change effects, as well as a discussion of the validity of the effective charge approximation [cf. Eq. (3)], will be presented in the future.

I wish to thank B. Baxter for assistance in programming of the numerical integration, Dr. M. Mittleman for pointing out the possibility of inclusion of the exchange effects in the theory, and Dr. A. Temkin for valuable discussions.

---

[1] L. Vainshtein, L. Presnyakov, and I. Sobelman, Zh. Eksperim. i Teor. Fiz. 45, 2015 (1963) [translation: Soviet Phys.—JETP 18, 1383 (1964)]. Similar calculation with total wave function approaching the final state asymptotically is given by D. Crothers and R. McCarroll, Proc. Phys. Soc. (London) 86, 753 (1965).

[2] L. Presnyakov, Zh. Eksperim. i Teor. Fiz. 47, 1134 (1964) [translation: Soviet Phys.—JETP 20, 760 (1965)].

[3] L. Presnyakov, I. Sobelman, and L. Vainshtein, Proc. Phys. Soc. (London) 89, 511 (1966).

[4] L. D. Landau and E. M. Lifshitz, Quantum Mechanics (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 505. Equation (7) is also given by M. R. C. McDowell, in Proceedings of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, Canada, August, 1965 (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1965), p. 22.

[5] K. Omidvar, Phys. Rev. 113, A970 (1964).

[6] R. Damburg and M. Gailitis, Proc. Phys. Soc. (London) 82, 1068 (1963).

[7] G. E. Chamberlain, S. J. Smith, and D. W. O. Heddle, Phys. Rev. Letters 12, 647 (1964); S. J. Smith, in Proceedings of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, Canada, August, 1965 (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1965), p. 377.

[8] D. Hils, H. Kleinpoppen, and H. Koschmieder, Proc. Phys. Soc. (London) 89, 35 (1966).

[9] W. L. Fite and R. T. Brackmann, Phys. Rev. 112, 1141 (1958).

[10] J. W. McGowan, M. A. Fineman, E. M. Clarke, and H. P. Hanson, to be published; J. W. McGowan and M. A. Fineman, in Proceedings of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, Canada, August, 1965 (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1965), p. 429.

[11] E. P. Wigner, Phys. Rev. 73, 1002 (1948).

[12] Similar differences in energy dependence occur in close coupling and Born calculations [cf. M. Gailitis and R. Damburg, Proc. Phys. Soc. (London) 82, 192 (1963)].

[13] G. H. Wannier, Phys. Rev. 90, 817 (1953).

[14] M. R. H. Rudge and M. J. Seaton, Proc. Roy. Soc. (London) A283, 262 (1965).

[15] A. Temkin, Phys. Rev. Letters 16, 835 (1966).

[16] R. K. Peterkop, Proc. Phys. Soc. (London) 77, 1220 (1961).

VANISHING KNIGHT SHIFT IN SUPERCONDUCTING ALUMINUM

R. H. Hammond and G. M. Kelly
General Atomic Division of General Dynamics Corporation,
John Jay Hopkins Laboratory for Pure and Applied Science, San Diego, California

(Received 28 December 1966)

We report here a new measurement of the Knight shift in superconducting aluminum which differs from a previous result[1] in that now the Knight shift extrapolates to a value at $T = 0°\mathrm{K}$ which is essentially zero, as predicted by the BCS theory of superconductivity,[2] according to which the ground state consists of a coherent superposition of Cooper pairs in singlet spin states.

Previous measurements of the Knight shift in superconductors have all shown that the spin susceptibility at $T = 0$ remains finite, contrary to the prediction of the BCS theory. In the elements tin,[3] mercury,[4] and vanadium[5] these results have been explained either on the basis of spin-orbit scattering or on the basis of contributions to the Knight shift that are unaffected by the transition to the superconducting state.[6,7] Aluminum, however, was expected to be one example where these effects might not play a significant role: (1) Spin-orbit coupling (both to displaced surface atoms and to the crystalline field) should be small because aluminum is the superconducting metal with the smallest atomic weight, and (2) aluminum has no d electrons so that one can assume that the paramagnetic susceptibility is entirely due to conduction electrons. The result[1] of a measurement made on one sample of aluminum films a number of years ago was that the Knight shift at $T = 0°\mathrm{K}$ was about 75%. In considering this unexpected result, Appel[7] concluded that all of the possible contributions to the Knight shift in superconducting aluminum should nearly vanish at $T=0°\text{K}$, and that a possible explanation for the finite shift was the presence of paramagnetic centers due to the presence of nonstoichiometric aluminum oxide.[8] This provided the motivation to produce another sample which would avoid as far as possible the inclusion of oxygen within the film thickness.

The results of the present measurements are shown in Fig. 1. The experimentally determined quantity is the difference in frequency between the nmr frequencies of copper and of aluminum. The data extrapolate roughly to 82 kc/sec at $T=0°\text{K}$, which corresponds to a change in the aluminum frequency of about 6.7 kc/sec, and which at the value of the magnetic field used, 3.8 kG, corresponds to a change $\Delta f/f=0.16\%$ in the aluminum shift. This is just the value ascribed to aluminum as the Knight shift.[9] An uncertainty is the amount of the chemical shift, which for aluminum is of the order of 0.01 %.[9]

The sample was made by the flash evaporation of precut pieces of aluminum wire (6-9's Cominco) dropped into an electron-beam–heated tantalum cup at about 1600°C. The vacuum was $<10^{-7}$ Torr. The aluminum condensed onto $\frac{1}{8}$-mil-thick Mylar, which was then cut and stacked as described previously,[1] again with copper foil inserted at intervals.

Initial measurements of the nmr in the aluminum and copper at temperatures below the transition temperature gave very broad and asymmetric lines, despite apparent alignment of the films with the magnetic field based on the minimization as a function of angle of the inductance of the rf coil of the Pound-Knight-Watkins marginal oscillator. It was finally determined that alignment is extremely critical, beyond the magnet-angle scale resolution of 0.1°, and only determined by sweeping repeatedly through the copper line at different adjustments of the magnet angle (there were some indications that we had to cool down the sample through the transition after each adjustment of the angle, rather than change the angle at a given superconducting temperature). When finally aligned, the copper and aluminum line shapes did not change upon cooling through the superconducting transition. The aluminum line was first-order quadrupole broadened, presumably either because of field gradients in the otherwise cubic crystal arising from oscillations in the charge density due to the film surfaces[10] or because of strains in the film.

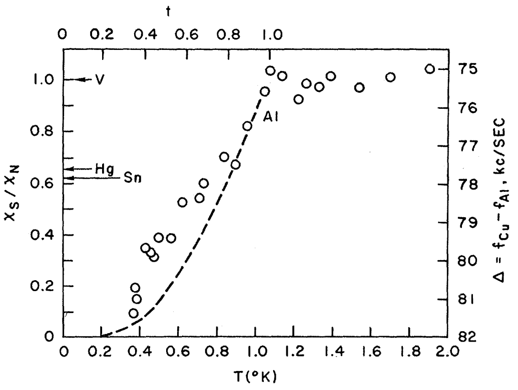

FIG. 1. Experimental data showing the change in the Knight shift in aluminum films through the superconducting transition. The ordinate at the right is the difference between the nmr frequencies of Cu and Al in a magnetic field of 3.8 kG. The left-hand ordinate refers to the dashed curve which is the spin susceptibility as calculated by Yosida for a BCS superconductor. The results of other measurements at 0°K are indicated by the arrows (see Refs. 3-5).

The temperature dependence of the observed shift differs from the one calculated by Yosida[11] on the basis of the BCS theory. An explanation for this might be found in the consideration of Fulde and Maki,[12] who have calculated the depairing effect of the magnetic field, which even in the limit of vanishing spin-orbit interaction will give rise to a finite susceptibility at $T=0$ if the superconductor is in the "gapless region" (when very close to the critical field), and which, at smaller fields, gives rise to a field-dependent susceptibility that, although vanishing at $T=0°\text{K}$, is larger at intermediate temperatures than that calculated by Yosida. This is shown in Fig. 1 of Ref. 12. These curves cannot be applied directly to our results, however, since the parameter H/H_c is actually a function of temperature, as the phase diagram of a superconductor illustrates. Unfortunately, our knowledge of the phase diagram of the sample is not complete enough at present to compare quantitatively our temperature dependence with one derived from the curves of Fulde and Maki. The critical temperature at zero magnetic field $T_c(H=0)$ is between 1.3 and 1.4°K, as determined by the change in the inductance of the rf coil. A "best-guess" phase diagram is obtained by fitting a temperature dependence of $[(1-t^2)/(1+t^2)]^{1/2}$, which is very close to what is found for a thin film,[13] through $T_c(0)=1.4°\text{K}$ and through $T_c(3.8\text{ kG})$

$=1.08$°K (obtained from Fig. 1). This gives a $H_c(T=0)$ value of 7.6 kG, which would be obtained if the film thickness were $d=136$ Å, using the formula[13] $H_c/H_{cb}=5.8\xi_0^{1/2}\lambda_L(0)/d^{3/2}$. This thickness is reasonably close to our estimate of 120 Å based on optical measurements. This phase diagram results in the following values of H/H_c at the respective temperatures: $H/H_c=0.79$ at 0.9°K, 0.65 at 0.7°K, and 0.57 at 0.5°K. Using these values of H/H_c at the corresponding reduced temperatures, one sees that the results of Fulde and Maki fall below our results. However, until the phase diagram is known with more certainty, no real conclusion can be made concerning the temperature dependence.

Unfortunately, a determination of the phase diagram of a sample consisting of a large number of films is difficult (the sample consists of about 3000 film layers). Even if the resistivity of a large sampling of individual films were measured, the gapless region would not be made evident since a gapless superconductor still has zero resistance.

Considerations of gapless superconductivity and magnetic-field depairing also apply to the previous measurement on aluminum.[1] In addition, the effects of paramagnetic impurities have to be considered in that sample. The fact that the transition temperature was not also lowered, and that the aluminum nmr linewidth was not broadened, might be related to the possibility that the distribution of paramagnetic centers due to a suboxide of aluminum could have been nonhomogeneous because of the techniques used then in the evaporation of the aluminum. A critical test for paramagnetic impurities would be a measurement of the nuclear spin-lattice relaxation time T_1, using the field-cycling technique,[14] where the relaxation is at zero magnetic field. Then the competing effect on T_1 of magnetic-field depairing[15] could be eliminated.

We wish to express our appreciation to Dr. Joachim Appel for his assistance and stimulation in this work, and to Dr. F. Wright, Jr., W. A. Hines, and Professor W. D. Knight for illuminating discussions of their work. We wish to acknowledge the assistance of Pendyala Subrahmanyam in operating the equipment and in analyzing the data and our thanks to Dr. G. W. Hinman and Dr. P. H. Miller, Jr., for their encouragement.

---

[1] R. H. Hammond and G. M. Kelly, Rev. Mod. Phys. 36, 185 (1964).

[2] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[3] G. M. Androes and W. D. Knight, Phys. Rev. 121, 779 (1961); Fulton Wright, Jr., thesis, University of California, 1966 (unpublished); F. Wright, Jr., W. A. Hines, and W. D. Knight, Phys. Rev. Letters 18, 114 (1967).

[4] F. Reif, Phys. Rev. 106, 208 (1957).

[5] R. J. Noer and W. D. Knight, Rev. Mod. Phys. 36, 177 (1964).

[6] R. A. Ferrell, Phys. Rev. Letters 3, 262 (1959); P. W. Anderson, Phys. Rev. Letters 3, 325 (1959); A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 39, 1781 (1960) [translation: Soviet Phys.–JETP 15, 752 (1962)] .

[7] J. Appel, Phys. Rev. 139, A1536 (1956).

[8] As suggested by Professor B. T. Matthias.

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

[10] R. J. Charles and W. A. Harrison, Phys. Rev. Letters 11, 75 (1963).

[11] K. Yosida, Phys. Rev. 110, 769 (1958).

[12] P. Fulde and K. Maki, Phys. Rev. 139, A788 (1965).

[13] P. G. de Gennes and M. Tinkham, Physics 1, 107 (1964).

[14] L. C. Hebel and C. P. Slichter, Phys. Rev. 113, 1504 (1959); Y. Masuda and A. G. Redfield, Phys. Rev. 125, 159 (1962).

[15] K. Maki and P. Fulde, Phys. Rev. 140, A1586 (1965).