among themselves, and more important, were obtained with bulk samples which are known to undergo a partial martensitic transformation[22] at low temperatures. This transformation is probably inhibited in dispersed samples.[23] Despite these uncertainties, when measured values of the Knight shift,[6] the nuclear spin-lattice relaxation time,[10,11] and the average of the reported values of electronic specific heat are combined, one infers from the Korringa relation a value $X_s = (2.30 \pm 0.20) \times 10^{-6}$ cgs volume units for lithium, and $X_s = (1.06 \pm 0.10) \times 10^{-6}$ cgs volume units for sodium, in good agreement with the values given in Table II.

The relative values of X_s in lithium were the same at 300, 77, and 1.5°K, within an estimated uncertainty of 3%, and were the same in sodium at 77 and 1.5°K, within an estimated uncertainty of 5%. This result for sodium is in agreement with that reported by Schu-

macher and Vehse.[2] Feldman and Knight[24] have reported an anomalously large decrease of the Knight shift in sodium at low temperature, which could be accounted for by about a 2% decrease of X_s in sodium at 4.2°K, or conversely, by an additional 2% decrease in P_F over its estimated decrease. Unfortunately, neither the measurements of Schumacher and Vehse nor our measurements are sufficiently precise to resolve this uncertainty.

ACKNOWLEDGMENTS

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Overhauser Effect in Metallic Lithium and Sodium*

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The overhauser polarization of nuclear spins in Li and Na metal has been precisely measured at 1.5°K and 10.4 G. The electron spin resonance was saturated for a time long compared to the nuclear spin relaxation time, and the resulting Overhauser polarization was then measured by adiabatically applying a high field and sweeping through nuclear resonance in a time short compared to the nuclear relaxation time. The degree of electron saturation was determined with precision by comparison with the change in electron spin magnetization longitudinally measured under the same experimental conditions. For Na the polarization ratio is $100 \pm 3\%$ of its high-field theoretical value γ_e/γ_n; for Li, $84 \pm 3\%$. At 10.4 G correction must be made for polarization leakage via the nuclear spin-spin energy; the predicted ratios are 98.5% for Na and 90% for Li, of the high-field values. The remaining discrepancy in Li is presumably a result of conduction electron orbital contribution to the relaxation which is important because of the predominantly p character of the lithium conduction electron wave functions. The orbital relaxation rate is estimated theoretically for Li, and the result agrees with experiment.

INTRODUCTION

THAT the nuclear spin polarization in a metal would become greatly enhanced if the conduction electron spin resonance were saturated has been shown by Overhauser.[1] Of the several methods[2,3] of dynamic nuclear polarization, the Overhauser effect is the one

which goes most strongly against intuition, so that its experimental observation by Carver and Slichter[4] was of considerable interest. Overhauser predicted that the maximum enhancement of the nuclear spin polarization would be γ_e/γ_n times its thermal equilibrium value, where γ_e and γ_n are the electronic and nuclear gyromagnetic ratios. Quantitative confirmation of this prediction in Li can be inferred indirectly from measurement of the Overhauser-enhanced electronic Knight shift, the electronic spin susceptibility, and the nuclear Knight shift.[5] It is directly confirmed with precision

[1] A. W. Overhauser, Phys. Rev. 92, 411 (1953).
[2] A. Kastler, J. Phys. Radium 11, 255 (1950).
[3] R. V. Pound, J. Phys. Chem. 57, 743 (1953).

[4] T. R. Carver and C. P. Slichter, Phys. Rev. 102, 975 (1956).
[5] Ch. Ryter, Phys. Rev. Letters 5, 10 (1960).

in the present experiment, as well as in the independent research of Reichert and Townsend.[6]

It is perhaps surprising that Overhauser's prediction was quantitatively so good, since it was based on the independent particle model of the conduction electrons. It is well known that this model usually gives only approximately correct predictions, and that Coulomb interactions between electrons must be taken into account. Slichter[7] has given an elegant derivation of Overhauser's result which shows that the only assumption that has to be made about the electron gas is that electron spin resonance saturation changes the state of the electron gas to that corresponding to thermal equilibrium in a magnetic field smaller than the applied magnetic field. This condition presumably follows if total electron spin magnetization is a good quantum number. The observation of a narrow unshifted electron spin resonance in Li and Na is evidence that total magnetization is a good quantum number for these metals.

In the present measurement we were able to achieve a precise direct measurement of the Overhauser polarization by working at low temperature where the nuclear resonance signal was large and the nuclear spin relaxation time[8] long enough to permit us to polarize the spins at a conveniently low field, and subsequently cycle the field for a measurement of the nuclear polarization by nuclear resonance at high field. This permitted us to study the same samples at the same field and temperature as were used in the experiment described in the paper[9] immediately preceding this one (henceforth referred to as I). In both cases the rf was pulsed with a low duty cycle, and it was found that the Overhauser polarization dependence on rf power closely followed the saturation curves exhaustively studied in I, up to nearly complete saturation. Thus, by fitting to the same saturation curves as were used in I, which are already corrected for rf inhomogeneity and skin effect and are appropriate to the low dc field used, the nuclear polarization expected for full saturation was inferred.

EXPERIMENTAL METHOD AND DATA

The field sequence used to measure the Overhauser polarization is shown in Fig. 1(a). The sample was polarized in a dc field H_0 of 10.4 G and a strong 29-Mc/sec rf field for a time τ_0 long compared to the nuclear spin-lattice relaxation time T_1. The rf was then turned off and a time τ_a later the field was raised adiabatically to a field H^* of several hundred gauss. Subsequently, a field sweep was started and the nuclear resonance transmitter activated, and nuclear resonance was swept through at a time τ_b after turning on H^*. The nuclear resonance signal S thus obtained was pro-

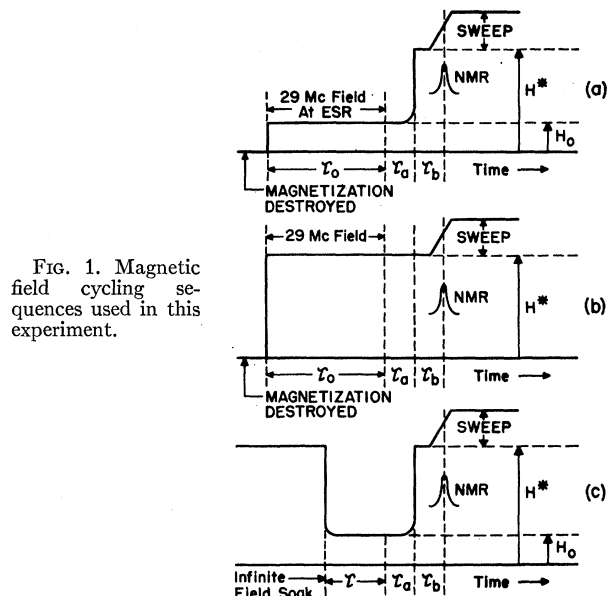FIG. 1. Magnetic field cycling sequences used in this experiment.

portional to the polarization at the end of τ_0, somewhat reduced by relaxation during the time $\tau_a + \tau_b$ ($=0.8$ sec), plus repolarization due to the field H^* during the time τ_b. The signal $S(V)$ was recorded as a function of the 29-Mc/sec rf amplitude in volts V, measured with a vacuum tube voltmeter of known linearity or with an oscilloscope.

The nuclear resonance frequency was 1.16 Mc/sec. To calibrate the nuclear resonance sensitivity the sequence in Fig. 1(b) was used. The sample was soaked in H^* for a long time, during which the 29-Mc/sec rf field was applied, not to produce a polarization but simply to duplicate rf heating effects which occurred in the Overhauser measurement sequence. The 29-Mc/sec field was cut off, and a time $\tau_a + \tau_b$ later a nuclear resonance calibration signal $S^*(V)$ was recorded. The temperature of the helium bath was also measured continuously and varied between 1.4 and 2°K. It was found that $S^*(V)$ varied inversely with bath temperature, which indicates that the sample temperature was always the same as the bath temperature, in I as well as in the present experiment.

The sequences of Fig. 1(a) and 1(b) were interspersed during a run as the rf voltage V was varied, and the quantity

$$R(V) = \frac{S(V) - S(0)}{S^*(V)} \frac{H^*}{H_0} \frac{\gamma_n}{\gamma_e} \exp\left(\frac{\tau_a + \tau_b}{T_1}\right) \quad (1)$$

was plotted. If the full Overhauser enhancement equals its theoretical maximum value γ_e/γ_n, then $R(V)$ should approach unity, and for less than complete electronic saturation $R(V)$ should equal the electron saturation parameter

$$Z = -(M_{sz} - \chi_s H_0)/\chi_s H_0. \quad (2)$$

In Eq. (1) we subtracted the signal $S(0)$ with no 29-

[6] J. F. Reichert and J. Townsend, Bull. Am. Phys. Soc. 8, 35 (1963).

[7] C. P. Slichter, Phys. Rev. 99, 1822 (1 55).

[8] A. G. Anderson and A. G. Redfield, Phys. Rev. 116, 583 (1959); L. C. Hebel and C. P. Slitchter, ibid. 113, 1504 (1959).

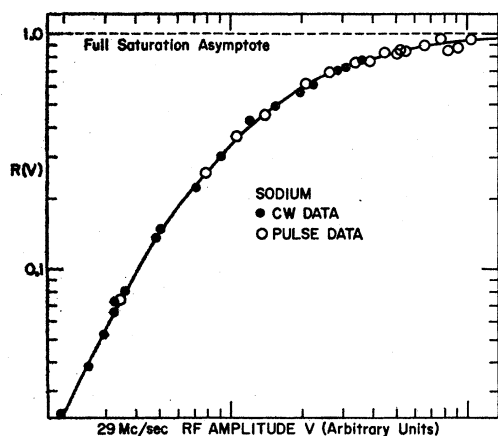[9] R. Hecht, preceding paper, Phys. Rev. 132, 966 (1963).

FIG. 2. The ratio of Overhauser enhancement in lithium as a function of rf amplitude, relative to its expected maximum value γ_e/γ_n at full saturation. The curve is derived from direct measurement of electron spin resonance saturation, whose known asympote gives the experimental full enhancement of 0.84 γ_e/γ_n.

Mc/sec power applied in order to obtain that part of the polarization due to the electronic saturation alone; this procedure also cancels the signal due to repolarization in H^* during the time τ_b. $S(0)$ is small compared to $S(V)$ except at the lowest power levels. The nuclear relaxation time T_1 was taken to be that appropriate to the bath for each measurement. The field dependence[8] of T_1 in Li was ignored in making this particular correction because the entire correction was small for Li.

At higher power levels rf heating of the bath became excessive so we resorted to pulsed operation, using the same repetition rate (280 cps) and pulse length (0.4 msec) as in I, and measuring the duty cycle D precisely with an oscilloscope and time-mark generator. When the rf is off the nuclear polarization will relax toward its equilibrium polarization; when the rf is on the polarization will relax toward the full Overhauser polarization. If T_1 is long compared to the time between rf pulses there will not be much variation (relaxation) between pulses and it is easy to see that the average polarization will be decreased by an amount D relative to the full Overhauser effect. This is expected if the buildup for the Overhauser effect equals the relaxation time T_1; we have measured the buildup time at low cw rf power by measuring $S(V)$ as a function of τ_0, and found both times equal, as is also expected theoretically. The pulse data were divided by the duty cycle D before plotting.

The field cycle in Fig. 1(c) was used to verify that the remagnetization of H^* was adiabatic and reversible, and to recheck the relaxation loss during the time $\tau_a + \tau_b$.

The samples were those used in I, and the nuclear resonance apparatus has been described elsewhere.[8,10] The 29-Mc/sec power was supplied by the same trans-

[10] Y. Masuda and A. G. Redfield, Phys. Rev. 115, 583 (1959); A. G. Anderson, ibid. 115, 863 (1959).

mitter and keying circuits as in I. A two-turn 29-Mc/sec coil was wrapped around the outside of the receiver coil and perpendicular to it. The 1.16-Mc/sec nuclear resonance transmitter coil was unchanged and was sufficiently large compared to the 29-Mc/sec coil to avoid loading it. As in I, the 29-Mc/sec power was limited by voltage breakdown. The 29-Mc/sec coil was tuned and matched locally using silver mica condensers, and powered from a 50-Ω microdot cable.

The field H^* was calibrated with a proton resonance, while H_0 was set by running at low 29-Mc/sec power and varying H_0 to plot out a resonance curve. This procedure was identical to that of I. The accuracy of this setting was about $\frac{1}{2}\%$.

Plots of $R(V)$ [or $R(V)/D$, for the pulse data] are shown in Figs. 2 and 3. Two Li samples were run, and we show the second of these. The first, less accurate, run was in agreement with the second within experimental error.

MAXIMUM ENHANCEMENT

Since the electron spin resonance was never fully saturated we cannot determine the full Overhauser polarization without some knowledge of the saturation of the electron spin resonance. The nuclear polarization increase is expected to be proportional to the change in z component of electron spin magnetization induced by the rf field. To test this expectation and to determine the full nuclear polarization we used the semiempirical determination of the fractional change in electronmagnetization $Z(H_1)$, as a function of rf power H_1, obtained in I for the same samples and frequency. $Z(H_1)$ was calculated from the modified Bloch equations using the observed electron spin relaxation time, and then empirically corrected for rf inhomogeneity and skin effect. The use of this saturation curve, rather than the usual high dc field solution to the Bloch equations, makes a few percent difference in the final result. In Figs. 2 and 3 are plotted the curves $\alpha Z(\beta V)$, where the scaling
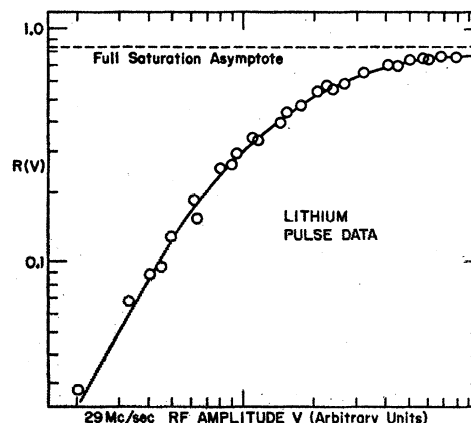

FIG. 3. The Overhauser enhancement in sodium as a function of rf amplitude.

constants α and β are chosen to best fit the data. The constant β is, of course, of no fundamental interest, but α is a measure of the nuclear enhancement; α should be unity if the full enhancement equals Overhauser's predicted value γ_e/γ_n. For Na, $\alpha=1.00$ while for Li, $\alpha=0.84$. Thus, the final experimental result of this research is that sodium shows the maximum Overhauser enhancement, while Li shows 84% of the full expected enhancement. We believe that the probable error of these measurements is 3%.

In the following two sections theoretical reasons for the reduced enhancement in Li are given. These remarks also apply to Na, but there the expected reduction is insignificant (1.5%) so we confine our remarks to Li. It should be understood that, had we measured the nuclear polarization directly at 10.5 G, rather than remagnetizing to high field, a smaller magnetization or enhancement would presumably have been observed. In adiabatically remagnetizing, a small increase in nuclear magnetization will occur, as discussed quantitatively in the next section.

NUCLEAR DIPOLE-DIPOLE CORRECTION

In lithium the rms local field which a nuclear spin feels due to its neighboring nuclei is about 2.7 G. This field is not negligible compared to the field H_0 of 10.5 G used in the present experiment. The energy of the nuclear spin system $\langle \mathcal{3C} \rangle$ can be conveniently divided into a Zeeman energy $\langle \mathcal{3C}_0 \rangle$ and spin-spin energy $\langle \mathcal{3C}_{ss} \rangle$:

$$\langle \mathcal{3C} \rangle = \langle \mathcal{3C}_0 \rangle + \langle \mathcal{3C}_{ss} \rangle. \tag{3}$$

At thermal equilibrium[11] the energy will be partitioned between these two contributions according to the relation

$$\langle \mathcal{3C}_0 \rangle = \langle \mathcal{3C}_{ss} \rangle H_0^2/H_L^2, \tag{4}$$

where H_L^2 is the mean square local spin-spin field, which can be shown to be 5/3 of the high-field angular average Van Vleck second moment of the nuclear magnetic resonance line. For Li, H_L^2 is 7.2 G^2; for Na, 1.05 G^2. Equation (4) follows easily from equilibrium statistical mechanics, but it is generally assumed to hold also when the spin system is not in equilibrium with the lattice, during a relaxation process or dynamic polarization. This assumption is reasonable if the spin-spin relaxation time is short compared to the spin-lattice relaxation time and if the nuclear system is not directly perturbed by the rf field.

During an Overhauser polarization the Zeeman part of the nuclear spin energy is pumped up by the conduction electrons, but it is reasonable to suppose that the spin-spin energy is not so pumped, being associated with a randomly oriented dipolar field. But both kinds of energy are relaxed by the conduction electrons; thus

the spin-spin energy acts as a leak for the Overhauser polarization. Abragam[12] has calculated the effect of this leakage. Abragam's result can be obtained from an intuitively reasonable rate equation for the total energy:

$$\frac{d\langle \mathcal{3C} \rangle}{dt} = \frac{\Omega_\infty}{T_{1\infty}} Z(V)\langle \mathcal{3C}_0 \rangle_0 - \frac{\langle \mathcal{3C} \rangle - \langle \mathcal{3C} \rangle_0}{T_1}. \tag{5}$$

Here $T_{1\infty}$ is the nuclear spin-lattice relaxation time at high field; T_1 is its value at H_0; Ω_∞ is the full Overhauser enhancement factor which would be observed at high dc field; and $\langle \mathcal{3C} \rangle_0$ is the thermal equilibrium value of $\langle \mathcal{3C} \rangle$. By "high field" we mean a field so large that spin-spin interaction can be ignored, thus $T_{1\infty}$ and Ω_∞ are quantities associated with an uncoupled spin system. Equation (5) says that the Zeeman energy is pumped up by the Overhauser effect at a rate appropriate to a single spin, and that the nuclear spin system is not otherwise affected by electron spin saturation. Solving Eqs. (3) to (5) we get Abragam's result that the fractional increase in magnetization is

$$Z(V)\frac{\Omega_\infty T_1 H_0^2}{T_{1\infty}(H_0^2+H_L^2)}. \tag{6}$$

It is found experimentally, and is theoretically predicted,[8,13] that

$$\frac{T_1}{T_{1\infty}} = \frac{H_0^2+H_L^2}{H_0^2+2.2H_L^2}. \tag{7}$$

Thus the low-field Overhauser effect is expected to be reduced, relative to high-field, by $H_0^2/(H_0^2+2.2H_L^2)$. This relation has been verified reasonably well at 2.88 G by Jerome and Galleron.[14] This correction is appropriate to a measurement made entirely at low field. But in the present case we remagnetized adiabatically to $H^*\gg H_0>H_L$, so we expect a resulting increase in polarization by a factor[11]

$$\left(\frac{1+H_L^2/H_0^2}{1+H_L^2/H^{*2}}\right)^{1/2} \approx \left(\frac{H_0^2+H_L^2}{H_0^2}\right)^{1/2}. \tag{8}$$

Combining both factors we conclude that the total spin-spin correction reduces the Overhauser enhancement by an amount

$$\frac{(1+H_L^2/H_0^2)^{1/2}}{(1+2.2H_L^2/H_0^2)}. \tag{9}$$

This expression equals 0.90 for Li and 0.985 for Na.

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[11] For a recent review of the application of statistical mechanics to spin systems see L. C. Hebel, in *Solid State Physics*, edited by F. Seitz and D. Turnbull [Academic Press Inc., New York, (to be published)].

[12] A. Abragam, Compt. Rend. **254**, 3848 (1962). The change in polarization caused by the presence of the Li^6 nuclei can be shown to be negligible because of the small specific heat of the Li^6 nuclei.
[13] See also A. Redfield and R. Blume, Phys. Rev. **120**, 1545 (1963), especially Ref. 18 of that article.
[14] D. Jerome and G. Galleron, J. Phys. Chem. Solids (to be published).

Thus, we conclude that the full Overhauser enhancement at high field would be greater than the value $0.84 \gamma_e/\gamma_n$ inferred by us in Li; we expect, from our measurements and the theory above, that it would be $(0.84/0.90)\gamma_e/\gamma_n$, that is, $0.93 \gamma_e/\gamma_n$.

ORBITAL RELAXATION

We have seen that for lithium we infer from our experiment that the full high-field enhancement will be $93\pm3\%$ of the maximum possible value γ_e/γ_n. As was emphasized by Overhauser, this maximum enhancement is expected only if the sole relaxing interaction for the nuclei is the contact-hyperfine interaction. Other relaxation mechanisms will lead to a reduced polarization.

It is possible that impurity-induced nuclear relaxation is present here, but we find that conduction-electron relaxation processes can entirely explain our result. Korringa[15] included the effect of two other interactions besides contact hyperfine interaction in his treatment of nuclear spin relaxation via conduction electrons. These are nuclear dipole-electronic dipole interaction with the p character of the conduction electron wave function, and interaction of the nuclear moment with the orbital angular momentum (moving charge) of the conduction electrons. We will see that the orbital contribution dominates. Other conduction electron interactions, such as electric quadrupole relaxation, are probably negligible. We conclude that about 6% of the conduction electron relaxation of Li nuclei is orbital in origin. Orbital relaxation is expected to be more important than this for the transition elements.

In order to get a rough estimate of these small contributions to the relaxation time we use a simplified spherical model for the conduction band. The electron wave function can be expanded in spherical harmonics and we suppose that the first two terms are

$$\varphi_k(r) = f(r) + h(r) \cos\theta + \cdots , \quad (10)$$

where θ is the angle between $\mathbf{r}$ and $\mathbf{k}$. Then the matrix elements of the interaction responsible for relaxation are[15]

$$\langle m_I, m_S, \mathbf{k} | \mathcal{H}^1 | m_I', m_S', \mathbf{k}' \rangle$$
$$= \gamma_e \gamma_n \hbar^2 \langle m_I, m_S | (8\pi/3) P_F \mathbf{I} \cdot \mathbf{S}$$
$$+ F k^{-2}(-\tfrac{2}{3} \mathbf{k} \cdot \mathbf{k}' \mathbf{I} \cdot \mathbf{S} + \mathbf{k} \cdot \mathbf{S} \, \mathbf{k}' \cdot \mathbf{I} + \mathbf{k} \cdot \mathbf{I} \, \mathbf{k}' \cdot \mathbf{S})$$
$$+ (10/3) F k^{-2}(\mathbf{k} \times \mathbf{k}') \cdot \mathbf{I} | m_I', m_S' \rangle . \quad (11)$$

Here $P_F = f(0)^2$ and

$$F = \frac{1}{5} \int h^2(r) r^{-3} d^3 r . \quad (12)$$

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[15] J. Korringa, Physica **16**, 153 (1963). Equation (10) of this article is in error, as has been kindly acknowledged by Professor Korringa (private communication). The factor 17/90 should be 2/9, and the factor 50/27 should be 400/27. See also A. H. Mitchell, J. Chem. Phys. **26**, 1714 (1957). The quadrupolar relaxation mechanism considered by Mitchell is probably completely negligible for Li and Na.

$\mathbf{I}$ and $\mathbf{S}$ are the nuclear and electronic spin operators. We are assuming in (11) that $\mathbf{k}$ and $\mathbf{k}'$ are nearly equal in magnitude. The second term in (11) is the p-character dipolar interaction, and the last term is the orbital interaction.

To calculate the relaxation time, (11) must be squared and averaged over all m_S and m_S', and over all $\mathbf{k}$ and $\mathbf{k}'$ on the Fermi surface, which is assumed spherical. Cross terms between the different parts of (11) average to zero, and consequently we are able to divide the relaxation rate into various parts:

$$T_1^{-1} \equiv W = W_s + W_L + W_1 + W_2 + W_3 . \quad (13)$$

The first term W_s arises from the first (contact or s-hyperfine) term of (11). It is the only part of the relaxation which is considered in the often-used "Korringa relation." We are only interested in the ratios of this term to the others.

W_L is the orbital relaxation contribution. It arises from the last term of (11) and is given by

$$W_L = W_s(800/81) F^2/(8\pi P_F/3)^2 . \quad (14)$$

W_0, W_1, and W_2 are contributions of the second (p-character dipolar) term of (11); they result, respectively, from terms in the dipolar interaction of the form $\mathbf{I} \cdot \mathbf{S}$, $I_+ S_z$ or $I_- S_z$, and $I_+ S_+$ or $I_- S_-$. They are smaller than the orbital relaxation term W_L and are given by

$$W_L = 400 W_0/3 = 400 W_1/9 = 400 W_2/8 . \quad (15)$$

Turning to the Overhauser effect, W_s should by itself produce the maximum Overhauser effect γ_e/γ_n, and so should W_0. W_1 and W_L should produce no polarization, only a leakage, since they involve no electron spin flip. W_2 acting alone would produce a *negative* Overhauser effect—this follows readily if one applies Overhauser's theory or Slichter's argument[7] to the interactions $I_+ S_+$ and $I_- S_-$ alone. When all these relaxation processes act simultaneously it is not hard to show that the full predicted Overhauser polarization is

$$\Omega_\infty = (\gamma_e/\gamma_n)(W_s + W_0 - W_2)/W . \quad (16)$$

It is worthy of note that if only dipolar relaxation were present $(W_L, W_s=0)$ then (15) and (16) predict that $\Omega_\infty = -\tfrac{1}{2}\gamma_e/\gamma_n$. The same result has been obtained by Abragam[16] in a different, though presumably equivalent way.

In practice, because W_L is so much larger than W_0, W_1 and W_2, (16) can be written

$$\Omega_\infty \cong (\gamma_e/\gamma_n) W_s/(W_s + W_L) . \quad (17)$$

This approximation is appropriate for the spherical model but it is probably also valid for most real metals. Orbital relaxation is much more important than non-contact dipolar relaxation.

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[16] A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), p. 312.

We have estimated the ratio of W_s to W_L for Li; in Na, W_L is negligible because P_F is considerably larger for Na than for Li. Unfortunately, a complete wave function is not given in the literature for Fermi electrons in Li, so we made various approximations. For P_F we used the value of 0.11 atomic unit inferred from Knight shift and spin susceptibility measurements, and also obtained theoretically for a wave function normalized over the unit cell.[17] For $h(r)$ we used a p function derived from calculations[17,18] of Callaway and Kohn:

$$h(r) = iC3j_1(rk)[u_0 + k^2\phi_0] + ku_1 j_0(kr). \qquad (18)$$

Here j_0 and j_1 are spherical Bessel functions, and u_0, u_1, and ϕ_0 are tabulated radial wave functions.[18] C is a normalization constant such that $[h(r)\cos\theta]^2$ integrated over the Wigner-Seitz sphere is equal to 0.7. The normalization is chosen to agree with Kohn's[17] result that there is 70% p character of the wave function, and the wave function was chosen because the p part of the wave function at the Fermi surface is probably not too different from the p part of the wave function at the bottom of the band.

The integral (12) is over all space, whereas (18) is defined only inside the Wigner-Seitz sphere. To simplify the calculation, outside the sphere we used a free-electron wave function, for which $h(r) = \Omega^{-1/2} 3ik j_1(kr)$; here Ω is the volume of the unit cell. This is probably a reasonable approximation since the interaction of a nucleus with an electron outside its own unit cell is probably not much affected the details of the electronic motion. About 30% of F is thus estimated to arise from the part of the integral outside the unit cell.

Using these assumptions we get the result that $W_L = 0.06\ W_s$ and $\Omega_\infty = 0.94\gamma_e/\gamma_n$, in fortuitous agreement with our experimental result.

CONCLUSION

Aside from confirming Overhauser's prediction quantitatively, these results are relevant to the interpretation certain other experiments, which we now discuss.

Ryter measured the lithium "day shift," that is, the shift in the electron spin resonance due to enhanced nuclear polarization.[5] By comparing day and Knight shifts Ryter obtained a value of P_F in good agreement with that inferred by Schumacher and Slichter from measurements of the Knight shift and conduction elec-

tron spin susceptibility. His conclusions, however, rest on the assumption that the full enhancement factor is γ_e/γ_n rather than $0.94\gamma_e/\gamma_n$ as we infer. Using our enhancement factor with Ryter's measurements we obtain a value of P_F 6% greater than that quoted by Slichter and Schumacher but in agreement with that obtained from the χ_s measurement in I. The experimental error on all these measurements is, of course, of the same order of magnitude as the 6% discrepancy.

This experiment also permits a less ambiguous test of the Korringa relation which, in its most useful form,[19] is

$$\chi_s = \left(\frac{C_{Ve}}{T}\right)\left(\frac{\gamma_e}{\gamma_n}\right)\left(\frac{\Delta\nu}{\nu}\right)\left(\frac{T}{W_s}\right)^{1/2}\left(\frac{36\mu^4}{\pi^3 k_B^3 \hbar}\right)^{1/2}. \qquad (19)$$

Here C_{Ve} is the electronic contribution to the specific heat, $\Delta\nu/\nu$ is the fractional Knight shift, μ is the Bohr magneton, and k_B is Boltzman's constant. The form (19) is likely to be correct even if there is some exchange interaction between conduction electron spins, because χ_s and $\Delta\nu$ will both be equally increased. Normally the low temperature value of T_1^{-1} is used in place of W_s and the present research shows that this substitution is correct for Na while for Li $W_s = 0.94T_1^{-1}$. The relation (19) is very well obeyed for Na, while for Li the measured χ_s is lower by about 15% than the right-hand side of (19) when typical measured values of $\Delta\nu$, C_{Ve}, and T_1 are substituted.[9] This discrepancy may be caused in part by the martensitic transformation which Li and Na undergo at low temperatures, as discussed in the previous article.[9]

Perhaps the most important fact which this experiment and the theory outlined above help confirm is that in most metals W_s will be very close to T_1^{-1}, so that (19) can be used to infer χ_s for many metals for which it cannot be directly measured. Such inferred values of χ_s may not be completely reliable since (19) is valid presumably only for weakly interacting quasi-electrons. In the transition metals, for which orbital contributions to $\Delta\nu$, χ_s and W may be important, (19) is not expected to hold.

ACKNOWLEDGMENTS

[17] W. Kohn, Phys. Rev. **96**, 590 (1954).
[18] J. Callaway and W. Kohn, Phys. Rev. **127**, 1913 (1962).

[19] See, for example, R. Schumacher and Vehse, J. Phys. Chem. Solids. **24**, 297 (1963).