Study of Superconducting Hg by Nuclear Magnetic Resonance Techniques*

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Since nuclear magnetic resonance techniques can provide rather microscopic information about conduction electrons in metals, their application to the study of superconducting metals is of considerable interest. The difficulties associated with the failure of magnetic fields to penetrate inside superconductors can be overcome by the use of dense colloids consisting of particles mostly less than 500 A in diameter. The preparation and characteristics of such Hg colloids are described and some comments are made about the experimental equipment. Experiments show that the superconducting particles give rise to a resonance line with a Knight shift less than that of the line in the normal metal. Considerations affecting the analysis of the data are discussed at some length. Calculations are given for the resonance line shape due to a single spherical superconducting particle and also for that expected from a distribution of such particles of different sizes. A criterion is developed for determining the Knight shift from the observed superconducting line. Corrections for the microscopic broadening of the resonance line and for the bulk diamagnetism of the sample are derived. It is pointed out that the bulk magnetization curve of the superconducting colloid can also readily be measured by means of the nuclear resonance equipment. In measurements ranging from 750 to 2300 gauss the Knight shift K_s in the superconductor at 1.20°K is found to be 1.6%, or about $\frac{2}{3}$ of its value in the normal metal. Experiments designed to elucidate the temperature dependence of the Knight shift K_s are also discussed. Some general quasi-thermodynamic comments are made to relate the Knight shift to some properties of the electron interaction energy responsible for superconductivity. Remarks based on the two-fluid model lead to some speculative predictions concerning the temperature dependence of K_s which seem to be in at least qualitative agreement with the temperature dependence suggested by experiment. The need and interest of some further experiments is pointed out.

I. INTRODUCTION

THE method of nuclear magnetic resonance[1,2] can be applied to the study of normal metals provided that, to allow penetration of the radio-frequency field, one works with samples consisting of particles small compared to the skin depth (i.e., $\lesssim 10^{-3}$ cm). One finds that in a given external magnetic field H the frequency ν_m at which the nuclear resonance is observed in the metal is higher than the frequency ν_i at which it occurs for the same nucleus in an insulator; the ratio $K\equiv(\nu_m-\nu_i)/\nu_i$ is known as the Knight shift. Furthermore, the relaxation time T_1 necessary for the nuclear spin system to attain thermal equilibrium in the metal tends to be appreciably shorter than it would be in an insulator. Both of these effects[3] are caused by the presence of conduction electrons in the metal. The frequency shift $\nu_m-\nu_i$ is due to the nonvanishing expectation value of the local magnetic field at the nucleus produced by its hyperfine interaction with the conduction electrons. If $\psi(0)$ is the wave function at the nucleus of a conduction electron with energy near the Fermi level and $\mathfrak{M}$ is the spin paramagnetic moment of the conduction electrons, then $(\nu_m-\nu_i)\sim\langle|\psi(0)|^2\rangle_{\text{Av}}\mathfrak{M}$ and

$$K\equiv(\nu_m-\nu_i)/\nu_i\sim\langle|\psi(0)|^2\rangle_{\text{Av}}\mathfrak{M}/H. \quad (1)$$

One can write $\mathfrak{M}=\chi H$, where χ is the paramagnetic susceptibility of the conduction electrons. The elementary Pauli theory[4] applied to the degenerate electron assembly of a normal metal yields $\chi\sim\rho_F$, the density of one-electron states at the Fermi surface. Hence the Knight shift K_n in a normal metal is given by $K_n\sim\langle|\psi(0)|^2\rangle_{\text{Av}}\rho_F$ which, like χ, is essentially independent of the magnetic field H. The short nuclear relaxation time T_1 is also due to interaction with the conduction electrons via (the off-diagonal matrix elements of) the hyperfine interaction. Indeed, in a normal metal the Korringa relation[5] predicts a close connection $(1/T_1\sim K^2)$ between the relaxation time produced by the conduction electrons and the Knight shift.

It is apparent that observation of the nuclear resonance in a metal provides chiefly information of a fairly microscopic kind concerning the conduction electrons near the Fermi surface. As a result, nuclear magnetic resonance techniques have proven themselves fruitful in the study of normal metals and alloys.[3] An extension of these techniques to the investigation of *superconducting* metals, where they could yield microscopic information about the electrons thought to be responsible for the superconducting behavior, would seem to be of considerable interest.[6] There is, however, a fundamental difficulty which might seem to preclude the possibility of observing nuclear magnetic resonance in the superconducting state. This is the Meissner effect,[7] i.e., the fact that the magnetic induction **B** vanishes inside a superconductor so that neither the static nor the rf magnetic fields can penetrate to the

* This work was supported by a grant from the Alfred P. Sloan Foundation.

[1] E. R. Andrew, *Nuclear Magnetic Resonance* (Cambridge University Press, Cambridge, 1955).

[2] G. E. Pake, in *Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 2, pp. 1–91.

[3] W. D. Knight, in *Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 2, pp. 93–136.

[4] C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1956), second edition, p. 260.

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

[6] F. Reif, Phys. Rev. **102**, 1417 (1956). This reference will hereafter be referred to by the letter R.

[7] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), second edition.

nuclei inside the superconducting metal. It is clear, however, that in a more detailed description of this effect there must exist a rather small but finite penetration depth λ characterizing the distance within which $\mathbf{B}$ decreases from its value at the surface to its value $\mathbf{B}=0$ well inside the superconductor. Measurements indicate that λ is of the order of 5×10^{-6} cm.[8] Hence, if one were to work with superconducting particles or films with at least one dimension small compared to the penetration depth λ, one could achieve substantial penetration of external magnetic fields and nuclear magnetic resonance experiments might then become possible. Furthermore, the use of samples consisting of such small particles should simultaneously help to overcome another difficulty since it allows one to work in magnetic fields large enough to avoid a prohibitively poor signal-to-noise ratio in the nuclear resonance experiment. The reason is that, though the critical field H_c sufficient to destroy the superconducting state in the bulk metal is rather small (413 gauss for Hg at $T=0°K$), the critical fields for small particles can be substantially higher, and are the larger the smaller their size.[8] This behavior of the critical field is a thermodynamic consequence of the fact that in these small particles the penetration of the magnetic field reduces their diamagnetic moments correspondingly. Finally, one might question to what extent experiments performed on particles comparable in size to λ can be expected to yield results of significance for the understanding of macroscopic superconductors. It should be pointed out in this connection that experiments designed to study the superconducting penetration depth λ have, as a matter of fact, been performed on colloidal particles of this size.[9,10] These colloids exhibit critical temperatures for the superconducting transition almost identical with the transition temperature of the bulk metal and yield results for the temperature dependence of the penetration depth consistent with those obtained from experiments on bulk superconductors. Investigations of films as thin as 20 A show that even these do become superconducting and with a transition temperature nearly the same as that of the bulk metal.[8,11] Furthermore, the microwave and infrared experiments on such thin films can be interpreted in terms of concepts and parameters significant for the understanding of bulk superconductors.[12] Evidence of this kind seems to indicate that studies of small particles of the size envisaged in our discussion can indeed be useful in elucidating some of the essential properties of macroscopic superconductors.

Although the use of samples consisting of very small metal particles seems to make nuclear resonance experiments in the superconducting state possible, it should be apparent that such experiments present, nevertheless, considerable difficulty. Most important, the preparation of dense samples with particle sizes in the range $10^{-6}-10^{-5}$ cm constitutes a major problem. Further, it is desirable and often necessary to make measurements in rather low magnetic fields where the signal strength available for the observation of the nuclear resonance is unfavorable. Finally, the incomplete penetration of the magnetic field into the superconducting particles complicates the analysis of the experimental results and makes the extraction of the experimental information of primary interest, such as the Knight shift, rather difficult.

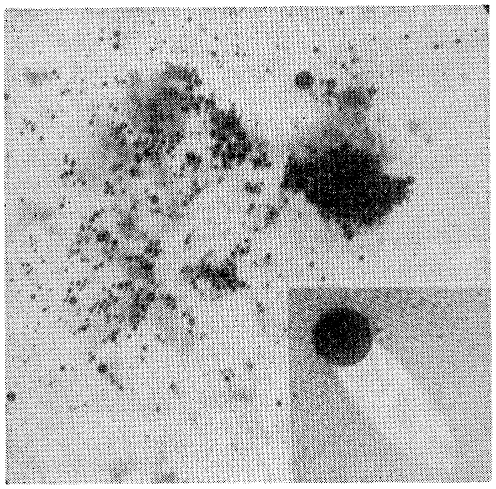
II. EXPERIMENTAL ASPECTS

(a) The Sample

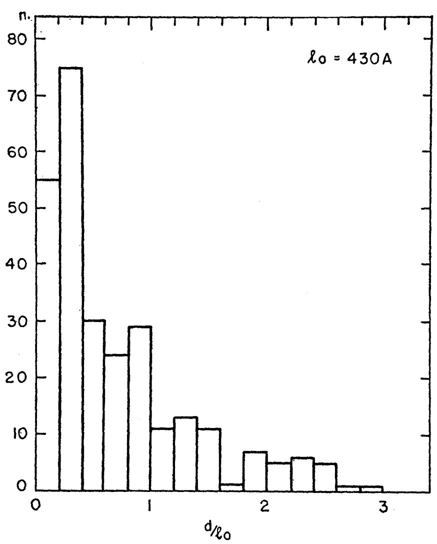
The sample desired for these experiments is one consisting of an aggregate of colloidal metal particles each of a characteristic linear dimension l. The fundamental requirements on the sample are the following: (a) One needs $l\lesssim\lambda\approx500$ A for most particles to allow sufficient penetration of the magnetic field in the superconducting state. (b) A large effective density, i.e., a large number of particles per unit volume of the sample, is necessary to provide a number of nuclei sufficiently large to make the detection of the small nuclear resonance signal possible. (c) The metal should have a superconducting transition temperature which is high compared to the lowest temperature (1.2°K) readily accessible by pumping on liquid helium. (d) The metal must have an isotope of sufficiently large abundance and with a sufficiently large nuclear magnetic moment to permit observation of the nuclear resonance. Preferably this isotope should have nuclear spin $I=\frac{1}{2}$ so as to avoid the possibility of its possessing a nuclear electric quadrupole moment the existence of which might further complicate the interpretation of the experimental results. (e) It is desirable that the Knight shift K_n in the normal state of the metal be large so as to make any change in this quantity more readily measurable.

Mercury seemed to fulfil all of these requirements, particularly since as a result of Shoenberg's work[9] it appeared possible to prepare dense colloids of this metal with particle sizes lying in approximately the desired range. Furthermore, since Hg is liquid at room temperature, one can expect the particles to have regular spherical shapes, a feature which simplifies the analysis of the data. The transition temperature for Hg is 4.15°K.[7] The Hg^{199} isotope has nuclear spin $\frac{1}{2}$, and its natural abundance of 16.8% and nuclear magnetic moment (0.179 that of the proton)[13] are, though rather small, adequate for the experiment.[14] Preliminary measurements at liquid nitrogen and also

[8] Reference 7, Chap. V.
[9] D. Shoenberg, Proc. Roy. Soc. (London) **A175**, 49 (1940).
[10] C. S. Whitehead, Proc. Roy. Soc. (London) **A238**, 175 (1956).
[11] R. E. Glover and M. Tinkham, Phys. Rev. **104**, 844 (1956).
[12] M. Tinkham, Phys. Rev. **104**, 845 (1956).
[13] W. G. Proctor and F. C. Yu, Phys. Rev. **81**, 20 (1951).
[14] The only other Hg isotope with a nuclear moment is Hg^{201} which is 13% abundant and has nuclear spin $\frac{3}{2}$ with a nuclear g factor only 0.4 that of Hg^{199}.



(a)



(b)

FIG. 1. (a) An electron microscope photograph showing Hg droplets sampled from one of our colloidal preparations. The inset in the lower right corner shows, with the same magnification, a latex sphere (shadow-cast) 2600 A in diameter. (b) A representative size distribution obtained for one of our samples. The histogram shows the number n of Hg drops *vs* their diameter d measured in units of $l_0=430$ A.

liquid helium temperatures showed that the Knight shift K_n in normal Hg metal is $2.46\pm0.05\%$; this is probably the largest Knight shift which has been observed in any metal. Parenthetically, it may be mentioned that mercury has a rhombohedral crystal structure.[15] As a result there is an asymmetric part of the Knight shift[16] which makes the nuclear resonance line in the normal metal at high fields asymmetric with a line width proportional to the field. However, at the low magnetic fields of interest in the present experiments, the line in the normal metal becomes nearly symmetric with a residual field-independent width (between points of maximum slope) of about 3.2 kc/sec; this is appreciably larger than the width of 0.28 kc/sec calculated from nuclear magnetic dipole-dipole interactions alone and is presumably due to electron-coupled nuclear exchange interaction.[17]

The actual Hg samples used in these experiments are similar in nature to some of those used in Shoenberg's work.[18] They were prepared by us by reducing a solution of $HgNO_3$ with hydrazine in the presence of a protecting colloid consisting of a solution of egg albumen hydrolyzed with NaOH. The albumen serves to coat the Hg particles when they are formed and thus to prevent their coalescence into bigger drops. Further, if the solution is finally acidified so as to bring it to the isoelectric point of the albumen, the latter coagulates and precipitates together with the embedded mercury droplets. This precipitates can then be filtered off and dried to provide a colloidal Hg sample of the required high density. Several chemical preparations are necessary to provide the amount of colloid desirable (about 30 grams packed into a polystyrene sample container of $\frac{3}{4}$-in. diameter and 1.5-in. length) for good signal-to-noise ratio in these low-field nuclear resonance experiments. Samples were stored at liquid nitrogen temperature to prevent slow growth of the Hg droplets.

Chemical analysis shows that these samples contain 70 to 80% by weight of mercury. Examination of the suitably diluted colloid with the electron microscope allows one to observe the spherical mercury droplets and to investigate the distribution of their sizes (see Fig. 1). If $l_0\equiv4.3\times10^{-6}$ cm, representative size distributions obtained by us indicate that about 55% of the Hg drops have diameter $d<\frac{1}{2}l_0$, about 75% of them (representing roughly 5% of the total mass of Hg) have $d<l_0$, and about 95% (representing about 40% of the mass) have $d<2l_0$. Measurements on macroscopic Hg samples yield for the penetration depth at temperature $T=0°$K the value $\lambda_0=l_0$,[19] though recent experiments[10] on colloidal Hg drops lead to results more consistent with a penetration of the magnetic field in these particles nearly twice as large.[20]

(b) Cryogenics and Electronics

An all-glass double Dewar contains the sample assembly and fits between the poles of the magnet. Temperatures between 4.20°K and 1.20°K are accessible

[15] C. S. Barrett, Acta Cryst. (to be published).

[16] N. Bloembergen and T. J. Rowland, Acta Metallurgica **1**, 731 (1953).

[17] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954); N. Bloembergen and T. J. Rowland, Phys. Rev. **97**, 1679 (1955).

[18] I am particularly indebted to Dr. D. Shoenberg and Dr. C. S. Whitehead for information concerning the preparation of this colloid. I also wish to thank Mr. R. T. M. Haines of Crookes Laboratories Ltd. for correspondence on this subject.

[19] E. Laurman and D. Shoenberg, Proc. Roy. Soc. (London) **A198**, 560 (1949).

[20] I.e., if these colloid experiments were to be interpreted in terms of an exponential decay of the field as predicted by the London equations, then the distance λ_0 within which the field falls to $1/e$ of its value should be about 8×10^{-6} cm.

by pumping on the liquid helium bath. Mercury and oil manometers allow temperature measurement in terms terms of the vapor pressure of liquid helium. The Varian electromagnet is powered by a well-regulated current supply and has pole faces of 12-in. diameter and a useful gap $4\frac{3}{4}$ in. wide. Suitable shims serve to make the field homogeneity over the rather large samples used in these experiments more than adequate. The wide gap is convenient since it provides ample working space for large samples and glass Dewars while still permitting one to reach fields of 7000 gauss, much higher than needed in the experiments. The radio-frequency spectrometer is of the Pound-Watkins type[21] and is connected by a specially constructed coaxial cable to the rf coil inside the Dewar. The frequency of the spectrometer is varied by mechanically rotating a condenser while the static magnetic field is kept constant. This feature is of some importance in the present experiments since, if the field were varied in order to sweep through the resonance line, the superconducting properties of the sample would simultaneously be affected. A narrow-band detecting system is followed by a recording meter which, with the small sinusoidal magnetic field modulation used, plots the *derivative* of the nuclear resonance absorption line. 10-kc harmonics derived from a frequency standard permit accurate frequency measurements to be made.

(c) Nature of Experimental Results

Experimental resonance lines are illustrated in R.[6] In a given magnetic field the larger particles in the sample find themselves in a field larger than critical. They remain, therefore, in the normal state and give rise to a "normal resonance line" with the normal Knight shift K_n of metallic Hg. On the other hand, the smaller particles with the higher critical fields do become superconducting and give rise to a "superconducting resonance line" which is found experimentally to occur at a lower frequency than the normal line. In general, then, both a normal and a superconducting line appear on the recording meter at somewhat different frequencies. If the magnetic field, or the temperature, is lowered the proportion of superconducting particles increases and the normal line is correspondingly observed to decrease in intensity at the expense of the superconducting one. At sufficiently low fields and temperatures only the superconducting line is observed. The superconducting line is found to be asymmetric, having a slowly decreasing tail on its low-frequency side and falling off more sharply on its high-frequency side.[6]

There are also indications that the relaxation time T_1 is longer in the superconducting than in the normal state.[6] In the following, however, our concern will be exclusively with the Knight shift K_s in the superconducting state. It is clear that, in order to discuss this quantity and the experiments bearing on its temperature and field dependence, it is necessary to understand the superconducting resonance line shape and to analyze the various corrections necessary to extract information about K_s. We now turn, therefore, to a somewhat lengthy discussion of the factors involved in the analysis of the experimental data.

III. CONSIDERATIONS AFFECTING ANALYSIS OF THE DATA

(a) Line Shape due to a Superconducting Sphere

Consider a metal sphere of radius a placed in a uniform magnetic field $\mathbf{H}_0$ in the z direction. We neglect, for the time being, the microscopic sources of broadening (e.g., interactions between nuclei) of the kind which endow the nuclear resonance line with a finite width in the normal metal. Then, if the sphere is in the normal state, the nuclei in it give rise to a sharp resonance line at the frequency $\nu_n=\nu_i(1+K_n)$; here $\nu_i=g\mu_nH_0$ (g= nuclear g factor and μ_n= nuclear magneton) is the frequency at which the resonance would occur in an insulator and, by Eq. (1), K_n is the Knight shift in the normal metal. If the sphere is in the superconducting state and its size is such that $a\ll\lambda$, then the external field $\mathbf{H}_0$ penetrates essentially uniformly throughout the sphere and the nuclei in it again give rise to a sharp resonance line at the frequency $\nu_s=\nu_i(1+K_s)$; here K_s is, by definition, the Knight shift in the superconducting state and may differ from K_n. If, however, a is more nearly comparable to λ, the diamagnetic effects cause an incomplete penetration of the field so that the field (or magnetic induction) $\mathbf{B}$ varies from region to region in the sphere. Nuclei in different parts of the sphere then have different resonance frequencies and thus give rise to a resultant observed resonance line which has a finite width and a shape which we should like to calculate.

If the phenomenological equations describing the electromagnetic behavior of a superconductor are known, one can calculate the field $\mathbf{B}(\mathbf{r})$ acting on the nuclei in an element of volume surrounding the point $\mathbf{r}$. At the frequencies used in these experiments ($\approx10^6$ cps) the rf field can also be considered quasi-static in computing its penetration into the superconductor.[22] Irrespective of the (not very well known) form of the equations describing the penetration of the magnetic field, one can profitably make a few general qualitative statements about the resonance line to be expected from the nuclei in the superconducting sphere. Since the sphere acts like a diamagnetic body and tends to expel magnetic flux from its inside, there is a shape effect which should cause B to attain its maximum value B_2,

[21] R. V. Pound and W. D. Knight, Rev. Sci. Instr. **21**, 219 (1950); G. D. Watkins, thesis, Harvard University, 1952 (unpublished).

[22] Relaxation effects in superconductors do certainly not become important at frequencies less than 10^7 cps [see reference 23; also A. B. Pippard, Proc. Roy. Soc. (London) **A203**, 215 (1950)]. Note, incidentally, that all the particles in the sample are much smaller than the skin depth in the normal metal.

somewhat greater than the external field H_0, at the equator of the sphere. (For perfect diamagnetism, or when $a\gg\lambda$, $B_2=\frac{3}{2}H_0$.) Similarly, since B tends to fall off in the interior of a superconductor, B should attain its minimum value B_1 ($<H_0$) at the center of the sphere. (For $a\gg\lambda$, $B_1\rightarrow 0$.) Hence the resonance line should extend from a highest frequency $\nu_2>\nu_s$ corresponding to nuclei at the equator to a lowest frequency $\nu_1<\nu_s$ corresponding to nuclei at the center of the sphere. Since, as a result of the limited field penetration, most nuclei in the sphere find themselves in fields less than H_0, the maximum of the resonance absorption line can also be expected to occur at a frequency $\nu_0<\nu_s$. In the limit $a\rightarrow 0$, one gets B_2, $B_1\rightarrow 0$ and hence ν_1, ν_1, ν_0 all approach ν_s to give a resonance line of negligible width. On the other hand, if a is comparable to λ, ν_1 and ν_0 should decrease and ν_2 should increase as a increases; i.e., one predicts that, as the sphere becomes larger, the resonance line becomes wider and the position of its maximum shifts to lower frequency as compared to ν_s. Furthermore, since B anywhere inside the sphere can be expected to be proportional to H_0, the width of the resonance line should be proportional to the external field.

It is instructive to calculate explicitly the resonance line shape to be expected if the London equations[23] are assumed to be valid. Then $\mathbf{B}$ inside the superconductor satisfies the equation $\nabla^2\mathbf{B}-\lambda^{-2}\mathbf{B}=0$. The solution of this equation for a sphere in a uniform field is well known.[24] In the case $a\ll\lambda$, a condition which is satisfied by most of the drops in our samples and which simplifies the analysis considerably, this solution can be written in the form:

$$B_z=C_0[1+\tfrac{1}{10}(1+\sin^2\theta)(r/\lambda)^2], \tag{2}$$

$$B_\rho=-\tfrac{1}{10}C_0\sin\theta\cos\theta(r/\lambda)^2, \tag{3}$$

where

$$C_0\equiv H_0[1-\tfrac{1}{6}a'^2],\quad a'\equiv a/\lambda. \tag{4}$$

Here B_ρ is the component of $\mathbf{B}$ perpendicular to the z axis and pointing radially outward from it, while θ is the angle between $\mathbf{r}$ and the z axis.

Nuclei in the volume element dv surrounding the point $\mathbf{r}$ have a resonance frequency $\nu=g\mu_m(1+K_s)\times|\mathbf{B}(\mathbf{r})|$ at which they contribute to the nuclear power absorption an amount[25] $\mathcal{P}(\mathbf{r})\sim dv\nu^2B_\perp'^2$ where $B_\perp'(\mathbf{r})$ is the component of the rf field $\mathbf{B}'(\mathbf{r})$ perpendicular to the static field $\mathbf{B}(\mathbf{r})$. In the case $a\ll\lambda$, Eq. (2) shows, however, that ν differs from ν_s and $\mathbf{B}'$ from the applied rf field $\mathbf{H}'$ only by terms of order $(a/\lambda)^2$. Thus in first approximation $\mathcal{P}(\mathbf{r})$ can be taken as independent of $\mathbf{r}$ and as simply proportional to dv, i.e., to the number of nuclei lying in this element of volume. Also, since B_ρ is of order $\frac{1}{10}a'^2B_z$, $|\mathbf{B}|\approx B_z$ and $\mathbf{B}$ is always very nearly orthogonal to the rf field $\mathbf{B}'$. Hence the problem of computing the line shape is reduced simply to ascertaining the volume of the sphere contained between two neighboring (ellipsoidal) contours $B_z=$constant. In symbols, the intensity $I(\nu)d\nu$ of the resonance line lying in the range $(\nu,\nu+d\nu)$ is then, neglecting terms of order $(a/\lambda)^2$, given by

$$I(\nu)d\nu\sim\int r^2\sin\theta drd\theta, \tag{5}$$

where the integration is extended over the range of r and θ for which

$$\nu=g\mu_n(1+K_s)B_z \tag{6}$$

as given by Eq. (2), lies in the range $(\nu,\nu+d\nu)$. The integration over the infinitesimal range dr consistent with the restriction (6) is immediate, and Eq. (5) then becomes

$$I(\nu)\sim\int_{\theta_{\min}}^{\pi/2}d\theta\left\{r^2\sin\theta\left|\frac{\partial\nu}{\partial r}\right|_\theta^{-1}\right\}_{r=r(\theta,\nu)}, \tag{7}$$

where, in choosing the upper limit of θ, we have made use of the fact that $B_z(\theta)=B_z(\pi-\theta)$. Equation (2) shows that $I(\nu)=0$ unless ν lies in the range $\nu_s(1-a'^2/6)<\nu<\nu_s(1+a'^2/30)$. The lower limit $\theta_{\min}$ is zero for ν in the range $\nu_s(1-a'^2/6)<\nu<\nu_s(1-a'^2/15)$ when the contours $B_z=$constant are closed surfaces lying entirely within the sphere. For values of ν in the range $\nu_s(1-a'^2/15)<\nu<\nu_s(1+a'^2/30)$, only nuclei in the equatorial region of the sphere contribute and $\theta_{\min}$ is determined by Eqs. (6) and (2) with r put equal to a. The integrals (7) are readily evaluated and the result is most conveniently expressed in terms of the function $f(x)$ defined by

$$\begin{aligned}f(x)&=(1-|x|)^{\frac{1}{2}}\quad\text{for}\quad 0<|x|<1\\&=0\quad\text{otherwise.}\end{aligned} \tag{8}$$

Equation (7) then yields, apart from irrelevant normalizing constants, the line shape due to a single sphere:

$$\begin{aligned}&I(\nu)\sim\lambda^3a'f[(30\eta+2a'^2)/3a'^2],\\&\eta\equiv(\nu-\nu_s)/\nu_s.\end{aligned} \tag{9}$$

This line shape is shown in Fig. 2 and exhibits all the features which our general qualitative discussion led us to expect. Note that the width of the line is proportional to a^2 while its peak intensity is proportional to a. The integrated intensity under the curve is thus properly proportional to a^3, i.e., to the volume of the sphere. The rather slow dependence of peak intensity on radius is helpful since it implies that in the resonance experiments (unlike the situation encountered in measuring the total diamagnetic moments of colloidal samples[9]) the *number* of small drops present is much more important than their rather small contribution to the mass might indicate.

[23] F. London, *Superfluids* (John Wiley and Sons, Inc., New York, 1950), Vol. 1.

[24] Reference 23, p. 34.

[25] See, for example, Eq. (6) in Bloembergen, Purcell, and Pound, Phys. Rev. 73, 679 (1948).

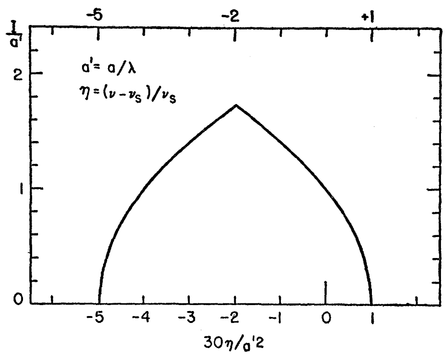


FIG. 2. The nuclear resonance line shape $I(\eta)$ calculated for a superconducting spherical particle of radius a by means of the London equations. Here λ is the superconducting penetration depth and $a' \equiv a/\lambda$. ν_s is the frequency at which the resonance line would occur if there were complete penetration of the magnetic field ($a/\lambda \to 0$). $I(\eta)$ is shown plotted as a function of the dimensionless frequency parameter $\eta \equiv (\nu-\nu_s)/\nu_s$.

(b) Line Shape due to a Distribution of Spheres

If $n(a)$ denotes the relative number of spheres in the sample with radii in the range $(a, a+da)$, then the intensity $w(\nu)$ of the nuclear resonance due to all these particles is given by

$$w(\nu) = \int_0^\infty I(\nu,a)n(a)da, \tag{10}$$

where $I(\nu,a)$ is the intensity due to a sphere of radius a. Using an experimentally determined size distribution and expression (9) for $I(\nu,a)$ with an assumed value of λ, one can compute the expected line shape $w(\nu)$. The result is a curve of the type shown in Fig. 3 of R.[6] Since the position of the maximum of $I(\nu,a)$ shifts to lower frequencies as a increases, $w(\nu)$ has a long tail on its low-frequency side and a more sharply defined slope on its high-frequency side. This is the kind of asymmetry which is experimentally observed for the superconducting line.

The experimental data present one with the problem of determining from the resultant nuclear resonance line $w(\nu)$ the frequency ν_s which determines the Knight shift K_s in the superconductor. Curves constructed like that of Fig. 3 in R[6] by using Eq. (9) and representative size distributions suggest strongly that, while the maximum of $w(\nu)$ lies at a frequency less than ν_s because of the limited field penetration, the point of minimum slope (i.e., maximum negative slope) of the curve $w(\nu)$ occurs very nearly at the frequency ν_s. We should like to give a simple argument showing how this comes about.

It is convenient to work with the dimensionless frequency parameter $\eta \equiv (\nu-\nu_s)/\nu_s$; the frequency ν_s then corresponds to $\eta = 0$. Since our argument concerns the slope or derivative of w, we get by Eq. (10), denoting differentiation with respect to ν (or η) by a prime,

$$w'(\eta) = \int_0^\infty I'(\eta,a)n(a)da. \tag{11}$$

The essence of the argument becomes clearer by phrasing it in rather general terms transcending the special assumptions involved in the use of the London equations and in the approximations leading to the shape function of Eq. (9). Consider, therefore, the shape function $I(\eta,a)$ due to a single sphere to have the following properties. $I(\eta,a)$ vanishes outside the range $-\eta_1 < \eta < \eta_2$ and has its maximum at $\eta = -\eta_0$. We can represent it schematically by a triangle [see Fig. 3(A)] with slope $s_1(a) > 0$ for $-\eta_1 < \eta < -\eta_0$ and slope $-s_2(a) < 0$ for $-\eta_0 < \eta < \eta_2$.[26] The *essential* characteristic of I is that, because of the finite field penetration, each of the three parameters η_k ($k = 0,1,2$) is a positive monotonically increasing function of a; also $\eta_k \to 0$ as $a \to 0$ [see Fig. 3(B)]. Conversely, therefore, given a particular η_k, a is determined; i.e., there is a functional relation $a = F_k(\eta_k)$, where F_k is a monotonically increasing function of its argument with $F_k(0) = 0$. Then Eq (11) becomes (the integration over a is indicated by the dashed lines in Fig. 3B):

$$\text{for } \eta > 0: \quad w'(\eta) = -\int_{F_2(\eta)}^\infty s_2(a)n(a)da, \tag{12a}$$

$$\text{for } \eta < 0: \quad w'(\eta) = \int_{F_1(-\eta)}^{F_0(-\eta)} s_1(a)n(a)da - \int_{F_0(-\eta)}^\infty s_2(a)n(a)da. \tag{12b}$$

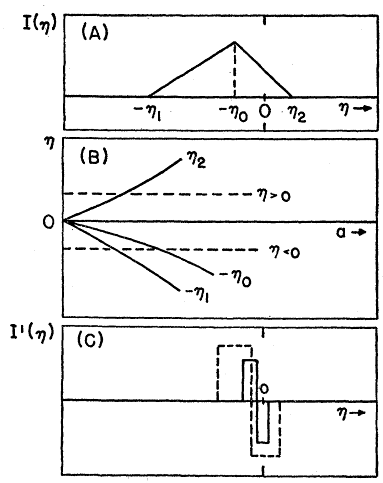


FIG. 3. (A) Schematic representation by a triangle of a general resonance line shape $I(\eta)$ due to a single superconducting sphere. η is the dimensionless frequency $\eta \equiv (\nu-\nu_s)/\nu_s$. (B) Behavior of the frequencies η_0, η_1, η_2, shown in Fig. 3(A), as a function of the sphere radius a. (C) Derivative line shapes $I'(\eta)$ obtained from $I(\eta)$ of Fig. 3(A) for a small sphere (solid curve) and a larger sphere (dashed curve). Note that the two curves, when added, tend to give a minimum at $\eta = 0$.

[26] In the particular case of the shape $I(\nu)$ obtained in Eq. (9) from the London equations this means approximating the shape of Fig. 2 by an isosceles triangle with slopes $s_1(a) = s_2(a) \sim a^{-1}$, i.e., putting $f(x) = 1 - |x|$ in Eq. (8).

Both of these expressions yield, as they should, the same value $w'(0)$ as $\eta \to 0$. Since the integrands are all positive, (12a) shows that $w'(0_+) > w'(0)$ and (12b) shows similarly that $w'(0_-) > w'(0)$. Hence $\eta = 0$ corresponds to the minimum on the derivative curve $w'(\eta)$.

This mathematical argument is more transparent when looked upon geometrically. Figure 3(C) indicates how derivative curves due to individual spheres are superposed to yield $w'(\eta)$. The frequency $\eta = 0$ is distinguished by the fact that there all drops, no matter how small, contribute to the intensity w. One sees that, for $\eta > 0$, the smaller drops no longer contribute to $w'(\eta)$ so that $w'(\eta)$ increases. On the other hand, for $\eta < 0$, the smaller drops begin to contribute to $w'(\eta)$ with opposite sign so that $w'(\eta)$ again increases. Hence $\eta = 0$ determines the minimum of $w'(\eta)$.[27]

Hence curves like that in Fig. 3 of R[6] and also these more general arguments both suggest a "minimum slope criterion"; this states that the frequency at which the derivative $w'(\nu)$ of the superconducting line has its minimum corresponds to the frequency ν_s of interest. Since experimentally we measure directly the derivative of the resonance line, this criterion is also very convenient to apply. The criterion ought to be particularly well applicable to particles with $a < \frac{1}{2}\lambda$ for which our discussion on the basis of the London equations leads one to expect, by Eq. (9), fractional line widths due to incomplete field penetration of less than 5%. The experimental size distributions indicate that in our samples about 75% or more of the number of drops (see comments at the end of Sec. IIIc) have radii $a < \frac{1}{2}\lambda$.[28] At higher fields or temperatures, where only the smaller drops are superconducting and where the penetration depth λ is larger, this statement about the superconducting particles ought to be true *a fortiori*. The larger drops, on the other hand, will give rise to rather widely smeared out resonance lines the contribution of which is unlikely to affect appreciably the position of the fairly sharply defined point of minimum slope of the line due to the many smaller drops. Finally, the considerable degree of generality of the properties of $I(\nu,a)$ assumed in our discussion of the minimum slope criterion suggests that this criterion may well be valid even if the London equations do not describe adequately the penetration of the magnetic field and even if the drops have radii of the order of λ.

[27] In the general case the sides of the line $I(\eta,a)$ are not straight as in the triangle approximation of Fig. 3(A), but are curved [so that s_1 and s_2 become functions of η in Eqs. (12)]. It is unlikely that these curvatures will cause the minimum slope of w to occur at a frequency differing appreciably from $\eta = 0$. Exceptions might occur if the magnitude of the slope of $I(\eta,a)$ for the particles contributing most to the intensity is very significantly larger for $\eta > 0$ than for $\eta < 0$. For example, if instead of using a triangle, one approximates the line by a trapezoid with slope $s_1(a)$ for $-\eta_1 < \eta < -\eta_{10}$, zero slope for $-\eta_{10} < \eta < -\eta_{20}$, and slope $-s_2(a)$ for $-\eta_{20} < \eta < \eta_2$, then $\eta = 0$ still corresponds to the minimum slope of w provided that $\eta_{20} > 0$.

[28] On the basis of the evidence mentioned in footnote 20, the number of drops with $a < \frac{1}{2}\lambda$ may be closer to 90%.

(c) Corrections for Microscopic Broadening

Up to now we have neglected the fact that microscopic interactions similar to those present in the normal metal give the resonance line in the superconductor a shape $g(\nu - \nu_s)$ with a finite width 2σ (measured between points of maximum and minimum slope) even in a case where there would be complete penetration of the field H_0 in the superconductor. If this microscopic broadening is taken into account, the resonance line shape due to all the drops becomes

$$W(\nu) = \int_0^\infty n(a)da \int_{-\infty}^\infty g(\nu - \nu_0) I(\nu_0,a) d\nu_0 = \int_{-\infty}^\infty g(\nu - \nu_0) w(\nu_0) d\nu_0. \quad (13)$$

$W(\nu)$ corresponds to the experimentally observed line, while the minimum slope criterion applies only to $w(\nu)$. If, as is the case at low temperatures and fields, the width of $w(\nu)$ is large compared to 2σ, then W does not differ appreciably from w and the point of minimum slope of W will correspond very nearly to ν_s. In the other limit, when 2σ is much larger than the width of w due to the limited field penetration, it is physically clear that it is the maximum of $W(\nu)$ which will occur close to the frequency ν_s. In the general case, ν_s will lie somewhere between the frequencies where the experimentally observed derivative $W'(\nu)$ vanishes and where it has its minimum. If, however, g is known one can, in principle, deduce $w'(\nu)$ from the measured derivative curve $W'(\nu)$ and the minimum slope criterion can then be applied to $w'(\nu)$ to yield the frequency ν_s.

The mathematical procedure is as follows. By (13) one obtains for the derivative curve of interest

$$W'(\nu) = \int_{-\infty}^\infty [dg(\nu - \nu_0)/d\nu] w(\nu_0) d\nu_0 = \int_{-\infty}^\infty g(\nu - \nu_0) w'(\nu_0) d\nu_0, \quad (14)$$

where the last integral follows from the first as a result of integration by parts. One now can take Fourier transforms of all the functions. We denote the Fourier transform of $g(x)$ by $\bar{g}(k)$ and use similar notation for the transforms of the other functions; thus

$$g(x) = \int_{-\infty}^\infty \bar{g}(k) e^{ikx} dk, \qquad \bar{g}(k) = (2\pi)^{-1} \int_{-\infty}^\infty g(x) e^{-ikx} dx. \quad (15)$$

The *faltung* theorem for Fourier transforms[29] applied to

[29] See, for example, P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (John Wiley and Sons, Inc., New York, 1953), p. 464.

(14) then yields immediately the algebraic equation

$$\bar{W}'(k)=2\pi\bar{g}(k)\bar{w}'(k) \tag{16}$$

and $w'(\nu)$ can then be obtained from $\bar{w}'(k)$ by taking the Fourier transform of the latter. If g is approximated by a Gaussian shape, then

$$g(x)=(2\pi\sigma^2)^{-\frac{1}{2}}\exp(-x^2/2\sigma^2),$$
$$\bar{g}(k)=(2\pi)^{-1}\exp(-\tfrac{1}{2}\sigma^2k^2), \tag{17}$$

and one gets simply

$$w'(\nu)=\int_{-\infty}^{\infty}\bar{W}'(k)\exp(\tfrac{1}{2}\sigma^2k^2+ik\nu)dk. \tag{18}$$

In practice we are only interested in the case when microscopic broadening constitutes a relatively minor correction, i.e., when 2σ is small compared to the observed width of $W(\nu)$. Approximations are then possible which allow one to exploit the Fourier transform procedure outlined above in a simple way (see appendix). For the width 2σ of g we have used the width of the resonance line in the normal metal.[30] In estimating the frequency ν_s the microscopic broadening corrections are in our experiments essentially negligible at 1.2°K and become of some importance only at higher temperatures where the superconducting line is narrower.

(d) Bulk Diamagnetic Moment of Sample

The field H_0 in which a given drop in the sample finds itself is not quite equal to the externally applied field H_e since the sample as a whole is slightly diamagnetic if some of the drops are superconducting. If the field and temperature are such that an appreciable fraction of the drops remain normal so that both a normal and a superconducting line are observed under the same conditions, the superconducting Knight shift K_s can be directly compared with the normal shift K_n since it is reasonable to assume that H_0 is the same at the position of a normal or superconducting drop. In other cases it may be of interest to estimate the correction needed to relate H_0 to H_e. If the sample is looked upon as a diamagnetic medium with bulk diamagnetic moment per unit volume M ($M<0$), the correction is readily made. One has

$$H_0=H_e-2\pi M+\tfrac{4}{3}\pi M, \tag{19}$$

where the first term in M represents the demagnetizing correction for the sample regarded as a long cylinder perpendicular to H_e and where the second term in M represents the Lorentz local field correction.[31] Hence

$$(H_0-H_e)/H_e=-\tfrac{2}{3}\pi(M/H_e). \tag{20}$$

The question of determining M as a function of H_e (i.e., the magnetization curve of the colloid) is interesting in its own right since it represents precisely the type of experiment carried out by Shoenberg *et al.*[9,10] to study the superconducting penetration depth and since it also provides an independent indication of the particle size distribution in the colloid. It is therefore useful to point out that the nuclear resonance equipment is capable of measuring simultaneously, and without any modifications, the magnetization curve of the colloid sample. It is only necessary to measure the change in the frequency of the rf oscillator as a function of the external field H_e.

To make these remarks more precise, we recall that the rf coil surrounding the sample produces a rf field H_x along its axis in the x direction which is perpendicular to the external field H_e in the z direction. The inductance L of the coil, together with an external capacitor C, determine the oscillator frequency

$$\nu=[2\pi(LC)^{\frac{1}{2}}]^{-1}. \tag{21}$$

At high fields all of the sample is in the normal state. The inductance L then has a certain value L_0 and the corresponding oscillator frequency is ν_∞. But in lower magnetic fields, where the sample is partially superconducting, the rf field H_x gives rise to a component M_x of the colloid diamagnetic moment. As a result the inductance of the coil becomes $L=L_0(1+4\pi f\chi_x)$, where $\chi_x\equiv M_x/H_x$ is an effective diamagnetic susceptibility and where f is the fraction of coil volume occupied by the colloid. The corresponding oscillator frequency is $\nu(H_e)$ and, using (21) and $\chi_x\ll 1$, is related to ν_∞ by

$$[\nu(H_e)-\nu_\infty]/\nu_\infty=-2\pi f\chi_x>0. \tag{22}$$

Now the magnetic moment $\mathbf{M}(\mathbf{H})$ in any field $\mathbf{H}$ points along this field so that $\mathbf{M}(\mathbf{H})=M(H)\mathbf{H}/H$, where $M(H)$ is the magnetization curve relating the magnitude of M to that of H. The rf field can be regarded as quasi-static[22] and $H_x\ll H_e$. Hence, in the presence of the rf field, $\mathbf{H}=\mathbf{H}_e+\mathbf{H}_x$ and $H=(H_e^2+H_x^2)^{\frac{1}{2}}\approx H_e$; thus the vector $\mathbf{M}$ is simply rotated without change of magnitude through the small angle H_x/H_e with respect to its original direction along $\mathbf{H}_e$. As a result there arises an x component of M given by $M_x=M(H_e)H_x/H_e$, so that

$$\chi_x\equiv M_x/H_x=M(H_e)/H_e. \tag{23}$$

Combination of this relation with Eq. (22) shows immediately how knowledge of the external field H_e together with the oscillator frequency shift $[\nu(H_e)-\nu_\infty]$ permits one to find $M(H_e)$ and thence also to compute the correction (20). Indeed, Eqs. (20) and (22) yield

[30] It should be pointed out, however, that, since the width of the normal line appears to be due predominantly to electron-coupled nuclear exchange interaction, it is hard to estimate the validity of the assumption that the microscopic broadening in the normal and superconducting states is the same. In view of this uncertainty and the fact that the microscopic broadening is itself only a correction, the assumption of a Gaussian shape for g ought to be quiet adequate.

[31] The corrections made in Eq. (19) are similar to those encountered in high-resolution nuclear magnetic resonance work. See reference 1, p. 78.

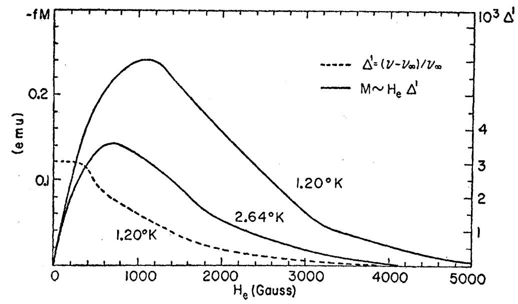


FIG. 4. Dashed curve: variation of oscillator frequency ν as a function of the external field H_e at 1.20°K. As H_e becomes very large, the superconducting properties of the colloid are destroyed and ν reaches a limiting value ν_∞. The actual ordinate for this curve is the dimensionless oscillator frequency $\Delta' \equiv (\nu-\nu_\infty)/\nu_\infty$. Solid curves: magnetization curves showing the magnetic moment per unit volume of a colloid sample *vs* external field H_e at two different temperatures. These curves were obtained by measuring the change of oscillator frequency as a function of H_e.

the simple relation

$$(H_0-H_e)/H_e=\tfrac{1}{3}f^{-1}[\nu(H_e)-\nu_\infty]/\nu_\infty. \tag{24}$$

Figure 4 shows how the oscillator frequency changes as a function of field in one of our samples at 1.20°K. (No such frequency shift of the oscillator is, of course, observed at 4.2°K which is above the transition temperature.) Also shown are magnetization curves obtained by this method at two different temperatures. These curves are similar to those studied by Shoenberg.[9] If the proportion of small particles in the sample is larger, the maximum of the magnetization curve should shift to higher fields. Indeed we observed this for a different sample which had a slightly better size distribution and which showed, at a given field and temperature, a somewhat smaller relative intensity of normal to superconducting resonance lines. The maximum oscillator frequency change in going from large fields to zero field is of the order of 0.3%. Frequency changes of one part in 10^5 are readily measurable. The maximum field correction (20) in our experiments amounts to about 0.06% which is quite small compared to the Knight shift.[32]

IV. EXPERIMENTAL RESULTS

After this lengthy discussion dealing with the analysis of the data the experimental results can now be summarized rather briefly. Some representative observed resonance lines are illustrated in R.[6] Experiments were performed at our lowest attainable temperature of 1.20°K over a range of magnetic fields such as 750, 970, 1530, and 2300 gauss. The observed superconducting line has the expected asymmetry and a width proportional to the field; i.e., its fractional width (measured between points of maximum and minimum slope) is field independent and amounts to about 1.6%. This behavior of the width is as expected since the discussion in Secs. IIIa and IIIb involves only the fractional frequency η. The observed width is also of the anticipated order of magnitude; e.g., the calculated Fig. 3 of R[6] leads to a width of 2%. Applying the minimum slope criterion and some of the other minor corrections, the Knight shift K_s in the superconducting state can be deduced from these data. One finds that, at 1.20°K, the results in this range of fields (750 to 2300 gauss) are all consistent with a value

$$K_s=(1.6\pm0.1)\%; \tag{25}$$

i.e., as compared with the Knight shift K_n in the normal state, $K_s/K_n=0.65$.

It would thus appear that, at least in this range of fields, K_s is independent of magnetic field just as is the case of the Knight shift in a normal metal. This is, of course, the behavior which one should expect, by Eq. (1), if the net spin paramegnetic moment $\mathfrak{M}$ of the conduction electrons is proportional to the applied field which gives rise to it. It should be pointed out, however, that near the upper end of this range of fields the superconducting line has become much less intense than the normal one and, since the two lines overlap slightly, reliable measurements on the superconducting line become increasingly difficult. It does not, therefore, seem possible to extend our measurements profitably to higher fields with our present samples. This is unfortunate in view of the recent result of Knight *et al.*[33] who, using a Hg colloid which presumably contains a larger proportion of very small particles than our samples do, find in experiments in fields of the order of 5000 gauss a Knight shift $K_s \lesssim 0.5\%$. Their method of analysis of the data appears to be essentially the same as ours so that, if one excludes the possibility of major systematic errors in either our own experiments or theirs, this decrease of K_s in high fields might be a real effect. It should be mentioned, in this connection, that for $H=5000$ gauss the interaction energy μH of the electron magnetic moment μ with the magnetic field begins to become more nearly comparable with the characteristic energy kT_c of the superconducting interaction ($\mu H/kT_c\approx 8\%$) and it is perhaps conceivable that peculiar effects might then set in. At the present time, however, the experimental situation on this point is very much in need of clarification.

We turn next to the experimental evidence on the temperature dependence of the Knight shift in the superconducting state. (It should be recalled that in a *normal* metal the Knight shift is, like the Pauli spin paramagnetism,[4] essentially temperature-independent.[3] Experimental results as a function of temperature in a fixed field of 967 gauss are shown in Fig. 5. Each experimental curve is, as is indicated in Fig. 6, a

[32] It is possible that the inhomogeneous nature of the sample may give rise to slightly different fields H_0 acting on different drops. This could lead to an additional resonance line broadening which, however, should not exceed in relative magnitude the field correction (20) and should thus be negligible compared to the microscopic broadening effects.

[33] Knight, Androis, and Hammond, Phys. Rev. **104**, 852 (1956).

superposition of a normal line due to the particles large enough still to be normal at the particular temperature and of a superconducting line due to the rest of the particles. Though it is qualitatively apparent that the superconducting line shifts to lower frequency as the temperature is decreased, it is rather more difficult to obtain quantitative information about the behavior of the Knight shift from these data. From each experimental curve it is first necessary to subtract off the normal line whose shape and position in frequency are well known but whose amplitude (proportional to the number of normal drops in the sample) is not known. Hence this subtraction procedure, illustrated in Fig. 6, can be carried out only within certain limits of possible ambiguity and becomes the less reliable the larger the normal line, i.e., the higher the temperature. After this subtraction, one is left with the superconducting line from which the Knight shift K_s can be deduced, as usual, by means of the minimum slope criterion. Increasing difficulty is, however, again encountered at the higher temperatures where the superconducting line becomes narrower so that the necessary microscopic broadening corrections of Sec. IIIc become increasingly important and uncertain. Figure 7 shows the behavior of K_s as a function of temperature as obtained from these data. The foregoing comments should make it apparent that no excessive quantitative significance ought to be ascribed to the points of this plot, especially near the high temperature end. One can expect, however, that at least the general trend of the temperature dependence of the Knight should be correctly indicated by the curve of Fig. 7.

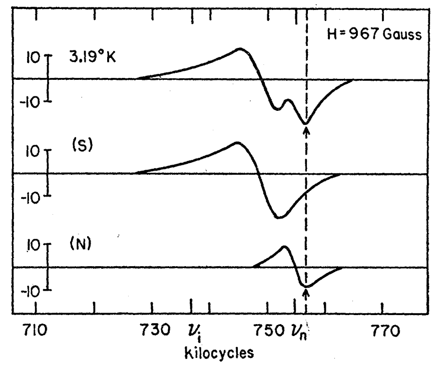


FIG. 6. Illustration showing how any plot in Fig. 5 (one of which is here reproduced at the top of the figure) can be decomposed into: (1) a normal line due to large drops which occurs at the frequency ν_n and has the shape of the normal line at 4.2°K (bottom), and (2) a remaining superconducting line (middle).

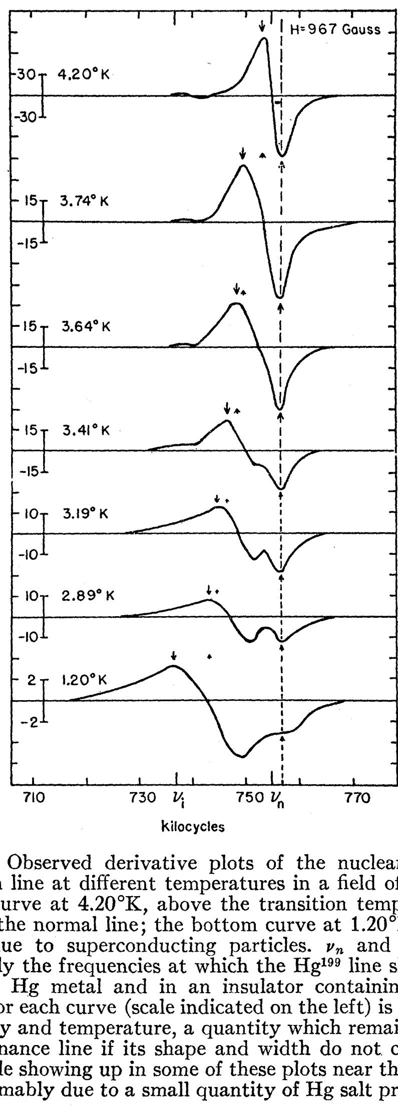


FIG. 5. Observed derivative plots of the nuclear resonance absorption line at different temperatures in a field of 967 gauss. The top curve at 4.20°K, above the transition temperature T_c, is simply the normal line; the bottom curve at 1.20°K is almost entirely due to superconducting particles. ν_n and ν_i indicate respectively the frequencies at which the Hg^{199} line should occur in normal Hg metal and in an insulator containing Hg. The ordinate for each curve (scale indicated on the left) is the product of intensity and temperature, a quantity which remains constant for a resonance line if its shape and width do not change. The little wiggle showing up in some of these plots near the frequency ν_i is presumably due to a small quantity of Hg salt present in the sample.

V. COMMENTS ON INTERPRETATION

In view of the lack of any satisfactory theoretical framework describing the superconducting state, any attempt at interpretation of the experimental results must be somewhat speculative in nature. A few minor comments might, however, not be out of place.

Since the energy involved in the superconducting transition is small, it is unlikely that the value $\psi(0)$ of the wave function of a conduction electron at the position of a nucleus is appreciably affected when the metal becomes superconducting. Hence, by Eq. (1), we are led to attribute most of the change in the Knight shift K to a change in the spin paramagnetism of the conduction electrons. Since reliable microscopic models for the superconducting state are lacking, it is helpful to consider the problem of calculating the electron paramagnetism of a metal (whether normal or superconducting) from a general quasi-thermodynamic point of view. Let N be the total number of conduction electrons, $N_+=\frac{1}{2}N+p$ of which have their spin pointing up and $N_-=\frac{1}{2}N-p$ of which have their spin pointing down. Consider the situation when any effects connected with the electron spin magnetic moment μ can be neglected, i.e. $\mu=0$. Then it is clear that the stable state of the system is one where $N_+=N_-=\frac{1}{2}N$, i.e.,

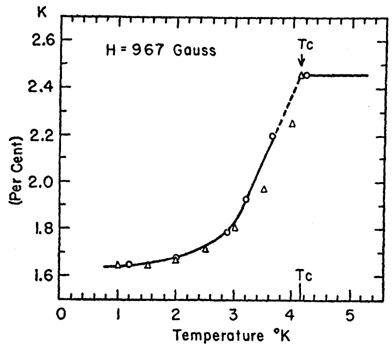


FIG. 7. Knight shift K as a function of temperature derived from measurements in a field of 967 gauss. In the normal state, above $T_c=4.15$°K, the Knight shift can be taken as temperature independent at its value K_n measured at 4.20°K. In the superconducting state the values K_s derived from experiment (open circles) become increasingly less reliable as $T\to T_c$. The triangles denote points computed from the interpolation formula $K_s(T)=K_s(0)(1-cT^4)^{-1}$, where $K_s(0)$ is the value of K_s as $T\to 0$ and c is chosen so that $K_s(T)=K_n$ at $T=T_c$.

$p=0$. Nevertheless one can meaningfully ask for the free energy $F(p,H)$ of the metal in a given field H for any number p of reversed spins, p being considered as an assumed parameter. Given any specific model of the metal (normal or superconducting), $F(p,H)$ can in the case under consideration ($\mu=0$) be calculated by a slight extension of the ordinary, computation yielding the free energy $F(0,H)$. A knowledge of F for small values of p ($p\ll\frac{1}{2}N$) is quite sufficient for our purposes since the paramagnetism of ultimate interest to us is known to be small. Any possible dependence of F on H in this case can arise only through diamagnetic effects connected with the electron orbital motion; its dependence on p, since there is no direct dynamic interaction of the spin for $\mu=0$, can arise only through the kinematic consequences of the exclusion principle. Once $F(p,H)$ is known, one can compute the spin paramagnetism in the case of nonvanishing μ if (as is customarily done in computing this quantity for a normal metal) one effectively neglects electron spin-orbit and spin-spin interactions. The energy due to the interaction of the magnetic moment μ is then purely additive, so that one gets for the total free energy

$$F'=F(p,H)-2p\mu H. \tag{26}$$

Minimizing this expression with respect to p, i.e., setting $\partial F'/\partial p=0$, yields the equilibrium value $\bar{p}=p(H)$ in the presence of the field H. The electron spin paramagnetic moment is then given by $\mathfrak{M}=2\bar{p}\mu$. Also, by Eq. (1), it follows that the Knight shift is characterized by the proportionality

$$K\sim\bar{p}(H)/H;\quad (\partial F'/\partial p)_{\bar{p}}=0. \tag{27}$$

We now proceed to apply these general considerations to the Knight shift K_s at absolute zero and at finite temperatures.

(a) Knight Shift K_s at Absolute Zero

Denoting the ground state energy of the superconducting metal by E_s and that of the normal metal be E_n, one can write

$$E_s=E_n-E_c, \tag{28}$$

where $E_c>0$ is the "condensation energy" representing the effective interaction between electrons and responsible for making the superconducting state the stable one at $T=0$°K. Disregarding entirely the existence of the electron spin magnetic moment μ, one may inquire how E_s would change if a small number p of electron spins were reversed so as to cause a departure from the usual situation $N_+=N_-=\frac{1}{2}N$. For a normal metal, i.e., for E_n, this question is readily answered since the one-electron approximation is then quite satisfactory. One has simply $E_n=E_++E_-$, where E_+ is the energy of the $N_+=\frac{1}{2}N+p$ electrons with spin up and E_- is the energy of the $N_-=\frac{1}{2}N-p$ electrons with spin down. Expanding E_+ in a Taylor series in p about $N_+=\frac{1}{2}N$, one gets $E_+(p)=E_+(0)+\epsilon_F p+\frac{1}{2}\rho_F^{-1}p^2$, where ρ_F is the density of one-electron translational states evaluated at the Fermi energy ϵ_F. Combining this with a similar expression for E_-, one obtains

$$E_n(p)=E_n(0)+\alpha_n p^2+\cdots,\quad \alpha_n\equiv\rho_F^{-1}. \tag{29}$$

Similarly for a superconducting metal the energy E_s must be, in our case when $\mu=0$, an even function of p since it should be immaterial whether the number p of reversed spins points up or down. We shall assume that, for small p, E_s can also be expanded in a power series: i.e.,

$$E_s(p)=E_s(0)+\alpha_s p^2+\cdots. \tag{30}$$

Equation (26) then gives for the total energy E_s' if $\mu\neq 0$:

$$E_s'(p)=E_s(0)+\alpha_s p^2-2p\mu H. \tag{31}$$

Minimizing this with respect to p, one obtains

$$\bar{p}=\mu H/\alpha_s. \tag{32}$$

In the limiting case of a normal metal, $\alpha_s=\alpha_n$ and Eq. (32) reduces simply to $\mathfrak{M}/H=2\bar{p}\mu=2\mu^2\rho_F$, the ordinary Pauli spin paramagnetic susceptibility.[4] Equation (27) then yields for the Knight shift K_s the relation

$$K_s=K_n(\alpha_n/\alpha_s). \tag{33}$$

The experimental evidence shows that the Knight shift is less in the superconducting than in the normal state so that $\alpha_s>\alpha_n$. Equations (28) through (30) then imply that the condensation energy E_c has an expansion of the form

$$E_c(p)=E_c(0)-\alpha_c p^2+\cdots;\quad \alpha_c=\alpha_s-\alpha_n>0. \tag{34}$$

It should be pointed out that, though the interaction energy E_c between conduction electrons in the superconducting state involves most probably only lattice vibrations and the translational degrees of freedom of the electrons, it can nevertheless markedly affect the electron spin paramagnetism indirectly through the Pauli exclusion principle.[34] Equation (34) shows that, in the absence of effects involving the spin magnetic moment μ, E_c is a maximum for the equilibrium case $N_+=N_-$. This situation is one which would ensue if the interactions responsible for superconductivity were particularly effective between electrons in similar translational states, e.g., between electrons within the same shell in k space. For then, if some of the electron spins are reversed so that $N_+\neq N_-$, the Pauli exclusion principle will demand that these electrons be put into different translational states where there are fewer electrons to interact with, and hence the total interaction energy E_c will decrease. It is apparent that if the interaction E_c thus favors keeping as many electrons as possible pointing up as are pointing down, the electronic paramagnetism, and thus the Knight shift, will be reduced as compared to what it would be in the absence of E_c.

Using the value (25) for K_s, Eq. (33) gives $\alpha_s/\alpha_n\approx 1.5$. The value of ρ_F, and hence that of α_c, can be roughly estimated from data on the electronic specific heat of normal Hg[35] ($\rho_F=1.3\times 10^{34}$ erg^{-1} cm^{-3}). It can be verified that, in Eq. (34), $\alpha_c p^2 \ll E_c(0)$ for all fields H of interest, as it should be for this expansion to be valid. [One has $E_c(0)=H_c/8\pi$ per unit volume, where H_c is the critical field of the bulk metal at $T=0$°K.] In addition, to the extent that the data give evidence for a field independent Knight shift, they verify that the correction term in Eq. (34) [or Eq. (30)] is quadratic in p with a constant α independent of H. If the next higher correction term $-\beta p^4$ were to become important in Eq. (34) it would lead, for $\beta>0$, to a saturation of the electronic paramagnetism, and consequent reduction of the Knight shift, in sufficiently high magnetic fields. It is uncertain whether this comment is pertinent to the small value of K_s observed by Knight *et al.*[33] (see Sec. IV).

(b) Generalization to Finite Temperatures

One can attempt to generalize these comments to finite temperatures by means of the two-fluid model of superconductivity.[36] In the usual case where $N_+=N_-$, the free energy of the normal metal is given by

$$F_n=E_n-\tfrac{1}{2}\gamma_0T^2,\quad \gamma_0=\tfrac{2}{3}\pi^2k^2\rho_F. \qquad (35)$$

Introducing an order parameter ω such that $\omega\to 1$ for $T\to 0$ and $\omega\to 0$ for $T\to T_c$ when $F_s=F_n$, one then writes the free energy of the superconductor in the form

$$F_s=E_n-E_c\omega-\tfrac{1}{2}\gamma_0T^2\mathcal{K}(\omega). \qquad (36)$$

Here $\mathcal{K}(1)=0$ and $\mathcal{K}(0)=1$ so that Eq. (36) reduces properly in the limiting cases to Eqs. (35) and (28). The specific form of $\mathcal{K}(\omega)$ is chosen so as to achieve the best agreement with the heat capacity and critical field data and characterizes the particular kind of two-fluid model which is used.

We now generalize to the situation when p is considered a fixed parameter, $p\neq 0$. The free energy of the *normal* metal is readily computed in terms of the density of states ρ and its derivatives evaluated at the Fermi energy ϵ_F. One obtains

$$F_n(p)=E_n(p)-\tfrac{1}{2}(\gamma_0+\gamma_1p^2)T^2, \qquad (37)$$

where

$$\gamma_1=\tfrac{1}{3}\pi^2k^2\rho_F^{-1}(d^2\ln\rho/d\epsilon^2)_F. \qquad (38)$$

Equation (28), where all energies are functions of p, is valid at $T=0$°K. The two-fluid model then suggests as a generalization of Eq. (36) to the case $p\neq 0$ the expression

$$F_s(p)=E_n(p)-E_c(p)\omega-\tfrac{1}{2}(\gamma_0+\gamma_1p^2)T^2\mathcal{K}(\omega). \qquad (39)$$

The condition $\partial F_s/\partial\omega=0$ determines the equilibrium value $\bar{\omega}$ of ω. Here $\bar{\omega}$ is a function of p and can be written in the form $\bar{\omega}=\bar{\omega}_0+\bar{\omega}_1p^2$, where $\bar{\omega}_0$ is the value of $\bar{\omega}$ for the usual case $p=0$. Substituting Eqs. (29) and (34) in Eq. (39), one finds that

$$F_s(p)=F_s(0)+[\alpha_n+\alpha_c\bar{\omega}_0-\tfrac{1}{2}\gamma_1T^2\mathcal{K}(\bar{\omega}_0)]p^2, \qquad (40)$$

where the terms in $\bar{\omega}_1$ have canceled. If one now takes into account the existence of the magnetic moment μ, Eqs. (26) and (27) yield

$$K_s=K_n(1+\rho_F\alpha_c\bar{\omega}_0)^{-1}. \qquad (41)$$

Here we have omitted the term in γ_1 since γ_1T^2/α_n is negligibly small of order $(kT/\epsilon_F)^2$; it is this term which gives rise to the negligible temperature dependence of the Pauli paramagnetism in a normal metal. Equation (41) becomes, of course, identical with Eq. (33) for $\bar{\omega}_0=1$.

If one uses the simple Casimir-Gorter form [$\mathcal{K}(\omega)=(1-\omega)^{\frac{1}{2}}$] of the two-fluid model,[36] one has[37] $\bar{\omega}_0=1-t^4$ where $t=T/T_c$. Equation (41) then suggests that

$$K_s(T)=K_s(0)(1-cT^4)^{-1}, \qquad (42)$$

with the constant c chosen so that $K_s(T_c)=K_n$, should be a suitable interpolation formula representing the temperature dependence of the Knight shift in the

[34] The manner in which such purely orbital effects can influence the electronic spin paramagnetism is quite similar to the way in which correlation and exchange effects between electrons lead to corrections to the electron spin paramagnetism in a normal metal. See D. Pines in *Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 1, p. 416. Incidentally these corrections for the normal metal can be considered included in α_n without affecting the discussion.

[35] E. Maxwell and O. S. Lutes, National Bureau of Standards Report NBS-3146, February, 1954 (unpublished).

[36] P. M. Marcus and E. Maxwell, Phys. Rev. **91**, 1035 (1953).

[37] Simple thermodynamic arguments applied to a small particle [e.g., see A. B. Pippard, Phil. Mag. 43, 273 (1952)] lead to $\bar{\omega}=1-qt^4$, where q is a function of H and of the penetration depth λ_0 at $T=0$°K, but Eq. (42) is unaffected by this. Since the critical field curve of Hg is quite accurately parabolic, the Casimir-Gorter model ought to describe its thermodynamic properties particularly well.

superconducting state. Points calculated by Eq. (42) are shown indicated in Fig. 7. Remembering the experimental uncertainties inherent in the experimental points of this figure, it is seen that the points obtained from Eq. (42) are not inconsistent with the general trend of the experimental results.

VI. CONCLUDING REMARKS

It would be desirable to perform these nuclear resonance experiments on superconducting particles of smaller size. This would facilitate the measurements and interpretation by reducing the width of the superconducting line; it would also allow one to extend these measurements to higher magnetic fields and thus to check the question of any possible field dependence of the Knight shift. Experiments on different metals, e.g., Pb, would also be worth while since they would show to what extent the results obtained are characteristic of all superconductors. The preparation of colloidal samples with sufficiently good size distributions constitutes, of course, the major difficulty in such experiments. The use of multiple thin films may, as suggested by Knight,[33] represent an alternative possibility of obtaining suitable samples for these nuclear resonance studies. If the films are all of uniform thickness, study of the resonance line shape might also yield information about the law governing the penetration of the magnetic field into the superconductor. On the theoretical side, it would be valuable to try to make some at least qualitative statements about the electrons spin paramagnetism [or $E_s(p)$] from the point of view of proposed microscopic models of superconductivity. Finally, though some preliminary experiments bearing on the nuclear relaxation time T_1 in the superconducting state were made in R,[6] systematic studies of this quantity have yet to be carried out and should be of considerable interest.

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APPENDIX

We want to estimate approximately, using the general discussion of Sec. IIIc, the correction due to microscopic broadening in the case that the latter is small, i.e., when 2σ is small compared to the width of $W(\nu)$. For any frequency ν_0 the value of $w(\nu_0)$ is determined by the behavior of $W(\nu)$ in a range of order $|\nu-\nu_0|\lesssim 2\sigma$ while the behavior of $W(\nu)$ far away from ν_0 is of no consequence. Since 2σ is relatively small, one can approximate $W(\nu)$ in the range of interest by a Taylor series

$$W'(\nu)=\sum_{m=0}^{\infty}(1/m!)W'^{(m)}(\nu_0)(\nu-\nu_0)^m, \qquad \text{(A-1)}$$

where

$$W'^{(m)}\equiv d^mW'/d\nu^m.$$

One can write the Fourier transform of $W'(\nu)$ in the form

$$\bar{W}'(k)=e^{-ik\nu_0}\sum_m (i^m/m!)W'^{(m)}(\nu_0)(d/dk)^m\delta(k), \qquad \text{(A-2)}$$

and Eq. (18) then yields

$$w'(\nu_0)=\sum_m (1/m!)W'^{(2m)}(\nu_0)(-\tfrac{1}{2}\sigma^2)^m. \qquad \text{(A-3)}$$

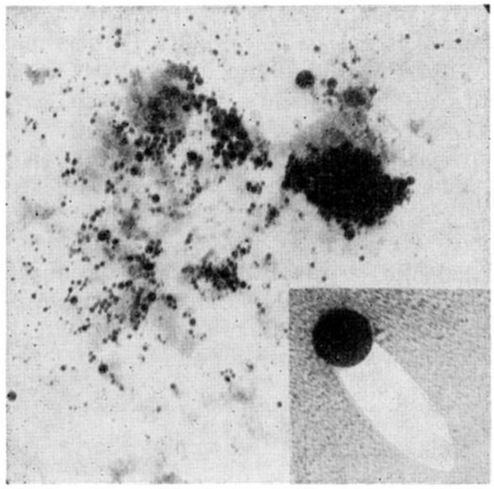
In particular, one can approximate the observed derivative curve $W'(\nu)$ near the frequency ν_1 of its minimum by

$$W'(\nu)-W'(\nu_1)=\sum_{n=2}^{5}a_nx^n, \quad x\equiv\nu-\nu_1, \qquad \text{(A-4)}$$

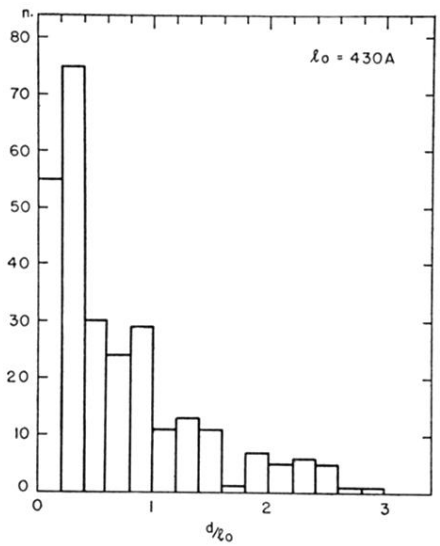
where the four coefficients a_n can be obtained, for example, by fitting this polynomial to $W'(\nu)$ for $x=\pm\sigma$, $\pm 2\sigma$. Using (A-4) in (A-3) and setting the derivative of the resulting expression to zero yields the approximate equation

$$3\sigma^2(-a_3+5a_5\sigma^2)+2(a_2-6a_4\sigma^2)x +3(a_3-10a_5\sigma^2)x^2=0 \qquad \text{(A-5)}$$

the solution of which determines the value x for which $w'(\nu)$ has its minimum, i.e., the desired frequency ν_s.



(a)



(b)

FIG. 1. (a) An electron microscope photograph showing Hg droplets sampled from one of our colloidal preparations. The inset in the lower right corner shows, with the same magnification, a latex sphere (shadow-cast) 2600 A in diameter. (b) A representative size distribution obtained for one of our samples. The histogram shows the number n of Hg drops *vs* their diameter d measured in units of $l_0 = 430$ A.