genic model. It is possible to fit the data reasonably with this expression by using values of a about twice as large: 22 A for B, 19 A for Al, and 24 A for Sb. It seems that the value estimated according to the hydrogenic model should be close to the proper value to be used. Kohn[25] has shown that the ground state wave function for acceptors in germanium can be represented by two terms, each of which has the form $\exp(-r/a)$. The calculated values of a are 43.3 A and 33.8 A. The larger value is close to the estimate 42 A given by the hydrogenic model for a typical ionization energy of 0.0108 ev. Thus, it appears that the form (21) is to be preferred.

ACKNOWLEDGMENT

One of the authors (R. K. R.) wishes to acknowledge his indebtedness to the late Professor K. Lark-Horovitz for his guidance and encouragement in the first part of this work.

PHYSICAL REVIEW VOLUME 121, NUMBER 3 FEBRUARY 1, 1961

Nuclear Magnetic Resonance in Superconducting Tin*

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(Received September 19, 1960)

The nuclear magnetic resonance (NMR) is investigated in small particles (~100 A diam) of β tin between 1.5 and 4.2°K, and in magnetic fields between 1.2 and 8.8 kilogauss. The critical temperature and critical field are 3.71°K and 25 kilogauss, respectively. The effective penetration depth for the superconducting particles is estimated to be 1500 A. The resonance linewidth is 0.34% of the magnetic field, and it is independent of temperature. With respect to α tin, the NMR shift for β tin is 0.77% in the normal state; it approaches 0.59% in the superconductor as $T \to 0$. (The largest known chemical shift is only 0.17%.) The variation with magnetic field is less than 0.03%. One may conclude that the electronic spin susceptibility in the superconducting particles at absolute zero is approximately three quarters of the normal value. The result for 1000 A particles, though less accurate, is substantially the same.

I. INTRODUCTION

THE feature which makes nuclear magnetic resonance (NMR) attractive as a method for studying solids is that the nuclear resonance frequency is quite sensitive to the local fields at the position of the nucleus. A principal source of local fields is the hyperfine interaction between electrons and nucleus which may be quite strong in a metal. The average local field, which is proportional to the polarization of the conduction electron spins, shifts the resonance line; fluctuations in the local field allow for the relaxation of the nuclear spins toward their equilibrium distribution. Moreover, the resonance line is broadened if the several nuclei are not found in a homogeneous magnetic field.

Because of the very local nature of the hyperfine interaction, we should expect the data to be useful in constructing a microscopic model of a metal. In particular, the method has considerable significance for a microscopic theory of superconductivity, which must consider electron spin polarization and density of states at the Fermi surface, since the resonance line shift and the nuclear spin relaxation time are measures of these quantities.

Although it was realized some time ago[1] that the nuclear resonance could provide unique information about superconductors, the attainment of experimental results was delayed by several difficult problems, principal among which was the fabrication of a specimen. This must consist of a dispersion of colloidal metallic particles or of a stack of thin films; the particle diameter or film thickness to be much less than the penetration depth; and the aggregate to contain one gram or more of the desired material. It is well known that the critical fields are high and that the internal fields are quite homogeneous in small specimens. Both of these conditions must be met for nuclear magnetic resonance (NMR), and, although the making of colloids and films is easy enough, it has been a major effort to concentrate a sufficient quantity of finely-divided material for the resonance experiments.

There are many methods for preparing the sample—ultrasonic disintegration, chemical reduction, electrolytic deposition, photochemical reduction, evaporation into an inert gas or liquid, and evaporation onto a solid surface—from among which we have chosen the last as being most generally applicable to all metals, most reproducible, and most capable of yielding a sample containing pieces of uniform size. We have been able to make multiple films, alternate layers of which are collections of quite uniformly-sized platelets of tin.

Tin is a good candidate for the investigation, since

* Supported in part by the U. S. Office of Naval Research and the Alfred P. Sloan Foundation.

[1] W. D. Knight, *Advances in Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 2, pp. 93–136. A preliminary account of the present work may be found in Phys. Rev. Letters 2, 386 (1959).

not only has its nuclear resonance in the normal state[2] been studied carefully, but also its properties as a superconductor[3] are well-known. Our problem has consisted in making several specimens by somewhat different methods, each containing a different size or distribution of particle sizes; in ascertaining that the end product was β tin possessing the recognizable properties of a superconductor; in verifying the consistency of the results among the several samples and the reproducibility in each for several magnetic fields and temperatures; in evaluating the importance of the chemical shifts; and in reconciling the experimental results with other related experiments and theories.

In Secs. II, III, and IV following, we shall present descriptions of the apparatus, the sample, and the results of the nuclear resonance experiments. We essay a comparison with other experiments and with some current theoretical models in Sec. V.

II. EXPERIMENTAL APPARATUS

Electronics. The nuclear resonance spectrometer system consisted of a marginal oscillator[4] associated with a lock-in detector, a modulating unit, and a recording potentiometer. This apparatus is quite conventional, and is described in detail elsewhere.[5] Frequency markers were put on the recording chart at one-kc/sec intervals, while the rf oscillator swept through the resonance in a fixed magnetic field. Since the sample volume was rather large, the correspondingly large region of homogeneous magnetic field was provided by a twelve-inch electromagnet with a two-inch gap. The magnet power supply gave short-time stability of approximately one part in 10^7, while the long-time or thermal-drift stability was approximately one part in 10^5. The field was monitored periodically by observing the nuclear resonance of sodium metal in a small sample mounted just outside the Dewar which contained the specimen.

Cryogenics. In order to utilize as much space as possible for sample volume, a Dewar of all-metal construction was used.[6] The inner wall consisted of a 1.500-inch diam stainless steel tube, with 0.016-inch wall, approximately 36 inches long. The outer wall was of brass. At a level about 6 inches below the top of the Dewar the inner wall was connected thermally to an annular reservoir containing liquid nitrogen. This reservoir was about 18 inches long, and attached to its bottom was a copper heat shield, which extended around the inner wall in the constricted part of the Dewar down the last 12 inches to the bottom. The power leak into the inner container was between 30 and 50 milliwatts. The Dewar was mounted so that it could be rotated through a 90° angle about the vertical axis. The sample was in direct contact with the helium bath, and was ordinarily mounted so that the films were parallel with both the steady field, H_0, and the rf field, H_1.

In attaining temperatures between 1.5 and 4.2°K a mechanical pump was applied through a Cartesian manostat pressure regulator. The T_{55E} vapor pressure scale for helium served as a standard.[7] Supplementary temperature readings were derived from a calibrated carbon resistance thermometer.

III. SAMPLE

A sample to be used for observing nuclear magnetic resonance in superconducting metals should have the following properties. First, the metal in the sample should be small enough in at least one dimension for the variation of the magnetic field to be less than the linewidth of the resonance in the metal in the normal state. Second, all of the metal particles should have the same size, so that they will all be at one time either in the normal or superconducting state: the transition between states should be sharp for the sample as a whole. It is particularly important to achieve the second of these conditions; otherwise the experimental results are difficult to interpret. For, if the sample contains a distribution of sizes, there are values of magnetic field and temperature ($T<T_c$) for which the sample will contain both normal and superconducting particles.[8] Then, if the resonant frequencies of the nuclei in the two different sizes of particle are not sufficiently different, the lines will overlap, in which case it is difficult to determine their separate positions. It is difficult to use any consistent criterion for untangling them, especially when the sample contains several particle sizes, because the intensities of the lines change differently with temperature in unpredictable ways. In particular, the ratio of the number of superconducting to number of normal particles changes in a fashion which depends in detail on the size distribution. Previous NMR experiments on superconductors[8,9] were plagued in varying degrees by this difficulty. In the present experiment, the final sample is more nearly ideal.

Preparation.[10] Alternate layers of tin and a dielectric (nylon) were evaporated onto a thin sheet of Mylar. The thickness of each layer was controlled by evaporating completely, during one cycle of operation, small unit amounts of both metal and dielectric. For this purpose, both materials were obtained in the form of strands or wire, from which small identical pieces could be cut. Nylon is obtainable commercially in this form; tin wire was extruded from an ingot of high purity

[2] N. Bloembergen and T. J. Rowland, Acta Met. **1**, 731 (1953); referred to hereafter as B.R.

[3] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952).

[4] R. V. Pound and W. D. Knight, Rev. Sci. Instr. **21**, 219 (1950).

[5] E. R. Andrew, *Nuclear Magnetic Resonance* (Cambridge University Press, Cambridge, 1955), pp. 49–53.

[6] We are indebted to Professor A. F. Kip for suggestions concerning the design of the Dewar.

[7] J. R. Clement, Phys. Rev. **100**, 743 (1955).

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

[9] W. D. Knight, G. M. Androes, and R. H. Hammond, Phys. Rev. **104**, 852 (1956).

[10] G. M. Androes, R. H. Hammond, and W. D. Knight (to be published).

(99.999%). Mylar film of 0.00025-inch thickness was the substrate material upon which the tin-nylon multiple film structure was deposited. The Mylar film was backed by a surface maintained at 77°K; however, because of poor thermal contact, and the heating from the evaporating boats, the average temperature of the Mylar was about 0°C. The multiple film structure tends to peel from the substrate after 300 or more layers have been deposited. For this reason the area of the film exposed to the evaporant was changed periodically by rolling the film from one cylinder to another as is done in a photographic camera. The final sample was composed of a stack of Mylar rectangles, upon each of which approximately 200 tin-nylon layers had been deposited. Oxidation and surface diffusion were minimized by keeping the completed films at low temperatures during storage in or after removal from the evaporation chamber. It is well known that evaporated thin films tend to break up into small pieces[11] at temperatures above 100°K. This occurred as expected in our samples. Fortunately the sizes of the platelets thus formed were quite uniform, and they were furthermore insulated from one another, partly because the evaporation of each tin bit took place before the preceding bit of nylon was completely boiled away.

The dimensions of the final stacked sample were $1.5\times1.5\times4.0$ cm, with the layer structure parallel to a long face. It contained an estimated one gram of tin in 60 000 layers. Approximately ten percent of the total volume consisted of tin; the remainder was apportioned about equally to nylon and Mylar.

X-ray analysis. An x-ray diffraction experiment showed the tin to exist in the β phase. There were slight deviations from the usual lattice spacings[12] by $\Delta d=-8.8\times10^{-3}$ A for the (200) planes, and by $\Delta d=+3\times10^{-3}$ A for the (301) planes. The amount of α tin present, if any, was less than 2%. The small-angle scattering of x rays from a portion of the sample (beam directed perpendicular to the layer structure) indicated that the metal layers had divided into platelets of quite uniform size. If the scattering centers are considered to be short cylinders with their axes parallel to the incident radiation, their diameters are calculated to be 140 A. Thus, the sample may be thought of as consisting of quite uniform layers of tin, each layer being composed of many separate platelets. Although the diameters of some of the platelets may be several hundred angstroms, the vast majority of them have diameters which fall in the range 100 A to 200 A. The thickness of the platelets is estimated to be 40 A.

Properties of the superconductor. The position and width of the superconducting transition temperature in zero magnetic field are good indications of the degree to which a particular sample approaches the behavior of a highly-pure, well-annealed specimen. For tin, transitions as narrow as 0.001°K have been observed by others,[13] and the mean value of T_c obtained from several independent measurements[14] is 3.735 ± 0.005°K.

The nuclear magnetic resonance apparatus may be used to determine changes in the susceptibility of the sample as it makes the transition to the superconducting state.[8] Experimentally this is measured in terms of a frequency shift $\Delta\nu$ of the oscillator as a function of T or H; $\Delta\nu/\nu=-2\pi f\chi$. Here f is the filling factor of the sample in the coil, and χ is the rf susceptibility of the sample. The critical temperature for the multiple-film sample was found in this way to be 3.712 ± 0.010°K in zero field; the half-width of the transition was approximately 0.05°K. Although the value of T_c is in fair agreement with the T_c of good bulk samples, the transition width is much greater than the ideal. It will only be mentioned that the addition of a small amount of impurity reduces the mean free path of the carriers, broadening the transition[3] and, for tin, reducing the transition temperature.[14] The mean free path of the electrons is certainly limited in our sample by the size of the platelets, and we should expect the effects to resemble those of impurities.

The particles of the sample were not completely uniform in size, and consequently we expect the transition to be smeared out somewhat when a field is applied. This was found to be so, for, using the rf susceptibility as an indicator, we measured a half-width of 0.17°K for the transition at 3.65°K in a field of 1.2 kilogauss. For this sample the rf susceptibility is very small, and this method of determining the transition temperature becomes unsatisfactory at larger fields. This comes about because the stability of the oscillator was inadequate over the longer times required to change the temperature through the wider transitions. The obvious alternative of varying the magnetic field at some temperature below T_c was attempted. However, the temperatures for these experiments were selected before it was appreciated that the critical fields exceeded 10 kilogauss at temperatures below 3°K. We also note that the rf susceptibility measurements will be affected somewhat by the presence of even a few larger particles. Consequently, we rely on the agreement between this and another method at low fields, and use the other methods, involving the NMR frequency, at higher fields. The critical field curve appeared to be parabolic, with $H_c(0)=25\pm3$ kilogauss.

The foregoing measurements might be used to estimate the correction to be applied to the external magnetic field to compensate for the diamagnetism of the sample. However, the sample employed in this experi-

[11] See, for example, J. P. Borel, Colloq. intern. centre nat. recherche sci. (Paris) **61**, 56 (1956).

[12] *Tables for Conversion of x-ray Diffraction Angles to Interplanar Spacing*, National Bureau of Standards, Applied Mathematics Series 10 1953 (U. S. Government Printing Office, Washington, D. C.).

[13] W. J. de Haas and J. Voogd, Communs. Phys. Lab. Univ. Leiden No. 214c (1931).

[14] E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids **3**, 165 (1957). Other references are given and the values of T_c discussed.

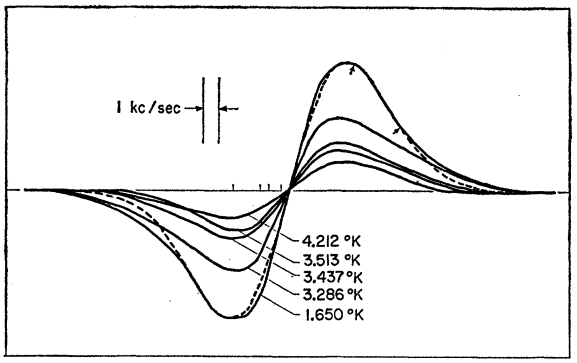

FIG. 1. Series of resonance lines in an external field of 1.2 kilogauss. Lines are traced from experimental recordings; centers are made to coincide in order to compare widths. The short marks on the horizontal axis denote the actual positions of the line centers; note that the maximum variation in line shift is about one half-width.

ment allowed the use of a more exact method of determining these demagnetization effects. We note that Mylar and nylon, which are part of the sample, contain protons. On the other hand, the coil form was constructed of Teflon, which is free of protons. The correction for demagnetization may be determined by observing the shift in the resonance frequency of the protons as the temperature is lowered through the superconducting transition. Although the proton resonance was 48 kc/sec wide, the accuracy of the frequency measurement was high; it was found that the frequency varied somewhat over the temperature range below T_c; but the maximum fractional frequency shift was 4×10^{-5}, which is small compared to other effects in the experiment. We may safely conclude that the gross demagnetizing factors are not important.

IV. EXPERIMENTAL RESULTS

Line shape. The nuclear resonance absorption in the small platelets was observed to have the following features, some of which contrast sharply with those of the resonance in micron-sized "bulk" pieces of tin. (Unless noted, the discussion relates to platelets in a plane parallel to the external field.)

1. The line is symmetric, nearly Gaussian, in all magnetic fields. By contrast the line shape in bulk material approaches exact symmetry only in the limit $H=0$, and it is quite asymmetric in fields of the order of several kilogauss. (The theory and experimental measurements for the bulk tin resonance have been given in some detail by Bloembergen and Rowland.[2] We shall refer to their paper in what follows as B.R.)

2. Aside from the enhancement of intensity to be expected from the Boltzmann factor, the characteristics of the line were independent of temperature. We may infer, then, that the distribution of field in the superconducting particles was less than the normal linewidth, and that the normal-to-superconducting transition had no effect on the linewidth. This lack of temperature dependence has of course been verified only in the range of temperature between 1.5 and 4.2°K, and to an accuracy obtainable with a signal-to-noise ratio of ten at the highest temperature.

TABLE I. NMR frequency shifts in tin.

Reference material	Frequency shift of β tin in constant magnetic field (%).
α Sn	0.773±0.005
$(C_4H_9)_4Sn$	0.676±0.005
SnI_4 in CS_2	0.847±0.005

3. The width of the line varies directly as the applied field. The same is true of the asymmetric line in bulk tin.

4. The width and symmetry of the line depend on the particle size. The sample of platelets to which we give primary emphasis here was the last in a series of samples. Some earlier ones, which contained particles as large as 1000 A, were made by evaporating tin into an atmosphere of helium gas. It was noticed that, as the mean of the particle size distribution became considerably less than 1000 A, the resonance line became broader and more symmetric. The linewidth, between points of maximum slope, in the final sample was 0.34% of the applied field, which is to be compared to $\nu_{11}-\nu_{\perp}=0.079\%$ for bulk tin.[2]

Evidence in support of points 1 and 2 above is shown in Fig. 1, for which the applied field H_0 is 1.2 kilogauss and $T_c(H)=3.68$°K. This sequence of lines was traced from the original recorder charts. Baseline noise varied somewhat from line to line, and the signal-to-noise ratio at the highest temperature was approximately ten. We show a Gaussian (dashed) line, which has been fitted to the 1.6-degree line at the positions of the two arrows. Although the fit here is not remarkably good, it is better at higher fields; at 8.8 kilogauss and 1.6°K, the line is almost exactly Gaussian.

There is obviously some variation of the linewidth among the members of the group of lines shown in Fig. 1. However, other experiments made it clear that the fluctuations are random. The linewidth at 1.2 kilograms is determined to an accuracy of 3%, while at 8.8 kilogauss, where the lines are much broader, the accuracy is 5%. Since the magnetic field distribution in the superconducting particles appeared to have little effect on the width and symmetry of the line, and since the approximate particle dimensions are known, an inequality may be established between the thickness of the platelets and λ, the penetration depth. If we assume that the solution of London's equations for thin plates is applicable, the requirement for the absence of observable field inhomogeneities is: $t(\text{thickness})<4\times10^{-2}\lambda$. On the other hand, the solution for spheres is: $d(\text{diam})<7\times10^{-2}\lambda$. The situation for the platelets is between these extremes. If it is assumed that the sample is composed of 40 A plates, then we find that $\lambda>1000$ A; for spheres of volume equal to that of the platelets

$\lambda > 1400$ A. Although λ is not precisely determined by these conditions, its value is certainly enhanced with respect to the value for bulk material. Using Tinkham's relation[15]

$$\lambda = \lambda_0(1+\xi_0/l_{\text{eff}})^{\frac{1}{2}},$$

with $\xi_0 = 2\times10^{-5}$ cm, $\lambda_0 = 500$ A, $l_{\text{eff}} = 100$ A, we obtain $\lambda = 2250$ A. We are reassured of the above conclusions by noting that rotation of the sample by 90° produced no marked change in the line.

The lines at an external field of 1.2 kilogauss, with a width of 6.31 ± 0.06 kc/sec, were the narrowest of those observed in the platelet sample; at 8.8 kilogauss, the width was 43.4 ± 0.3 kc/sec. Since the modulation amplitude was necessarily quite large, the peak-to-peak amplitude being approximately $\frac{3}{4}$ of the observed linewidth, the appropriate corrections[16] have been made in arriving at the true widths. The corrected line width may be expressed by the relation $\delta\nu_{pp} = a\nu + b$, where $\delta\nu_{pp}$ is the width between points of maximum slope, ν is the resonance frequency, and the constants have the values $a = 3.19\times10^{-3}$ and $b = 0.8$ kc/sec. B.R. calculated a dipolar linewidth of 0.71 kc/sec.

Line shift. The center of the resonance line for the films in the normal state coincided (to an accuracy of one part in 10^4) with ν_{iso} as determined for the bulk tin metal line in the same field. However, since the chemical shift varies considerably among the several tin compounds, it is difficult to assign a precise value for the line shift of the metal. Lauterbur[17] has investigated a large number of tin compounds. We have measured two of those which he found to be near the extremes in the variation of the chemical shift. We compare bulk β tin with these and with α tin. The results are shown in Table I. The lines in the chemical compounds were narrow; for α tin, the line was 2 to 3 kc/sec wide (B.R. reported 5 kc/sec.). The nonmetallic samples were investigated at room temperature, and, since the temperature dependence of the resonance frequency in the metal has not been investigated carefully between 4 and 300°K,[18] we must allow for an error of possibly as much as one percent of the value of the line shift at low temperatures. We shall see later on that the effect in the superconductor is much larger than this, and we may therefore draw our major conclusions, safely neglecting the small effects.

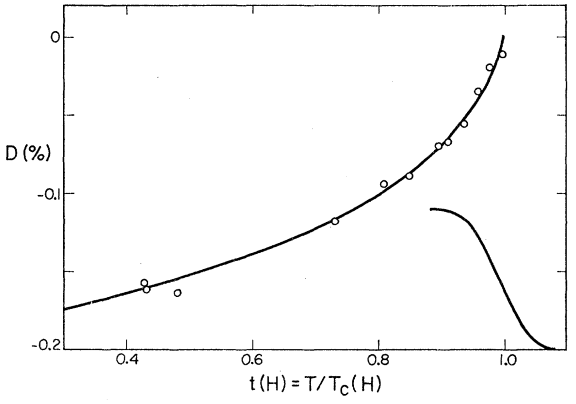

FIG. 2. Shift of resonance frequency as a function of reduced temperature. The curve at the lower right indicates the change in rf susceptibility during the superconducting transition.

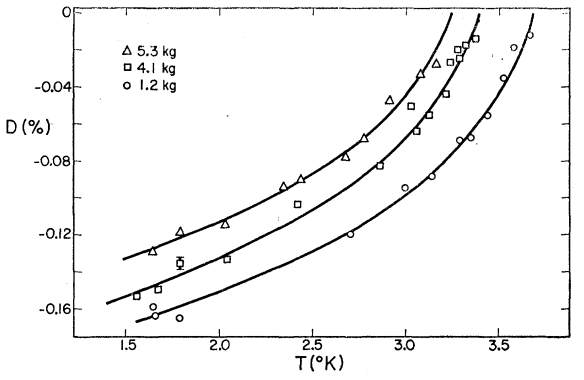

FIG. 3. Shift of resonance frequency for three magnetic fields as a function of absolute temperature.

Nevertheless, in order to avoid temporarily the uncertainties in the absolute value of the line shift, we shall measure the resonance frequency in the superconductor relative to the frequency of the normal resonance in the platelet sample at 4.2°K. Thus we define the quantity $D = (\nu_T - \nu_{4.2})/\nu_{4.2}$, where ν_T is the resonance frequency of any line measured at temperature lower than 4.2°K, and $\nu_{4.2}$ is the resonance frequency in the normal metal at 4.2°K. The quantity D was determined as a function of temperature in fields of 1.2, 1.8, 2.25, 4.1, 5.3, 6.8, and 8.8 kilogauss. The behavior of the Sn^{117} isotope was found, in a limited series of experiments, to give the same results as for Sn^{119}, for which the results are given here.

The procedure was to run through the 4.2° line several times, in order to obtain a reliable average value for $\nu_{4.2}$. Then the temperature was lowered in increments, and two lines were run at each temperature, each pair requiring about one hour.

Figure 2 is a plot of D vs reduced temperature $t(H)$ in a magnetic field of 1.2 kilogauss. We notice that the curve rises with increasing temperature, D approaching the value zero at a temperature which agrees nicely with the critical temperature as determined by the rf susceptibility. The agreement of the values of T_c determined by these two methods at low fields gives us some confidence that the first method may be valid at

[15] M. Tinkham, Phys. Rev. **110**, 26 (1958). For values of λ_0 and ξ_0, see J. E. Faber and A. B. Pippard, Proc. Roy. Soc. (London) **A231**, 336 (1955).

[16] E. R. Andrew, Phys. Rev. **91**, 425 (1953).

[17] P. C. Lauterbur (private communication), and P. C. Lauterbur and J. J. Burke, Abstracts of Papers Presented at the 133rd Meeting, Am. Chem. Soc. (1958), p. 15L.

[18] D. Feldman, thesis, University of California, 1959 (unpublished) has investigated the temperature dependences in Na, Al, and Pb.

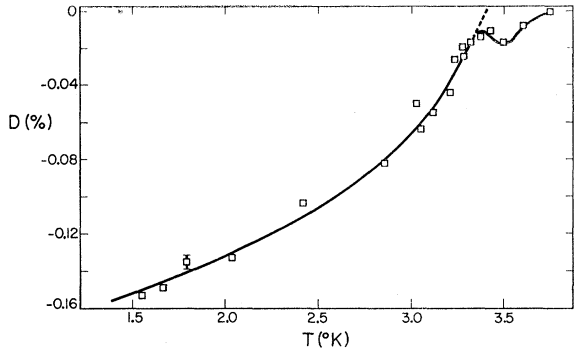

FIG. 4. Shift of resonance frequency for applied field of 4.1 kilogauss, showing dip near T_c.

higher fields where the rf susceptibility is more difficult to measure.

In Fig. 3 we compare the curves of D for external fields of 1.2, 4.1, and 5.3 kilogauss. The two principal features of the curves are (1) the critical temperatures are appreciably different, as we should expect, and (2) the average value of D, extrapolated to 0°K is approximately $D(0)=-0.18\%$. The data taken at several magnetic fields are consistent with $H_c=H(0)[1-(T/T_c)^2]$, where $H(0)=25\pm3$ kilogauss, and $T_c=3.71\pm0.01$°K; this is a reasonable behavior for a superconductor of small dimensions.

Since the lowest reduced temperature in the experiments was about 0.4, we are not able to ascertain to what extent $D(0)$ depends on magnetic field. However, at the lowest temperatures of the experiment, the variation of D among the several values of magnetic field is only one sixth of the probable average value of $D(0)$. The present data are not accurate enough to warrant a discussion in detail of the magnetic field dependence. We content ourselves by showing that it is small, and we pass on to another subject of interest.

Figure 4 is a more complete plot of D vs T for $H_0=4.1$ kilogauss. It is immediately obvious that D has not reached the expected zero value just above T_c. Moreover there appears to be a small minimum near 3.5°K; this will be referred to as the "dip." The effect is certainly rather small, and one might be inclined to regard it as an experimental error but for the fact that it is quite reproducible; furthermore, on close examination, the dip is found in all the curves for D and it is not peculiar to the data taken at any single value of the magnetic field.

Returning for a moment to consider Fig. 3, we notice that the curves are displaced from one another in a way which suggests that a plot on a reduced temperature scale would be useful. One might in fact hope to represent the data for the several magnetic fields in a single universal curve, where the reduced temperature scale is adjusted according to the value of $T_c(H)$, the critical temperature for each field. Figure 5 is constructed in this way, and it is to be observed that, although the data may not be reduced to a single curve, nevertheless the curves fall quite closely together. Furthermore, the dip in each curve appears near $T/T_c(H)=1.03$. In this plot we have determined $T_c(H)$ as is indicated in Figs. 2 and 3. The values are consistent, and correspond to $T_c(0)=3.71$°K.

On the basis of the presently available data, we conclude that the dip is real and that it occurs above the critical temperature. Its existence is, however, not understood, since it appears to be a kind of precursor to a phase transition which is otherwise noted for its abruptness.

V. DISCUSSION AND COMPARISON WITH THEORY

In this section we shall first propose a qualitative explanation for the shape and width of the absorption line in the platelets. After discussing the line shift in the superconductor, we shall compare the results on tin with previous work on mercury and with several theoretical proposals.

Linewidth and shape. Except for the symmetry and width, the resonance in the platelets seems to exhibit all of the properties of the normal bulk tin line. We now examine the existing theory (B.R.) for the bulk tin line, with the intention of demonstrating a particle-size dependence for the width. A qualitative picture is quite easily made; exact theoretical values for the width are more difficult to derive, and this will not be done here.

The B.R. calculation considers the effect of the p character in the conduction electron wave function on the energy levels of a nucleus in a uniform magnetic field. The net effect is to make the resonance frequency of the nucleus dependent upon the orientation of the magnetic field with respect to the crystal axes. The results can be described in the tetragonal case in terms of the extreme resonance frequencies which arise when

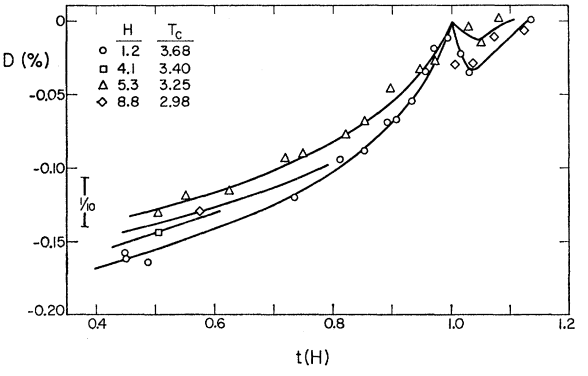

FIG. 5. Shift of resonance frequency, plotted against reduced temperature. The reduced temperature for each applied field is taken relative to $T_c(H)$, the critical temperature in that field. Note that the positions of the "dip" are coincident on this plot. The magnitude of one tenth the line width is shown at the far left. The experimental error is less than 0.01% at the lowest temperature.

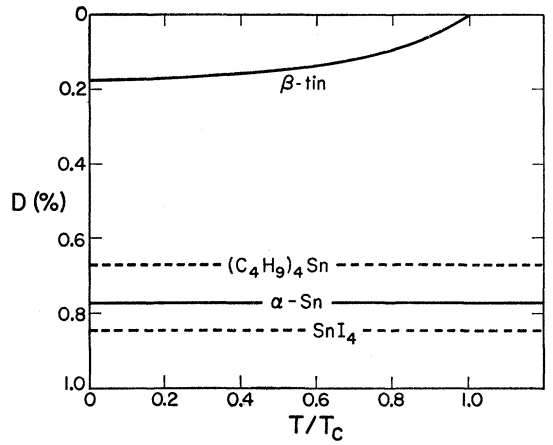

FIG. 6. Shift of resonance frequency in normal and superconducting β Sn compared to α Sn and diamagnetic compounds.

H is parallel ($\nu_{\parallel}$) or perpendicular ($\nu_{\perp}$) to the tetragonal axis. In practice, the sample is composed of many crystallites with randomly oriented axes, so that one may see contributions to the resonance at all points between these extremes.

The electronic wave function in the unit cell may be written

$$\psi=\exp(i\mathbf{k}\cdot\mathbf{r})(a_0\varphi_s+a_1\varphi_{px}+a_2\varphi_{py}+a_3\varphi_{pz}).$$

The p functions include a radial function, and an angular part of the form

$$\varphi_{px}=2^{-\frac{1}{2}}(\psi_+ +\psi_-),\quad \varphi_{pz}=2^{-\frac{1}{2}}(\psi_+ -\psi_-),\quad \text{and}\quad \varphi_{pz}=\psi_0,$$

the ψ_m being atomic-type functions for the angular momentum states m. The constants in this wave function may be evaluated by comparing the expressions for the isotropic and anisotropic line shifts with experiment.[19] In the following we define $A_i=\langle|a_i|^2\rangle_{\text{av}}$, the average to be taken over the Fermi surface; V_0 is the atomic volume; $N(E_F)$ is the density of states at the Fermi Surface; κ_s and κ_p are relativistic correction factors.[19]

In terms of the above wave function, the isotropic shift may be written as[2,19]

$$\Delta H/H=(16\pi/3)\mu_B{}^2V_0N(E_F)A_0\kappa_s\langle|\varphi_s(0)|^2\rangle_{\text{av}}.$$

The expression for the anisotropic shift is

$$(\nu_{\parallel}-\nu_{\perp})/\nu_0=(12/5)\mu_B{}^2V_0N(E_F)\kappa_p\langle r^{-3}\rangle_p(A_3-A_1),$$

where ν_0 may be the resonance frequency of a diamagnetic salt, and advantage has been taken of the appearance of the radial p function so that we may insert $\langle r^{-3}\rangle$. One may calculate $\varphi_s(0)$ from a value of the atomic hyperfine splitting; calculate $\langle r^{-3}\rangle$ from the atomic fine structure splitting; and, using the value of $V_0N(E_F)=0.19\times10^{12}$ erg^{-1} given by B.R. for tin, arrive at the following values: $A_0=0.34$, $A_1=A_2=0.13$, and $A_3=0.40$.

The case of orthorhombic symmetry is also considered by B.R. The discussion of the resulting line shape is made in terms of three frequencies, ν_1, ν_2, ν_3, corresponding to the resonant frequencies for the cases when H_0 is parallel to each of the three axes. In terms of the above wave function, one finds that

$$(\nu_3-\nu_2)/\nu_0=(12/5)\mu_B{}^2V_0N(E_F)\kappa_p\langle r^{-3}\rangle_p(A_3-A_1),$$

$$(\nu_2-\nu_1)/\nu_0=(12/5)\mu_B{}^2V_0N(E_F)\kappa_p\langle r^{-3}\rangle_p(A_1-A_2).$$

It may be seen that the resonance line becomes wider and more symmetric as A_2 departs in value from A_1, becoming twice as wide as in the tetragonal case and symmetric if $A_3-A_1=A_1-A_2$. Small distortions of the lattice along one of the axes in the plane perpendicular to the tetragonal axis by only 0.01 A (see Sec. III above) are insufficient to account for the observed line breadth.

However, we are able to give a qualitative account of the linewidth and shape by introducing the effects of the surface. Even if the lattice constants were unchanged throughout the body of the crystal, an electron near the surface atom would not see the regular tetragonal symmetry of the tin lattice: one or more of the near neighbors is likely to be missing. Since the cyrstal is certainly not perfect, especially near its surface, and since approximately half of the atom in one of the platelets are within 10 A of the surface, it is clear that the surface effects may be considerable. It is worthwhile to recall at this point that the line shape in the small particles begins to deviate from the behavior of bulk material only when the diameters of the particles become considerably less than 1000 A, which is just the range where the surface-to-volume ratio becomes appreciable.

In particular, the relative amounts of φ_{px}, φ_{py}, and φ_{pz} in the wave function and/or the value of $\langle r^{-3}\rangle$ may be expected to change in a manner depending on the position of the cell on the surface relative to the crystal axes. This last point may also be used to help explain the symmetry of the line, which will be a superposition of contributions from atoms for which the constants A_i take on all possible values consistent with $\sum_{i=1}^{3}|a_i|^2=0.66$ (assuming for the moment that a_0 does not vary). The fluctuations in these quantities from atom to atom will be random, and it is easily shown that a symmetrical line can result which is two to three times as wide as the line in bulk tin.

Doubtless one should also include the effects of the variation in $\varphi_s(0)$ among the surface atoms. However, although the effect may be appreciable, we believe it to be smaller than the effects discussed above, primarily because the value of $\varphi_s(0)$ is less affected by conditions at the periphery of a cell. Finally, as B.R. point out, anisotropy of the electronic g factor may influence the result. In view of these considerations, a fourfold increase in linewidth is not difficult to account for.

Line shift in the superconductor. The significance of the result is best appreciated if it is regarded to be a

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measure of the spin paramagnetism χ_S of the superconductor. In the normal state $\Delta H/H$ is directly proportional to χ_N, which represents the average departure from perfect spin pairing as "seen" by the nucleus. Comparison of the experimental values of $\Delta H/H$ among some twenty-four different metals has established the importance of the role of the spin paramagnetism. Precise comparisons of $\Delta H/H$ and χ_N have, however, not yet been made, except perhaps for the alkali metals, for which independent determinations are available for both the paramagnetism and the electronic wave functions. Our concern here is with the uncertainties that might be introduced by the chemical shifts, and we assume provisionally that the line shift in the metal, measured relative to an average of the known resonance positions for diamagnetic chemical compounds, provides a sufficiently accurate measure of χ_N for most purposes.

In particular, let us compare the resonance frequency in normal β tin (white) with the frequencies in the superconductor, and also in α tin (grey) and in some compounds, the latter being near the extremes of the chemical shifts. Table I displays the significant numbers, except for the effect in the superconductor, and Fig. 6 shows the situation graphically, including the behavior of the superconductor. It is first to be noted that the metallic shift, measured from the average position of the compounds, is greater than the range of chemical shifts; this behavior is typical of most of the elements which have been investigated. Moreover, it is clear that, regardless of which compound might be chosen as reference, the line shift in the superconductor (and consequently χ_S) does not vanish at the absolute zero of temperature.

If we choose α tin arbitrarily as a reference, we can state the results of the experiment as follows: in the normal state, $\Delta H/H=(0.773\pm0.005)\%$; in the superconductor $D(0)\approx-0.18\%$, so that the limiting value of $\Delta H/H$ is 0.59%; the limiting value of χ_S/χ_N is then $0.59/0.77=0.77$, or approximately three quarters. A comparable value (two thirds) was obtained for mercury by Reif.[8] We summarize the data in Fig. 7, where the curve for the tin platelets is shown slightly above that for Reif's mercury colloid; the solid line represents Yosida's calculation[20] for a model in which exact spin pairing at $T=0$ implies a vanishing χ_S.

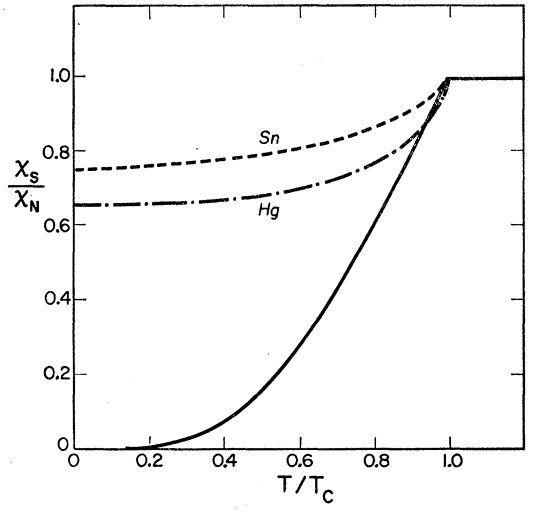

FIG. 7. Paramagnetic susceptibility of superconductors. The solid line is from the calculation of Yosida.

Recently a number of attempts have been made to account for these experimental results. The discussion concerns the ratio of the spin paramagnetism in the superconductor at absolute zero to its value in the normal metal.

Pippard and Heine[21] suggest that the Bardeen-Cooper-Schrieffer[22] restriction to pair states $\psi_{k'\uparrow}$ and $\psi_{-k\downarrow}$ be relaxed slightly by allowing that $k\neq k'$. As a consequence of this they obtain $\chi_S/\chi_N\sim\frac{3}{4}$. However, they have not yet developed an explicit wave function for their model.

Ferrell,[23] Martin and Kadanoff,[24] Schrieffer,[25] and Anderson[26] derive expressions, all of which may be approximately expressed by $1-\chi_S/\chi_N\sim l/\xi_0$, where l is a mean free path between electron spin reversals, and ξ_0 is the coherence length ($\sim2.5\times10^{-5}$). It is significant that the values of l are of the order of ten times the size of our experimental particles. One is therefore forced to consider the problem of spin flipping on reflection at the boundaries of the particles. Since the spin-orbit coupling is a principal mechanism involved in electron spin flips, the analysis will depend on a discussion of the strength of the spin-orbit effects, which are likely to be more important in the heavier metals. The point we wish to make with regard to the experimental results is, however, that the mean free path between collisions must somehow depend on the particle size of the sample. The fact that the experimental results do not indicate a strong size dependence leaves this interpretation in a provisional state.

Martin and Kadanoff[23] also propose a model in which the London λ rather than a scattering length enters as a determining parameter. In this approximation $(1-\chi_S/\chi_N\sim\lambda/\xi_0)$ the effect is independent of particle size; it also is in approximate agreement with experiment.

All of the above estimates are too crude to allow precise comparison with experiment. We can only say that they are not inconsistent with $\chi_S/\chi_N\sim\frac{3}{4}$. However, as we have already indicated, the present experiments have not revealed a strong dependence on size.

Let us examine the problem of the size dependence in more detail. Experimental evidence includes the present

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results on tin, Reif's data on mercury, and our earlier preliminary work on mercury. Reif obtained a value of approximately two thirds for χ_S/χ_N. The size distribution of his mercury particles was such that we believed our results[9] ($\chi_S/\chi_N \sim \frac{1}{2}$) to be typical of much smaller particles and higher magnetic fields. There is yet no direct evidence to contradict this belief. However, the present evidence for tin is quite strong that neither size nor magnetic field affects the result. In Sec. IV we referred to a preliminary series of experiments on larger particles of tin. The resonance lines from these samples showed broadening from the inhomogeneous fields in the particles, and the overlapping superconducting and normal resonance lines had to be separated, much as in Reif's experiment. The determination of χ_S/χ_N could not be as accurate as is our result for the sample of platelets. However, we can say with confidence that χ_S/χ_N lies between 0.70 and 0.85 for particles of the order of 1000 A diam. Thus, it appears that particle-size effects are not large in tin, and there is no reason to believe them to be important in mercury, except for the discrepancy in the results mentioned above, which is presently not understood.

We now consider the relation between the linewidth and the line shift. Since both these quantities depend on the electron paramagnetism, we should expect that changes of the one would be seen in the other as well. The line shift is reduced in the superconductor; the width is not. We must therefore seek a compensating mechanism for the decrease in line width which is expected to accompany the drop in χ_S. It is possible that the sample contains a number of larger particles, in which the variation of the magnetic field is observable as a broadening; this would be proportional to the applied field, but it would also tend to destroy the symmetry of the line. One might propose, alternatively, that the paramagnetic susceptibility in the superconductor is reduced for the s electrons (which produce the shift), but is not reduced for the p electrons (which produce the width). Since the theories of superconductivity are not explicit on this point, we must await further experimental and theoretical clarification.

Our understanding of the dip in the D vs t curve, discussed in Sec. IV, is also presently incomplete. Although the effect is similar to one predicted by Martin and Kadanoff, their effect takes place just below T_c. A more elaborate determination of T_c should be made in this sort of sample before the question is completely settled.

VI. SUMMARY

We have fabricated a sample containing one gram of β tin quite uniformly dispersed in small particles approximately 100 A diam. The critical field for the material is quite high (25 000 gauss), which is consistent with an enhanced penetration depth of approximately 1500 A. We had expected to observe relatively narrow NMR lines in either the normal or superconducting state, since the diamagnetic effects were small in the small particles. However, the lines were in fact quite broad, the width being proportional to the applied field and inversely proportional to the particle diameters below 1000 A. The extra width is explained in terms of the effect of the surface on the electronic wave functions.

We infer from the reduction of the resonance line shift in the superconductor that the spin paramagnetism of the conduction electrons is reduced, not to zero as is required in a theory of exact spin pairing, but rather to about three quarters of the normal value. This result is in agreement with that of Reif on a mercury colloid, and would be consistent with the theoretical estimates that $1-\chi_S/\chi_N \sim l/\xi_0$, but for the fact that there is no direct correlation between l in the formula and the experimental particle size. The variation of χ_S with magnetic field between one and nine thousand gauss is small compared to the apparent difference between χ_S and χ_N.

Further experiments on linewidths, line shifts, and also spin-lattice relaxation times are now in progress for the metals Al, Sn, V, and Pb.

ACKNOWLEDGMENTS

We acknowledge with thanks the assistance of Robert H. Hammond in constructing the nylon-tin evaporating device; of T. R. Carver in suggesting the technique of evaporating into an inert atmosphere, of D. W. Feldman in assisting in the preparation of samples of larger particles, and of J. Murchio (Cutter Laboratories) in preparing electron micrographs of the larger particles; of George Gordon and R. L. Wild in performing the x-ray analyses of the multiple films; of A. Ewald in providing a sample of grey tin; of John Thomas (California Research Corporation) in providing a sample of $(C_4H_9)_4Sn$; and of the Dupont Company for providing the nylon and Mylar material.

Our efforts have been encouraged and stimulated by conversations with P. W. Anderson, J. Bardeen, Robert H. Hammond, C. Kittel, J. C. Phillips, F. Reif, J. R. Schrieffer, and M. Tinkham.