, even in sample II with its high purity and careful preparation, some quadrupolar broadening of the resonance line remains. Other experimenters have also recorded this effect.[9–11]

The apparatus used to record the values of T_{1dd} was a three-pulse spectrometer incorporating coherent detection and with variable phase of rf in two of the pulses. It operated at 10 MHz with a crystal controlled oscillator supplying the reference for the detector (through an AD-YU variable delay line), the rf for the pair of pulses of the same phase (again through a delay line), and the rf for the single pulse. Gated amplifiers were used to supply the pulses of rf and the final pulse power was generated by a class-C power amplifier giving of the order of 3 kV peak to peak across the transmitter coil. The pulse sequence, into a nuclear induction head for T_{1dd} measurements was $^{0}90^\circ$-τ-$^{90}45^\circ$-τ'-$^{90}45^\circ$, i.e., a 90° pulse at zero time followed by a 45° pulse, shifted in phase with respect to the first pulse by 90° at time τ and a 45° pulse, again phase shifted by 90° with respect to the first pulse at time $\tau' > \tau$. With $\tau \sim T_2$ for the aluminum nuclei, the first two pulses convert some Zeeman to dipolar order, the decay of which is observed by monitoring the signal after the third pulse at variable time τ'.[4]

This experimental technique requires extremely fine adjustment of the phases and the field to ensure the absence of Zeeman signal after the third pulse. The Zeeman and dipolar signals are orthogonal in the rotating frame so that the dipolar signal is observed with the receiver reference phase adjusted to look at signals on the axis of the rotating frame along which the free-induction decay appears after the first, the $^{0}90^\circ$, pulse. If this is set accurately, no Zeeman signal should appear along this axis after the third pulse. Thus, with only the first present, the field and receiver phase is adjusted to maximize the free-induction decay following the pulse. Then, with only pulses 2 and 3 present, the phase of these pulses is adjusted so that no signal is observed after them. With all three pulses present, the widths of pulses 2 and 3 and the separation of pulses 1 and 2 are optimized for maximum dipolar signal. Finally, the third pulse is set at a time $\tau' \gg T_{1dd}$ and its phase finely adjusted so that no signal follows it, i.e., the boxcar output reads the same as in the absence of the applied static field B. With this technique of alignment, we were able to get strong dipolar signals in aluminum, close to the 59% optimum transfer efficiency for purely dipolar coupling, and a 100% abundant spin species calculated by Jeener *et al.*[4] The technique is very sensitive to any field instabilities, which can give rise to the mixing of a growing Zeeman signal with the decaying dipolar signal that one is attempting to measure. Continuous proton resonance monitoring of the field was used to minimize such effects in our system.

IV. RESULTS AND INTERPRETATION

Table I summarizes the results of our measurements of T_{1dd} at the various temperatures. The value of $T_{1z}T$ used to calculate δ in Table I was 1.85 sec °K. Both samples gave values within 1% of this value; since Spokas and Slichter[9] quote $(T_{1z}T) = 1.85\pm0.05$ sec °K,

TABLE I. Measurements of apparent δ against temperature.

Sample	Temperature °K	δ	Error
I	4.2	2.86	±0.05
I	80	2.30	±0.05
I	295	2.26	±0.05
II	1.42	2.87	±0.12
II	4.2	2.92	±0.12
II	65	2.54	±0.11
II	77	2.47	±0.06
II	295	2.25	±0.04

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[9] J. Spokas and C. P. Slichter, Phys. Rev. **113**, 1462 (1959).

[10] N. Fernelius, *Proceedings of the XIVth Colloque Ampere, Ljubljana* (North-Holland Publishing Co., Amsterdam, 1966).

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

we have assumed $T_{1z}T$ to be exactly the value quoted, so that the error bars on δ are derived only from the uncertainty in the measured T_{1dd}'s. All the measurements of T_{1z} and T_{1dd} at the various temperatures involved taking the mean of approximately eight values and the error bars on T_{1dd} correspond to two standard deviations on either side. No evidence was found to contradict the hypothesis that after the pulse pair creating the dipolar order a temperature for the dipolar subsystem is very rapidly established, i.e., in times <1 msec. This allowed us to measure the short relaxation times at room temperature.

The increase in δ with decreasing temperature exhibited by the results in Table I may be due to an explicit temperature dependence of $(T_{1dd}T)^{-1}$. We reject this possible explanation of the results, since it is difficult to conceive of an additional relaxation process which could reproduce the results. We have postulated an alternative explanation[12] for which there is support from independent sources. Aluminum of the highest purity must contain a certain minimum number of defects in its lattice structure which annealing cannot eradicate. These give rise to quadrupolar interactions for the nuclei close to them. In aluminum, the perturbation induced by substitutional impurities creates quadrupolar interactions greater than the dipole-dipole interactions for of the order of 100 host nuclei around the impurity.[13] Thus, such perturbations in the lattice are of very long range. The second-moment measurements quoted above provide further evidence for substantial quadrupole effects even in very pure samples. We suppose, therefore, that these quadrupolar interactions from a separate thermal reservoir in the sample in addition to the ones formed by the dipole-dipole interactions between nuclear spins and the Zeeman interaction between the spins and the applied magnetic field. Cross relaxation may then occur by spin diffusion processes between the quadrupolar spins around defects and the dipolar spins well away from the defects. Thus, the measured δ will be distorted due to the presence of both cross-relaxation and spin-lattice relaxation processes and will not be a true measure of T_{1z}/T_{1dd}. Hebel[14] has discussed the assumptions of this model and produced some experimental evidence in their support.

The experimental variation of δ with temperature can be reasonably simulated by a crude three-bath model of the combined dipolar-plus-quadrupolar systems, i.e., two thermal reservoirs of quadrupolar origin and the dipolar reservoir. The model is outlined in Fig. 1.

The coupled equations of Schumacher[15] may be easily extended to include the extra reservoir, showing that each bath relaxes as the sum of three exponentials, though the amplitude of each component exponential in the sum varies considerably with temperature, i.e., with the relative values of the cross-relaxation and the spin-lattice processes. R_{12}, R_{21}, R_{32}, R_{23} are assumed to be temperature-independent, while R_1 and R_2 are assumed to have a fixed temperature-independent ratio with R_0, the spin-lattice relaxation rate for the Zeeman system. The observation at 1.42°K of a rapid cross-relaxation process in sample II, proceeding at a rate ~ 50 sec^{-1} and of small amplitude and superimposed on the much longer decay used as an estimate of T_{1dd} in Table I, enabled us to estimate approximately the values of R_{12} and R_{21} and the relative heat capacities of systems 1 and 2. The heat capacity of system 3 and the strength of its coupling with system 2 were then used as adjustable parameters. We estimate that the relative heat capacities are as 2:1:5 for systems 1, 2, and 3, respectively, and that $(R_{23}+R_{32})$, the cross-relaxation rate between 2 and 3, is ~ 2 sec^{-1}.

With $R_2/R_0=3$ and $R_1/R_0=2.15$, the values of the model predictions for δ are noted in Table II, with, for comparison, the experimental values. These values refer to sample II.

Given the crudeness of the model, the agreement is satisfactory. The model also clearly shows the possibility of apparently exponential decays with rates greater than $3R_0$, such as have been observed by other experimenters.[8,14] This can occur because of the possibility of two of the exponential decays in the composite sum being of similar amplitudes and having similar decay constants; the combined decay can then appear to be a pure exponential within experimental error with a characteristic decay constant greater than $3R_0$.

For temperatures >65°K, the results for the two-bath (Schumacher) model and our own three-bath model are effectively identical, which is to be expected physically since the cross-relaxation rate between baths 2 and 3 is negligible compared to the other relaxation processes at these temperatures. At all temperatures, with the parameter values inserted in this analysis, the model predicts that the relaxation rates observed should appear as pure exponentials within experimental error, apart from the rapid cross relaxation observed at helium temperatures, even though they are, in fact, composite decays, the components of which differ in their decay constants by sufficiently small amounts for their sum to appear as a pure exponential (within experimental error). This is not true for the measurement at room temperature where the model predicts that, in the composite decay of the order in the dipolar bath, only one of the exponentials in the sum has a significant amplitude.

The conclusion of our analysis is, therefore, that δ in aluminum takes the value 2.15 ± 0.07, and that previously reported values of this ratio have failed to take account of the cross relaxation to the quadrupolar bath which apparently exists in all samples of the metal. Because of the more rapid spin-lattice relaxation of nuclear spins on sites where the quadrupole interaction

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[12] D. P. Tunstall and D. Brown, Phys. Letters **27A**, 273 (1968).

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

[14] L. C. Hebel, Phys. Rev. **128**, 21 (1962).

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

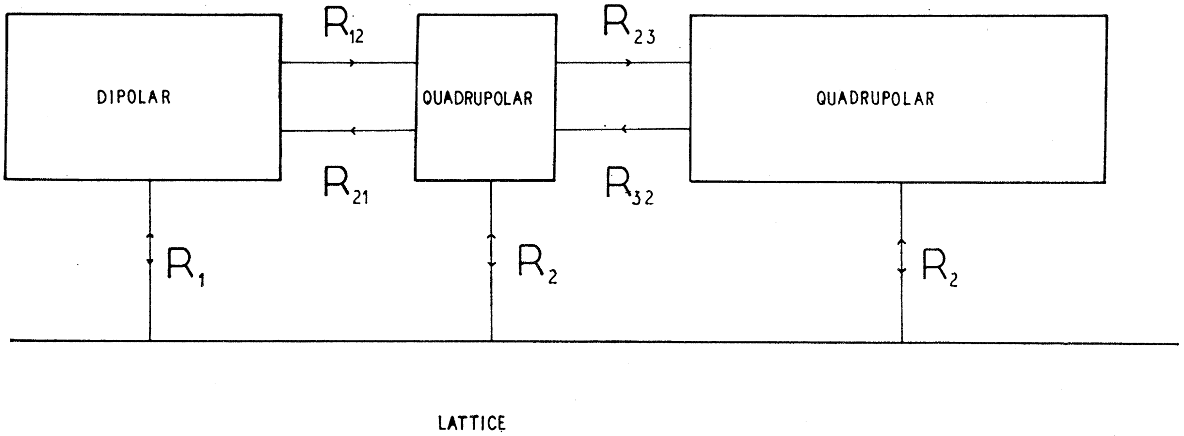

FIG. 1. Model of the relaxation processes in a combined quadrupolar plus dipolar system, with temperature-independent cross relaxation at rates R_{12}, R_{21}, R_{23}, R_{32}, and thermal couplings between each bath and the lattice at rates R_1, R_2, R_2. R_1 and R_2 are assumed to be proportional to temperature.

is greater than the dipole-dipole interaction, low-temperature measurements, where the T_1's are long, thus, permitting more time for the cross-relaxation processes to occur, give rise to anomalously large values of δ.

The pulse-pair technique for the transfer of Zeeman to dipolar order has been analyzed by Jeener and Broeckart[4] for the case of a single-spin species with only Zeeman and dipolar terms in the Hamiltonian. They calculate the coefficients K_{z-d}, K_{z-z}, etc., where, for example, K_{z-d} is the coefficient representing the conversion of Zeeman to dipolar energy on application of a pulse pair. Pursuing the model that we have used above to explain the cross-relaxation effects, we consider that the spins around a defect can be described by Zeeman plus quadrupolar Hamiltonians, while those spins far from a defect are described by Zeeman plus dipolar Hamiltonians. For the latter spins, Jeener *et al.*[4] have calculated K_{z-d}. For the quadrupolar spins, we have calculated expressions for K_{z-Q}, approximating the quadrupole interaction by a small axially symmetric term $\mathcal{H}_Q=-ahI_z{}^2$ in the rotating frame; a is assumed to vary randomly between limiting values over the quadrupolar spins. In the limit $B_1\gg$(all values of a), K_{z-Q} is effectively zero, showing that no order is transferred to the quadrupolar term. In our calculation of the effects of cross relaxation above, we have, therefore, assumed that immediately after the application of the pulse pair the quadrupole terms in the Hamiltonian still have the lattice temperature. In the cross-relaxation processes between quadrupole and dipole subsystems, the quadrupole temperature will deviate from the lattice temperature, so that it might appear as a contribution to the signal after the third pulse. However, the time-independent[16] term normally associated with quadrupole free-induction decays can, in this case, be shown to be zero, and the other oscillating terms will destructively interfere to give a net zero signal.

V. ELECTRON-ELECTRON EFFECTS IN ALUMINUM

$(T_{1z}T)$, as noted in Sec. IV, is measured as 1.85 sec °K in agreement with the value of Ref. 9. Taking 0.162% as the measured Knight shift,[17] the experimental Korringa ratio equals 1.26A [Eq. (1)], an apparent enhancement of 1.26. Other shifts and relaxation effects should, however, first be separated from those due to the contact term to which Eq. (1) applies. We now consider these other contributions.

Core polarization effects are first separated into those due to conduction electrons having s-wave and p-wave character. Both affect T_{1z} and K, but there is a cross term in the expression for $(T_{1z}T)^{-1}$ involving the direct contact interaction and the core-polarization (s wave) interaction; this implies that the direct and core-polarization (s wave) contributions to the Korringa product are inseparable and that, taken together, they satisfy the Korringa relation, which should, therefore, be modified to

$$(K_{c+\mathrm{cps}})^2(T_{1z}T)_{c+\mathrm{cps}}=A\,. \tag{5}$$

Modifications to this equation when electron-electron interactions are considered will be unaffected by this addition of cps terms.

TABLE II. Three-bath model predictions for δ against temperature.

Temperature (in °K)	Model δ	Experimental δ
1.42	3.00	2.87±0.12
4.2	2.72	2.92±0.12
65	2.52	2.54±0.11
77	2.47	2.47±0.06
295	2.23	2.25±0.04

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[16] I. Solomon, Phys. Rev. **110**, 61 (1958).

[17] Y. Masuda and A. G. Redfield, Phys. Rev. **133**, A944 (1964).

The p-wave contribution does not have a cross term in the expression for $(T_{1z}T)^{-1}$, so that direct contact and core-polarization (p wave) interactions contribute separately to both K and $(T_{1z}T)^{-1}$. Contributions from this source should, therefore, be subtracted from the measured K and $(T_{1z}T)^{-1}$ before any effects due to electron-electron enhancements of the direct and core-polarization (s wave) interactions are deduced. The calculation of Shiu, Das, and Gaspari[18] gives a separation of the relative importance of the core-polarization (p wave) and direct-contact contributions to the Knight shift, showing clearly that the total contribution from the p-wave character of the conduction electrons is negligible. We conclude that contributions to both K and $(T_{1z}T)^{-1}$ due to this source may be neglected.

There is some evidence that the measured Knight shift and relaxation rate contains little or no contribution from the orbital motion of the conduction electrons or from the spin-orbit interactions:

(i) The measured g factor of the conduction electrons 1.997 is very close to that for a free electron.[19]

(ii) The conduction-electron diamagnetic susceptibility calculation,[20] the measured g value,[19] and the ionic-core susceptibility,[21] may be inserted into the expression for K_{orb} derived by Appel[22]; the ensuing prediction for the orbital contribution to the Knight shift is negligible.

(iii) The measured resonance frequency in the superconducting state, extrapolated to zero temperature, differs from that in the normal state by 0.16%.[23] Since the experimental Knight shift in the normal state quoted earlier is very close to this value, orbital contributions, which are unchanged at the superconducting transition, must be very small.

Finally, there may be a contribution to $(T_{1z}T)^{-1}$ due to spin-dipolar interactions; the cubic symmetry rules this interaction out as a possible shift mechanism. A very approximate estimate of this may be obtained from the tight-binding calculation of Obata.[24] With a free-electron density of states, assuming that all the conduction electrons are in a p band and estimating $\langle r^{-3}\rangle$ from the known hyperfine splittings $a_{1/2}$, $a_{3/2}$ in atomic aluminum, the resultant rate is of the order of 0.4% of the observed rate. Since the assumptions lead to an overestimation, the relaxation due to spin-dipolar interactions may be neglected.

It seems plausible to assume, therefore, that both the Knight shift and the relaxation rate in aluminum are dominated by interactions between the nuclei and conduction electrons of s-wave character, with the consequence that the Korringa enhancement is given by 1.26±0.08. This is much smaller than any of the enhancements observed in the alkali and noble metals.[7]

TABLE III. Summary of known data in aluminum and sodium.

Metal	$(K_c^2T_{1z}T)/A$	δ	α
Na	1.60±0.07[a]	2.12±0.03[b]	0.42±0.03[a]
Al	1.26±0.08	2.15±0.07	···

[a] Reference 7.
[b] Reference 3.

Table III summarizes the experimental data in aluminum, with the corresponding values for sodium included for comparison. The value of the enhancement parameter α, obtained by direct measurement, is also included for sodium; the experiment measuring α has yet to be performed in aluminum.

Both δ and the Korringa product in aluminum show significant enhancements over the values expected from one-electron theory. We may suppose that these enhancements both stem from electron-electron effects, as outlined in Sec. II. With the δ-function interaction between electrons, agreement between the experimental value of the Korringa product and the theoretical expression[7] is attained if $\alpha=0.38$. Pointing out that the theory developed in Sec. II for the description of the effects of electron-electron interactions is not strictly applicable to aluminum, most obviously because of the requirement of a spherical Fermi surface, we may, nevertheless, make some attempt to calculate an approximate value of δ using the theory with the value of α above. Applying Eqs. (2) and (3), using the values of k_F noted in Ref. 18 as providing the dominant contribution to the Knight shift, and taking the sum in Eq. (3) out to third-nearest neighbors, a value of $\delta\sim 2.06$ results.

An estimate of the enhanced spin susceptibility in aluminum, using the effective mass quoted by Ashcroft and Wilkins[25] (excluding electron-phonon effects) may be made with $\alpha=0.38$, resulting in $\chi_s=2.08\times 4\pi\times 10^{-6}$ mks volume units. Taking the total measured susceptibility[26] and subtracting off the diamagnetic contributions[20,22], the spin susceptibility comes out at $2.33\times 4\pi\times 10^{-6}$ mks volume units; in this calculation, we have assumed a conduction-electron contribution to the diamagnetic susceptibility three times the value quoted in Ref. 20, allowing for the valence of three.

VI. ELECTRON-ELECTRON EFFECTS IN SODIUM

As an indication of the relevance of the discussion in Sec. V, it is of interest to review the extent of the agreement between the enhancement theory and experi-

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[18] W. M. Shiu, T. P. Das, and G. D. Gaspari, Phys. Rev. **152**, 270 (1966).

[19] S. Schultz, G. Dunifer, and C. Latham, Phys. Letters **23**, 192 (1966).

[20] P. K. Misra and L. M. Roth, Phys. Rev. **177**, 1089 (1969).

[21] J. H. Van Vleck, in *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).

[22] J. Appel, Phys. Rev. **139**, A1536 (1965).

[23] R. H. Hammond and G. M. Kelly, Phys. Rev. Letters **18**, 156 (1967).

[24] Y. Obata, J. Phys. Soc. Japan **18**, 1020 (1963).

[25] N. W. Ashcroft and J. W. Wilkins, Phys. Letters **14**, 285 (1965).

[26] J. Reekie and T. S. Hutchinson, Phys. Rev. **74**, 610 (1948).

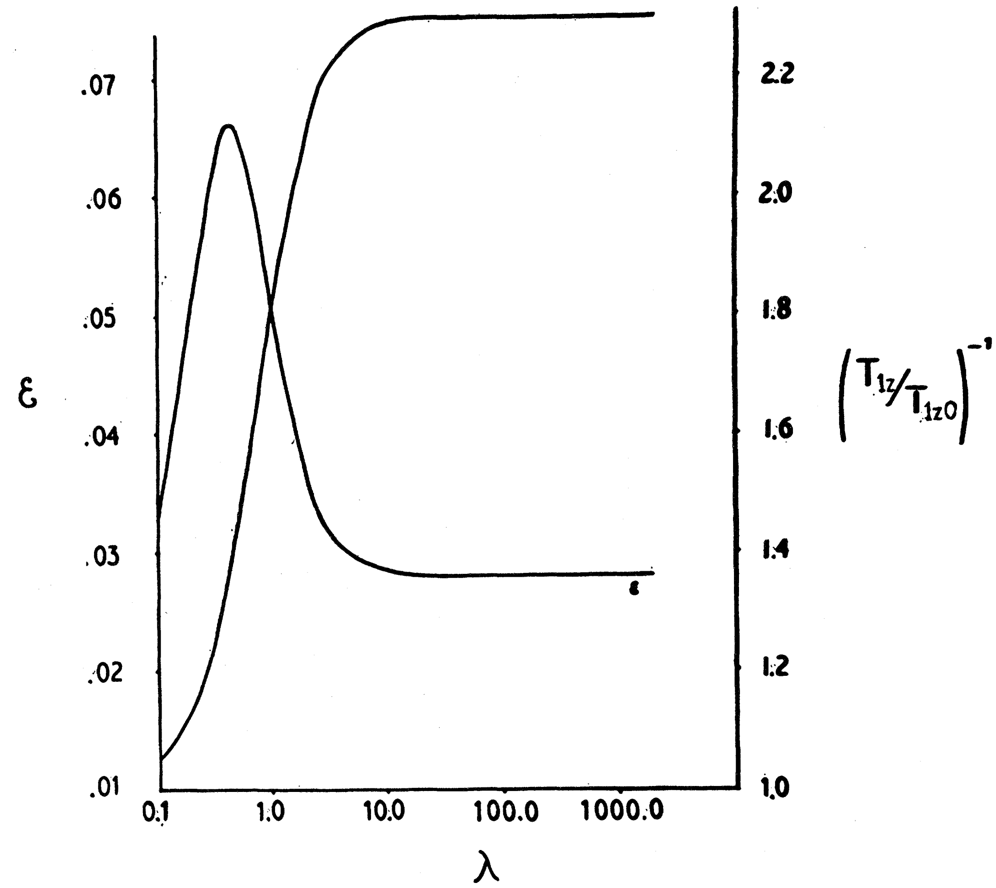

FIG. 2. The theoretical predictions for ϵ and $(T_{1z}/T_{1z0})^{-1}$ as a function of the screening parameter λ (in units of $2k_F$) in sodium.

ment for a particular case for which the theory may be expected to be more accurate. The experimental data for sodium are in Table III.

The δ-function interaction theory, as developed by Wolff[2] and represented in Eqs. (2) and (3), when applied using the internuclear distances and the Fermi wave vector k_F, pertaining to sodium, with the experimental value of α given in Table III, yields a value of $\delta=2.03$ and a $(T_{1z}T)^{-1}$ enhancement of 2.30 over its value in the absence of interactions, i.e., $\alpha=0$. The theoretical $K_c^2T_{1z}T/A$ product is then only 1.29, since the K_c^2 enhancement is 2.97. As Narath and Weaver[7] point out, the theory of the enhancement of the spin-lattice relaxation rate overcompensates, bringing theoretical prediction below experiment for the Korringa product. The prediction for δ is also well below the experimental value. It seems, therefore, a possibility that the δ function is not an accurate simulation of the electron-electron interactions. Narath and Weaver[7] postulate a finite range for the interactions, assuming a potential of screened Coulomb form, while emphasizing that the theory of the $(T_{1z}T)^{-1}$ enhancement is strictly only applicable to the δ-function representation. With the same degree of validity, so that only qualitative meaning may be ascribed to the results, we have supposed that α in Eq. (2) can be replaced by the following formulations. If the electron-electron interactions are of (a) screened Coulomb type, then $\alpha\rightarrow\alpha(0)/[1+(q/\lambda)^2]$, or of (b) Gaussian type, then $\alpha\rightarrow\alpha(0)\exp(-q^2/4\beta^2)$, with q the wave-vector difference between interacting electrons. The motivation for this analysis lay in the hope that the introduction of this finite range might improve agreement between theory and experiment for δ as well as for $K_c^2T_{1z}T/A$.

With numerical integration of Eq. (2), and the sum in (3) taken out to the third-neighbor shell, the resulting $\epsilon:\lambda$ curve, case a, is shown in Fig. 2, together with the corresponding enhancement of $(T_{1z}/T_{1z0})^{-1}$ obtained by similar numerical integration of the denominator in Eq. (2); λ is in units of $(2k_F)$. The corresponding curve for the Gaussian approximation, case b, is not shown. It exhibits a sharper peak, going up to $\epsilon=0.08$, but the conclusions from it are not very different from those to be gained from consideration of the $\epsilon:\lambda$ curve.

In discussing Fig. 2, note first that $\lambda=\infty$ corresponds to the δ-function interaction, with $\epsilon=0.03$ and $(T_{1z}/T_{1z0})^{-1}=2.3$, as quoted earlier. Remembering that the enhancement of K_c^2 is determined by $\alpha(0)=0.42$

and is therefore independent of λ with the enhanced value 2.97 $(K_{c0})^2$, then agreement with the experimentally observed value of $K_c^2T_{1z}T/A$ (Table III) is obtained when $\lambda=(1.0)2k_F$ and $\epsilon=0.05$. Best agreement between theory and experiment for δ is obtained at $\lambda=(0.42)2k_F$, with $\delta=2.07$, almost within range of the error in the experimental value. Unfortunately, agreement is then lost between theoretical prediction and experiment for the Korringa product, with $(K_c^2T_{1z}T)/A=2.23$. The same difficulty is encountered with the Gaussian interaction.

VII. CONCLUSION

In sodium, the electron-gas theory of electron-spin correlations, including electron-electron interactions of δ-function type, fails to explain the experimentally observed enhancements of the Korringa product and the ratio of Zeeman to dipolar spin-lattice relaxation times. Closer agreement between experiment and theory is obtained by imposing a finite range for the electron-electron interactions on to the theory.

In aluminum, we have discussed in some detail the different contributions to the relaxation time and the Knight shift and have measured δ at 2.15 ± 0.07. A δ-function electron-electron interaction produces quite reasonable agreement between theory and experiment in this case, where the Korringa enhancement is abnormally low. Taken with the susceptibility analysis, this leads us to conclude tentatively that the conduction electrons in aluminum interact over a shorter range than in sodium, but that the enhancement of the Knight shift and spin susceptibility is very similar in the two metals.

There has been one other recent determination[27] of δ in Al, finding a value of 2.07 ± 0.02 at 273°K. This value and ours overlap, though we think this fortuitous since the analysis leading in Ref. 27 to the value quoted took no account of the quadrupole interactions which have played a fundamental role in our analysis.

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[27] J. H. Pifer, Phys. Rev. 166, 540 (1968).

PHYSICAL REVIEW B VOLUME 1, NUMBER 7 1 APRIL 1970

Specific Heat of Antimony and Bismuth between 0.03 and 0.8 K†

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The specific heats of the semimetals antimony and bismuth have been measured from 0.03 to 0.8 K. The best fit to the antimony data yields $C_p=4.55T^{-2}+119T+180T^3$ μJ/mole K. The T^{-2} term associated with the nuclear quadrupole interaction is in good agreement with NMR measurements and also with theoretical predictions of the electric field gradient at the nucleus. The best fit for bismuth gives $C_p=0.0064T^{-2}+8.5T+1120T^3$ μJ/mole K. The value of the coefficient of the electronic specific heat is in agreement with predictions from Fermi-surface parameters. Slow spin-lattice relaxation in bismuth prevents the nuclear quadrupole Schottky anomaly from being observed in a calorimetric measurement.

I. INTRODUCTION

THE semimetals antimony and bismuth crystallize in similar rhombohedral structures,[1] the "arsenic structure," and exhibit many similar properties. By virtue of a small band overlap, which spills a small number of electrons into the conduction band, both metals show weak metallic properties. The Fermi surfaces consist of small pockets of electrons and holes with low densities of states at the Fermi level resulting in electronic specific heats considerably lower than those of normal metals. Both metals also have isotopes with sizable nuclear quadrupole moments which interact with the electrical field gradient (efg) at the site of the nucleus giving rise to hyperfine splittings of the order of a few tenths of a milli-Kelvin.

The quadrupole coupling constants e^2qQ have been measured by resonance techniques for both metals.[2,3] No precise calorimetric confirmation of the resonance figures has been made for antimony except for estimates[4,5] from measurements in the He^3 range which are, of necessity, rather inaccurate owing to the smallness of the nuclear specific heat at these temperatures. Calorimetric measurements on bismuth[6] have been extended

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[1] W. B. Pearson, *Lattice Spacings and Structures of Metals* (Pergamon Press, Inc., New York, 1958).

[2] R. R. Hewitt and B. F. Williams, Phys. Rev. **129**, 1188 (1963).

[3] B. F. Williams and R. R. Hewitt, Phys. Rev. **146**, 286 (1966).

[4] D. C. McCollum and W. A. Taylor, Phys. Rev. **156**, 782 (1967).

[5] R. S. Blewer, N. H. Zebouni, and C. C. Grenier, Phys. Rev. **174**, 700 (1968).

[6] N. E. Phillips, Phys. Rev. **118**, 644 (1960).