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Interaction of Conduction Electrons and Nuclear Magnetic Moments in Metallic Sodium*

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The electronic wave function at the Fermi surface of metallic Na has been calculated. The resulting value of $|\psi|^2$ at a Na nucleus is discussed with reference to measurements of the Knight shift and the paramagnetic susceptibility.

I. INTRODUCTION

The interaction of conduction electrons with nuclear magnetic moments in metallic lithium and its connection with the Knight shift and the paramagnetic susceptibility was discussed in detail in a recent paper,[1] to which the reader is referred for general background and notation. In the present paper, we wish to report the results of a similar investigation for metallic sodium.

The Knight shift is given, according to the theory of Townes, *et al.*,[2] by

$$\frac{\Delta H}{H}=\frac{hc\Delta\nu IM}{\mu_I\mu_0(2I+1)}\chi_p\frac{P_F}{P_A}. \qquad (1)$$

In their paper, (P_F/P_A) was calculated by perturbation theory and gave the value 0.81, while the then available value[3] of $\Delta H/H$ was 1.04×10^{-3}. When substituted into Eq. (1) this leads to $\chi_p=0.77\times10^{-6}$ cgs mass unit.

Meanwhile, a direct measurement[4] of χ_p at liquid nitrogen temperature has yielded a value of $(0.93\pm0.10)\times10^{-6}$ cgs mass unit, which is in fairly good agreement with a theoretical estimate by Pines[5] who finds 0.84×10^{-6} cgs mass unit, with an uncertainty of 10 to 20%.

It therefore appeared worth-while to report some of the details of a theoretical calculation[6] of the ratio (P_F/P_A) giving the value

$$(P_F/P_A)_{\text{theoret}}=0.81 \qquad (2)$$

at 77°K, in good agreement with reference 2. When this is combined with the value $\Delta H/H=1.09\times10^{-3}$ derived from more recent Knight shift measurements[7] one finds, from Eq. (1), the value $\chi_p=0.82\times10^{-6}$ cgs mass unit at 77°K.

It will be noticed that while this value agrees very well with the theoretical estimate of Pines, it is about 12% smaller than the best experimental value. A discrepancy of the same sign and similar magnitude exists in the case of Li.[1,4] This indicates that the calculated values of (P_F/P_A) may be too large or that Eq. (1) requires refinement.

We have also calculated the volume dependence of P_F in the vicinity of V_0, the room temperature volume per atom, and find

$$(\Delta P_F/P_F)=-0.26(\Delta V/V). \qquad (4)$$

This result is of interest in connection with the experiments of McGarvey and Gutowsky,[7] who have measured the temperature dependence of the Knight shift between 200° and 400°K, and those of Knight,[8] who has reported a strong temperature dependence between 25° and 75°K.

According to Eq. (1),

$$\text{Fractional change of Knight shift} =(\Delta\chi_p/\chi_p)+(\Delta P_F/P_F). \qquad (5)$$

Between 200° and 370°K, McGarvey and Gutowsky observe a 2.7% increase in the Knight shift. In this temperature range, V changes by 3.5% giving, by (4), $\Delta P_F/P_F=-0.009$, so that to obtain agreement with experiment we would require $\Delta\chi_p/\chi_p=0.036$. The theory of Pines leads to $\Delta\chi_p/\chi_p=0.022$ corresponding to this volume change.

Knight[8] has reported a 10% drop of the Knight shift between 75° and 25°K. This evidently cannot be attributed to a change of P_F resulting from a volume change, since by (4) it would require $\Delta V/V\sim0.4$. In addition, the fact that McGarvey and Gutowsky observe only a 3% change of the Knight shift on melting, makes it unlikely that Knight's result is due to a change of P_F as a result of a phase transformation.

II. DETAILS OF THE CALCULATION

The Quantity P_A

P_A in (1) equals $|\psi_A(0)|^2$, where ψ_A is the normalized $3s$ wave function of atomic sodium. Using the Prokofjew potential,[9] we find

$$(P_A)_{\text{theoret}}=0.685a_0^{-3}. \qquad (6)$$

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[1] W. Kohn, Phys. Rev. **96**, 590 (1954) hereafter called I.

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

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

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

[5] D. Pines, Phys. Rev. **95**, 1090 (1954).

[6] T. Kjeldaas, Jr. and W. Kohn, Phys. Rev. **99**, 622(A) (1955).

[7] H. S. Gutowsky and B. R. McGarvey, J. Chem. Phys. **20**, 1472 (1952); B. R. McGarvey and H. S. Gutowsky, J. Chem. Phys. **21**, 2114 (1953). These experiments were done at higher temperatures. The value of the shift quoted for 77°K is derived from an extrapolation based on volume contraction.

[8] W. D. Knight, Phys. Rev. **96**, 861 (1954).

[9] W. Prokofjew, J. Physik **58**, 255 (1929).

The measured[10] hyperfine splitting of the $3s$ state leads to

$$(P_A)_{\text{exptl}}=0.756a_0^{-3}. \tag{7}$$

The error in the quantity P_F/P_A occurring in (1) should be much less (perhaps 1–2%) than the 10% discrepancy of (6) and (7), especially since the energy at the Fermi surface is very nearly equal to the atomic $3s$ energy.

Metallic Wave Function in the Spherical Approximation

We write for the wave function on the Fermi surface, normalized in the equivalent sphere,

$$\psi=\sum_{l=0} a_l\varphi_l, \tag{8}$$

where φ_l is a similarly normalized wave function corresponding to angular momentum l. Using the same variational method as in I, and the radial wave functions calculated by Von der Lage,[11] we find with trial functions, including up to 7 terms,

$$|a_0|^2=0.45,\quad |a_1|^2=0.45,\quad |a_2|^2=0.09,$$
$$\sum_{l=3}^{6}|a_l^2|=0.01,$$

leading to the value for $(P_F/P_A)_{\text{theoret}}$ quoted in Eq. (2). The various checks described in I were also applied to the present calculation and indicate that as a solution for the potential chosen this result has an error of less than 2%.

The calculation was repeated for a slightly different lattice constant in order to obtain the volume dependence of P_F quoted in (4).

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[10] M. Fox and I. I. Rabi, Phys. Rev. 87, 472 (1951).

[11] F. Von der Lage, thesis, Cornell University, 1943 (unpublished). We are indebted to Dr. J. A. Krumhansl for making these results available to us.

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Nuclear Spin-Lattice Relaxation Time in Copper and Aluminum*

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Nuclear spin-lattice relaxation times of Al^{27} in pure Al and Cu^{63} in annealed pure Cu have been measured at 2 and 4.2°K, using the adiabatic fast-passage technique suggested by L. E. Drain. At 4.2°K, $T_1=260\pm100$ milliseconds for copper and 370 ± 40 milliseconds for aluminum. The relaxation time is apparently inversely proportional to temperature, as predicted by Korringa, from 2 to 300°K.

KORRINGA[1] has calculated the spin-lattice relaxation time T_1 in metals and has shown that T_1 should be inversely proportional to temperature and should be related to the Knight shift.[2] Early low temperature measurements[3–5] of T_1 in Cu, Al, and Li were in rather poor agreement with Korringa's theory, but recently Holcomb and Norberg[6] have found reasonable agreement in Li, Na, and Rb near room temperature. Using two independent techniques, the writer[7] found that $T_1=5.5\pm1$ milliseconds for Al^{27} in aluminum, and $T_1=3.55\pm0.7$ milliseconds for Cu^{63} in copper,[8] consistent with Korringa's theory. It seemed desirable to check the earlier low-temperature measurements on aluminum and copper to see if the discrepancy with theory is real.

The relaxation times were measured by the method of adiabatic fast passage previously used to study liquids by Drain[9] and by Ciaroti *et al.*[10] The fact that this method can also be applied to solids was discussed in a previous paper.[7] It is necessary that the time taken to sweep through resonance be short compared to T_1 and long compared to T_2 or $(\gamma H_1)^{-1}$, whichever is smaller. Also, H_1 (the rf field) must be several times the value of rf field required to saturate the resonance under steady-state conditions.

The apparatus was similar in principle to that of

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

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

[3] J. Hatton and B. V. Rollin, Proc. Roy. Soc. (London) A199, 222 (1949).

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

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

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

[7] A. Redfield, Phys. Rev. 98, 1787 (1955).

[8] These values of T_1 are quoted from Sec. IV of reference 7. The writer now feels that they are more reliable than those obtained conventionally and quoted in the abstract and Sec. II of reference 7.

[9] L. E. Drain, Proc. Phys. Soc. (London) A62, 301 (1949).

[10] Ciaroti, Cristiani, Giulotto, and Lanzi, Nuovo cimento 12, 519 (1954).