Discussion 28

Coles: One rather interesting thing about a very strongly energy dependent density of state is that Pauli paramagnetism or the straightforward spin paramagnetism would show field dependence. Magnetization should not be linear in field. Has there been any evidence of this in high fields in the normal state of V_3Ga?

Jaccarino: I think that you'll find that the field dependence of the susceptibility is of the order of $(g\beta H/\Delta)^2$, where Δ = effective width of the band. This is still a rather small number; you only have field energies at best of the order of a degree or a couple of degrees and the widths of the bands are of the order of several hundred degrees. It would be very difficult to discern.

Chandrasekhar: This very unusual shape of the density of states at the Fermi surface—does this lead to any unusual ordinary transport properties? What sort of effect does it have on the normal state resistivity as a function of temperature or the thermal power?

Weger: I don't know about thermal power, but you would expect the Hall effect to be very different. If the *d*-electrons contribute to the resistivity then you should expect a different Hall effect and different magnetoresistance and things like that. Experimentally I know the thermoelectric power was measured and nothing strange was found—that's the measurement by Mrs. Sarachik.

Mrs. M. P. Sarachik, *Bell Telephone Laboratories:* These measurements were made by George Smith and myself. I can just quote what the results are. We found a peak in the thermoelectric power of V_3Ge which looks like a phonon drag contribution, and we did not find such a peak in the thermoelectric powers of the other three that we measured, namely V_3Si, V_3Ga and V_3Sn. They were all positive and about 10 μV per degree at room temperature. I was wondering if you could comment on these results since you do have them at your disposal.

Weger: It is very complicated. You have both *s*-electrons and *d*-electrons, and the question is how much of the thermal power is due to the *s*-electrons and how much to the *d*-electrons.

Pippard: If I remember correctly, the Fröhlich model involves a lattice displacement equal to the wave number at the Fermi surface in the one dimensional model. It is a finite displacement, is it not? What I am not clear about is whether you are allowed to have three mutually orthogonal finite displacements without their getting in the way of one another. I would like to ask Dr. Weger if that is so. The second point: Is there any possible way of verifying by x-ray methods that this displacement occurs?

Weger: If you look at the lattice there is no reason why they should interfere with each other because they are different atoms; there are three array of lines. Now in regard to x-rays—I don't know whether it can be seen by x-rays, but I believe that one could do an experiment with neutron diffraction. The theory by Kohn and Woll about the distortion of the phonon spectrum interacting with the electrons gives some singularities from this interaction which in three dimensions are very, very weak—discontinuous in the derivative—or something like that. Actually it has been observed by Brockhouse and his group in Pb, but after very very hard work because they are very small. Now if this model is true, then the singularities here should be much larger; they should not be discontinuous in the derivative but should show logarithmic infinities. So this would certainly be a way to confirm it or rule it out.

H. E. Rorschach, *Rice University:* If the Fermi surface has this very unusual shape, which seems necessary in order to give a cusp which moves with the Fermi surface, then it seems to me that one could hardly avoid the conclusion that there should be a superlattice formed in which this material should become essentially an insulator.

Nuclear Magnetic Resonance and Relaxation in Superconducting Vanadium*

R. J. NOER† and W. D. KNIGHT

Department of Physics, University of California, Berkeley, California

I. INTRODUCTION

Earlier nuclear magnetic resonance (NMR) experiments in superconducting mercury[1] and tin[2] suggested that the conduction electron spin susceptibility χ_s might not vanish[3] at $T = 0$. We undertook the work on vanadium[4] expecting the spin–orbit interaction[5] to be small. During the investigation Orgel[6] suggested that orbital contributions to the NMR shift should be appreciable. In the following we show that orbital effects are certainly important in vanadium although not necessarily overwhelming. The interpretation of the NMR shift in superconducting vanadium is qualified accordingly. A more

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* Supported in part by the U. S. Office of Naval Research.

† Present address: Atomic Energy Research Establishment, Harwell, England.

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

[2] G. M. Androes and W. D. Knight, Phys. Rev. **121**, 779 (1961).

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

[4] R. J. Noer and W. D. Knight, Bull. Am. Phys. Soc. **2**, 122 (1961).

[5] P. W. Anderson, Phys. Rev. Letters **3**, 325 (1959); R. A. Ferrell, Phys. Rev. Letters **3**, 262 (1959).

[6] L. Orgel, J. Phys. Chem. Solids **21**, 123 (1961).

relevant test of the spin–orbit effects is provided by Hammond's experiment[7] with aluminum.

II. THEORY

In the case of most simple metals, it has long been felt that the measured values of magnetic susceptibilities are at least qualitatively understood, and that the simple expression for the contact hyperfine interaction adequately explains the experimental results on the nuclear resonance frequency shift. For the transition metals, however, things are much less clear. One is by no means sure how to apportion the several contributions to the large total measured susceptibilities. We now discuss the several contributions to the magnetization and the corresponding contributions to the NMR shift in vanadium.

A. Magnetic Susceptibilities

Kubo and Obata[8] (KO) gave a general theoretical treatment of the magnetic susceptibilities of metals. They began with the Hamiltonian for a conduction electron in an external field H, neglecting electron spin–orbit and nuclear spin terms. They obtained the usual Landau (χ_l) and Pauli (χ_p) contributions and in addition,

$$\chi_0 = \beta^2 \sum_{n \neq n'} \int \frac{d^3k}{(2\pi)^3} \frac{f(E_n) - f(E_{n'})}{E_n - E_{n'}} \langle nk|L|n'k\rangle \times \langle n'k|L|nk\rangle\,, \quad (1)$$

where k is the conduction electron wave vector, n represents the other quantum numbers of the electronic state, E_n is its energy, and $f(E)$ is the Fermi function.

This is an orbital susceptibility, about which several things should be noted. Since the wave functions in the matrix elements are Bloch functions, and since L when properly defined for a lattice has the periodicity of the lattice, these matrix elements exist only for $k = k'$, as written. Furthermore, if we use the tight-binding approximation, L has matrix elements only between states n and n' which differ only in m_l. S states, of course, give vanishing matrix elements. Thus, after the implied summation over all electrons, the only contributions to χ_0 (in this approximation) will come from matrix elements between full and empty states within the same partly filled band, i.e., in vanadium from the $3d$ band.

It can be seen that χ_0 is the metallic analog of the more familiar Van Vleck second-order paramagnetic susceptibility in nonmetallic crystals. Its order of magnitude can be estimated as $\beta^2/V\Delta \sim 5 \times 10^{-6}$ cgs per mole, where V is the atomic volume and Δ is an "average" bandwidth, of the order of 1 eV. A quantitative evaluation would require knowledge of metallic wave functions and is out of the question at present, and even any semirealistic approximation seems difficult. KO consider the case of p electrons in a simple cubic lattice, constrained to move in one direction only, and find that for this model, χ_0 is in fact about the same size as χ_p.

In the case of most simple metals this part of the susceptibility should not be large because the unfilled shells contain mostly s electrons. However, in transition metals, the experimental values of the susceptibility seem to have little relation to simple theory, as noted earlier, and here we have unfilled d states which furnish a significant χ_0. This has also been discussed by Clogston *et al.*[9]

B. Nuclear Shielding in Metals

Since a magnetic moment and thus a magnetic field should be associated with each type of susceptibility, a corresponding shielding of the external field at the nucleus is also anticipated. Thus we can use the formalism of KO to calculate the shielding constant σ,

$$\sigma = \Delta H/H = \mu^{-1}\,\partial F'/\partial H\,, \quad (2)$$

where F' is that part of the free energy proportional to the nuclear moment μ. Thus we must include in the Hamiltonian the electron–nuclear spin interaction terms:

$$\mathcal{H} = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A} - \frac{e}{c}\mathbf{A}_n\right)^2 + V(\mathbf{r}) + 2\beta\mathbf{S}\cdot \operatorname{curl}\mathbf{A} + 2\beta\mathbf{S}\cdot\operatorname{curl}\mathbf{A}_n\,, \quad (3)$$

where $\mathbf{A}_n = (\boldsymbol{\mu} \times \mathbf{r})/r^3$ is the potential at the electron due to the nuclear dipole moment $\boldsymbol{\mu}$.

Straightforward operations analogous to those of KO result in the following contributions to σ:

1. σ_l, the shielding due to χ_l, the Landau term. Das and Sondheimer[10] have treated this term for free electrons, and find $\sigma_l = (8\pi/3)\chi_l$.

2. $$\sigma_s = (8\pi/3)\chi_s\langle|\psi_F(0)|^2\rangle V\,. \quad (4)$$

This is the familiar expression for the metal shift.[11] (χ_s is that part of χ_p due to s electrons.) Another term, σ_{dipole}, gives the usual anisotropic part of the metal shift, equal to zero in cubic metals.

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[7] R. H. Hammond (private communication).

[8] R. Kubo and Y. Obata, J. Phys. Soc. Japan **11**, 547 (1956).

[9] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters **9**, 262 (1962).

[10] T. P. Das and E. H. Sondheimer, Phil. Mag. **5**, 529 (1960).

[11] W. D. Knight, *Advances in Solid State Physics* (Academic Press Inc., New York, 1956), Vol. 2, p. 93.

3. The orbital contribution is

$$\sigma_0 = 2\beta^2 V \sum_{n\neq n'} \int \frac{d^3k}{(2\pi)^3} \frac{f(E_n) - f(E_{n'})}{E_n - E_{n'}} \langle nk|L|n'k\rangle \times \langle n'k|L/r^3|nk\rangle\,, \quad (5)$$

$$\sigma_0 \cong 2V\langle 1/r^3\rangle \chi_0\,, \quad (6)$$

where the average is taken over the single radial wave function belonging to n and n'.

The spin–orbit interaction would, if included, give a term $\sigma_{s0} \propto \chi_{s0}$; we neglect this as small.

C. Correlation and Exchange Effects

The independent-particle treatment above neglects, by its very nature, the effects on χ and σ due to correlation between electrons. A complete many-body treatment would be extremely complicated and has not yet been made; however, on the basis of some simplified theoretical models, a few statements may be made.

Pines[12] has included exchange and correlation effects in calculations of χ and γ (coefficient of electronic specific heat) for the alkali metals. He finds that the two effects roughly cancel in their contributions to γ, leaving it close to its free electron value. However, their effect on χ is such as to increase it over the free electron value by roughly 20–50%.

Pratt[13] and Heine[14] have suggested that in addition to the usual contact hyperfine field at the nucleus caused by outer s electrons, a further possible important contribution may come from unfilled non-s shells or bands (such as the $3d$ band of vanadium) via an exchange polarization of filled core s shells. Thus a nucleus may be shielded from an external field by outer non-s electrons, not only via the weak non-contact interaction, but more importantly via an indirect contact interaction; the sign of the shielding will depend on the details of the wave functions of the various electrons.

Watson and Freeman[15] have calculated this effect for free atoms in the iron-group transition elements and find that the $3d$ shell produces a negative hyperfine field at the nucleus quite comparable with that from the $4s$ shell. They suggest that the situation should not be much different in the metallic state. Thus we should add a term,

$$\sigma_d = (8\pi/3)VD\chi_d\,, \quad (7)$$

where D is a constant perhaps comparable in size with $|\psi_F(0)|^2$, and probably negative.

D. Nuclear Spin–Lattice Relaxation

In a metal the most important means of relaxation of the nuclear spins is their interaction with the conduction electrons. Obata[16] has recently made a study of this for normal transition metals, and finds for the three major mechanisms:

$$\left(\frac{1}{T_1T}\right)_s = \frac{64\pi^3 k_B\mu^2 \langle|\psi_F(0)|^2\rangle^2}{9I^2\hbar} n_s(E_F)^2 \quad (8)$$

the familiar contact hyperfine relaxation [μ and I are the nuclear moment and spin, and $n_s(E)$ is the outer s electron density of states];

$$\left(\frac{1}{T_1T}\right)_d = \frac{64\pi^3 k_B\mu^2 D^2}{9I^2\hbar} n_d(E_F)^2\,, \quad (9)$$

a contribution from the core polarization discussed above (n_d is the d-band density of states); and

$$\left(\frac{1}{T_1T}\right)_0 = \frac{\pi k_B\mu^2 (2x)^2 \langle r^{-3}\rangle^2}{I^2\hbar} n_d(E_F)^2 \quad (10)$$

arising from the orbital effects mentioned earlier (x is a factor of order unity involving details of the d wave functions). Since in transition metals one often expects $n_d > n_s$, the latter two relaxation rates may be significant. For nontransition metals, where the core and orbital rates will more likely involve p electrons, the appropriate densities of states should be smaller, making the contact relaxation dominant as is usually assumed.

Hebel and Slichter[17] worked out the theory for the temperature dependence of $(1/T_1)_s$ in the superconducting state, using the BCS[18] theory. They find a marked peak in $1/T_1$ just below T_c associated with the enhanced density of states near the energy gap. We note that the other relaxation mechanisms above also depend on $n(E)^2$; furthermore the forms of the interactions involved are such that a calculation analogous to that of Hebel and Slichter would give the same sort of temperature dependence in the superconducting state.

E. Application to Experiment

We now make some estimates of the size of the above contributions to shielding, susceptibility, and relaxation, and attempt to fit them to experiment using for comparison Al, Sn, and Hg, for which similar measurements have been made. We have from

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

[13] G. W. Pratt, Rev. **102**, 1303 (1956).

[14] V. Heine, Phys. Rev. **107**, 1002 (1957).

[15] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

[16] Y. Obata (to be published).

[17] L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959).

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

the previous section, the contributions to the shielding,

$$\sigma = \sigma_s + \sigma_d + \sigma_l + \sigma_0 . \tag{11}$$

The shielding due to ion cores is the same in metals and insulators and is therefore not evident in measurements of metallic shifts.

In the effective mass approximation, since $\chi_l = -\chi_p/3$ for free electrons,

$$\sigma_l/\sigma_s = -\tfrac{1}{3}\left[(m/m^*)^2\chi_p/V|\psi_F(0)|^2\chi_s\right] , \tag{12}$$

where χ_p/χ_s is often somewhat larger than one. We assume $|\psi_F(0)|^2 \sim |\psi_A(0)|^2$, the corresponding quantity in the free atom, and calculate this quantity from the experimentally measured hyperfine splitting factor $a(s)$,

$$a(s) = (16\pi/3)(\mu/I)\beta|\psi_A(0)|^2 . \tag{13}$$

For V^{51}, $a(s) = 0.088 \text{ cm}^{-1}$, $\mu = 5.1$ nuclear magnetons, and $I = 7/2$, giving $|\psi_A(0)|^2V \sim 200$. Thus σ_l is insignificant unless $m/m^* \gtrsim 10$. Das and Sondheimer[10] point out that this condition may be fulfilled in metals such as Be where the Fermi surface comes close to a Brillouin zone boundary. Little is known about the band structure and Fermi surface in V but lacking any evidence for small m^*, we shall treat σ_l as small.

We may compare the orbital and contact terms,

$$\frac{\sigma_0}{\sigma_s} = \frac{2\langle r^{-3}\rangle}{(8\pi/3)|\psi_F(0)|^2}\,\frac{\chi_0}{\chi_s} . \tag{14}$$

For V^{51}, we can hope to get an estimate of $\langle r^{-3}\rangle$ from the Landé interval rule applied to the spectrum of V (iii) (in which the two $4s$ electrons have been ionized):

$$\Delta E \cong \tfrac{2}{3}\, J\langle r^{-3}\rangle Z\beta^2 ,$$

where ΔE is the energy separation between the J and $J + 1$ levels of a multiplet, equal to 145 cm^{-1} between the states ${}^4F_{3/2}$ and ${}^4F_{5/2}$.[19] Thus we find $\langle r^{-3}\rangle \sim 1.3$ atomic units. Furthermore $|\psi_A(0)|^2 \sim 2.3$ atomic units from Eq. (13), and Eq. (14) becomes

$$\sigma_0/\sigma_s \sim 0.14(\chi_0/\chi_s) . \tag{15}$$

The calculation of KO suggests that χ_0/χ_s may exceed unity. Suppose we examine measured susceptibilities and apportion the several contributions in order to estimate χ_0/χ_s. To the susceptibilities of part A we add the ion core contribution,

$$\chi_{\text{total}} = \chi_{\text{ion}} + \chi_p + \chi_d + \chi_0 + \chi_l . \tag{16}$$

Table I shows pertinent experimental and theoretical numbers.

Consider first the data for Sn, Hg, and Al, the other superconductors for which resonance data are available. It is to be noticed that: (a) $\chi_{\text{meas}} - \chi_{\text{ion}} \approx \chi_\gamma$, differences being attributable to χ_l; (b) $\chi_\gamma \gtrsim \chi_{\text{free}}$, differences being attributable to band effects; (c) $\chi_{\text{free}} \gtrsim \chi_\sigma$, differences being attributable to the fact that $|\psi_F(0)|^2 < |\psi_A(0)|^2$, usually; (d) $\chi_\sigma \approx \chi_{T_1}$, since the s electrons predominate, differences again being attributable to correlations among the conduction electrons; (e) in view of points (a)–(d) we may say that the gross magnetic and nuclear magnetic properties of these metals are understood at least approximately.

Vanadium is more complicated, for $\chi_{\text{meas}} > \chi_\gamma \gg \chi_{\text{free}}, \chi_\sigma, \chi_{T_1}$. It is fair to assume, however, that the Pauli contribution to the magnetization is as estimated, i.e., $\chi_{\text{free}} \sim \chi_\sigma/3$, which is reasonable on other grounds: In Eq. (16) we assume $\chi_d \sim \chi_\gamma$, $\chi_s \sim \chi_{\text{free}}$ and find $\chi_0 \sim 180 \times 10^{-6}$ cgs per mole. Equation (15) then suggests that $\sigma_0/\sigma_t \sim 3$. This estimate suggests that σ_0 predominates but is not overwhelming.

We may also infer from Table I and the foregoing argument that a major part of the relaxation is attributable to the contact interaction.

III. SAMPLE PREPARATION

Best results in evaporating vanadium were obtained using resistance-heated boats formed from 5-mil tungsten strip. Vanadium wets such boats nicely and evaporates well when a current of about 100 A is passed through the tungsten. However, at the very high temperatures reached, some alloying takes place between V and W; this alloy has a very low vapor pressure and thus does not contaminate the sample, but the simultaneous corroding of the W boat causes its eventual breakage. Typically, a boat

Table I. Magnetic susceptibilities ($\times 10^{-6}$ per mole).

	χ_{meas}[a]	χ_{ion}[b]	χ_γ[c]	χ_{free}[d]	χ_σ[e]	χ_{T_1}[f]
V	300	−6.6	126	7.9	26	10
Sn	3.1	−24	23	19	9.3	7.6
Hg	−34	−48	21	14	7.1	
Al	18	−2.5	19	12	13	11

[a] χ_{meas} = total measured bulk susceptibility.
[b] χ_{ion} = calculated ion core susceptibility.
[c] χ_γ = derived from measured heat capacity.
[d] χ_{free} = calculated from Pauli's formula with $m^*/m = 1$, and number of electrons per atom respectively: V, 1; Sn, 4; Hg, 2; Al, 3.
[e] χ_σ = derived from NMR shift measurements, with $\psi_F = \psi_A$.
[f] χ_{T_1} = derived from NMR spin relaxation measurements with $\psi_F = \psi_A$.

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[19] C. E. Moore, *Atomic Energy Levels*, Circular No. 467 of the National Bureau of Standards (Government Printing Office, Washington, D. C., 1949).

lasts for the evaporation of 20–40 mm^3 of V, or about 2000–4000 Å worth of films at a source-to-substrate distance of 11.5 cm. This was a short enough life to slow the sample-making procedure considerably.

All evaporation, aside from early trials, was done in the apparatus described by Androes, Hammond, and Knight.[20] The V wire was much too hard for the wire-chopping devices, and so the system had to be modified so it could be loaded with pre-cut lengths of wire which were dropped at the appropriate time by remote control.

With this modified apparatus the actual evaporation of enough films to make a sample was relatively easy but slow and tedious.

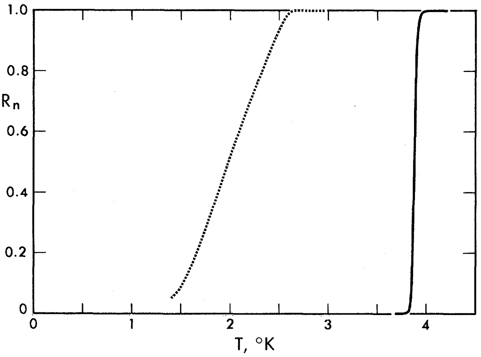

FIG. 1. Resistance vs temperature for impure 1000-Å vanadium film (dotted curve; $H = 0$) and more pure 500-Å vanadium film (solid curve; $H = 6700$ G).

The only special precaution necessary during the vaporizing of the V was to keep the evaporation rate slow enough to avoid overheating the Mylar substrate. The latter, held close to (but generally in poor physical contact with) the 77°K backing plate, was not affected appreciably by the radiation from the hot boat, but could be badly melted by the energy released on rapid condensation of a thick film of V. Care was taken to avoid this.

The resulting films were hard, uniform-looking, and when sufficiently thick, shiny and metallic in appearance. They could not be rubbed off the Mylar or scratched easily. The warping of the Mylar referred to above was not severe, and seemed not to affect the films macroscopically, although it is quite possible that it caused some strains.

The vanadium used for all samples was in the form of 0.028-in.-diam wire obtained from the Vanadium Corporation of America. The stated purity was 99.64% (impurities 0.16% oxygen, 0.0083% hydrogen, 0.062% nitrogen, 0.052% carbon, and 0.024% iron), the best commercially available. Its resistivity was found to be 1.6×10^{-5} Ω-cm, with a resistivity ratio $r = R_{\text{room temp.}}/R_{4.2°\text{K, normal}}$ of 7.6.

1. *1000 Å thickness.* These early films were evaporated in a starting vacuum of about 2×10^{-6} mm, with the pressure rising during evaporation to the low 10^{-5} range. Their thickness was estimated by making a typical evaporation onto a pre-weighed microscope cover glass and weighing the coated glass again (both times with a microbalance); the thickness was calculated assuming the bulk density of vanadium.

The resistance of one of these films was measured using a potentiometric method by attaching four fine copper leads with conducting silver paint. At room temperature, this resistance was about 30 times larger than that calculated from the measured bulk resistivity of the original *V* wire. The resistance at 4.2°K was only slightly less, $r = 1.3$. No superconducting behavior was observed down to about 2.6°K, when a broad transition set in over more than a degree, *R* decreasing by a factor of 20 as shown in Fig. 1. The field required to restore the resistance to 1/2 its normal value was about 8 kilogauss at 1.4°K. Similar measurements on a second film gave comparable results.

2. *500, 200, 100 Å thicknesses.* Since the poor superconducting behavior of the 1000-Å sample was most likely due to impurities introduced from the residual gas in the evaporating apparatus, it was decided to go to some effort to improve the vacuum both before and during evaporation. The former was accomplished by passing liquid nitrogen through the copper water-cooling tubes on the outside of the metal bell jar. This gave a minimum pressure of 5×10^{-7} mm. After this pressure was attained, several inches of titanium wire were partially evaporated as a getter (meanwhile the yet uncoated substrate was shielded). The final pressure was 2 or 3×10^{-7} mm. To keep the pressure as low as possible during evaporation of the V charge, the W boat was outgassed before loading with metal by preheating above the maximum vaporization temperature; after loading, the V was first heated slowly to its evaporating point to let it outgas as much as possible. With these precautions, it was possible to keep the pressure during evaporation in the high 10^{-7} range most of the time, with only rare rises above 2×10^{-6} and no loss in evaporation rate.

A rather dramatic improvement was found in the resistance of 500-Å films made under these conditions. The room-temperature resistance was about 10 Ω, now only slightly larger than the value calculated from the bulk resistivity. At 4.2°K, the re-

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[20] G. M. Androes, R. H. Hammond, and W. D. Knight, Rev. Sci. Instr. **32**, 251 (1961).

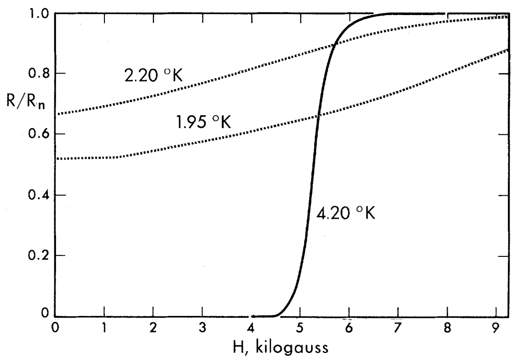

FIG. 2. Resistance vs field for impure 1000-Å vanadium film (dotted curves) and more pure 500-Å vanadium film (solid curve).

sistance was less than 0.005 Ω, the smallest measurable with the apparatus used. In a 10-kG field, enough to drive the films normal at this temperature, the resistance was about 3 Ω, giving a resistance ratio near 3. A plot of the resistance vs field for the normal-to-superconducting transition of a typical film is shown in Fig. 2. The transitions in zero field occurred at too high a temperature for their width to be observed conveniently; Fig. 1 shows R vs T for the same film in 6700 G as having a transition width of about 0.1°K (wider than the $H = 0$ transition because of nonuniformity in film thickness, edge effects, etc.). The critical field and temperature for these films were $H_0 = 23 \pm 1$ kG and $T_c = 4.5 \pm 0.1$°K.

Three NMR samples were then made with film thicknesses of roughly 500, 200, and 100 Å, estimated from V charge used for evaporation as compared with that for the 1000-Å sample, each consisting of 600 layers, 1 × 2 cm, making a total thickness of about 1 cm. These samples were stored in liquid nitrogen after assembly and between runs to reduce aging effects to a minimum.

We used a conventional NMR detection system supplemented by a pulse-height analyzer as described by Klein and Barton.[21]

IV. RESULTS OF NUCLEAR RESONANCE EXPERIMENTS

A. NMR Linewidth

1. *Normal state.* The data are collected in Table II. We consider the changes in width with time for the several samples. It is to be noticed that the less pure 1000-Å films showed first the width characteristic of the bulk metal, after which an increase was noted. The thinner more carefully prepared samples showed an initial extra broadening which decreased to the bulk value over a period of approximately one month. Since in no case was the broadening observed to depend on the applied field, we may eliminate paramagnetic impurities as a cause. Rather it is reasonable to attribute the extra broadening to first-order quadrupole effects which are independent of magnetic field. If we recall that the 1000-Å sample spent considerable time at room temperature, and also that it was prepared in a poor vacuum we may assume that most of the lattice defects were quickly annealed out. Repeated exposure to the atmosphere

TABLE II. NMR linewidth.

Sample	Time elapsed since sample completion	H(gauss)	$T_c(H)$	$\Delta\nu_N$(kc/sec) (4.2°K)	$\Delta\nu_{SC}$(kc/sec) (1.4°K)
1000 Å	1 week	5000		15 ± 1	(normal)
	2 months	1950		14 ± 1	(normal)
	14 months	2250		16 ± 1	(normal)
	23 months	8250		24 ± 1	(normal)
	25 months	8250		24 ± 1	(normal)
	25 months	4800		22 ± 1	(normal)
	25 months	2200		23 ± 1	(normal)
500 Å	1 day	7800	$\sim 4°$	25 ± 3	100 ± 25
200 Å	1 day	8250	$3.2° - 3.8°$	22 ± 2	
	2 days	8400	$3.2° - 3.8°$	20 ± 2	57 ± 3
	7 weeks	3600		16 ± 2	41 ± 5
	9 weeks	7900	3.65°	16 ± 1	24 ± 1
100 Å	5 days	8250		27 ± 2	28 ± 2
	6 days	8250		25 ± 2	
	2 weeks	7350	2.8°	18 ± 2	20 ± 1
	3 weeks	4600	2.8°	15 ± 1	17 ± 3
	9 weeks	7900	2.8°	15 ± 1	18 ± 1
Bulk				15	

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[21] M. P. Klein and G. W. Barton, Rev. Sci. Instr. **34**, 754 (1963).

could, however, be expected to facilitate the formation of oxides which then diffused throughout the material to produce lattice strains and the resulting quadrupole broadening. The later purer samples, however, were not allowed to remain at room temperature or in the atmosphere except for brief periods during which they were transferred from the liquid nitrogen storage Dewar to the measuring apparatus. We may then associate their line narrowing with a gradual relief of the strains produced when the films were deposited.

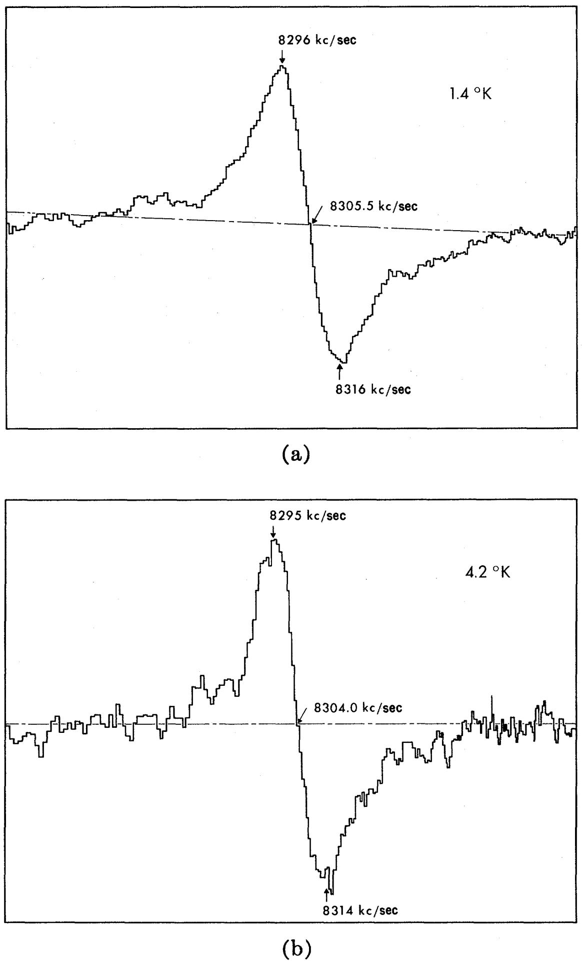

Fig. 3. Derivatives of NMR lines in 100-Å vanadium sample at 4.2°K (normal state) and 1.4°K (below superconducting transition) to show typical signals and noise. Steps are individual channels of pulse-height analyzer.

2. *Superconducting state.* We may associate the broadening in the superconducting state with magnetic field inhomogeneities resulting from a partial Meissner effect. This width may be estimated from the relation

$$\delta H/H \cong \tfrac{1}{2}(d/\lambda)^2 \,, \qquad (17)$$

where d is $\frac{1}{2}$ the film thickness and λ is the penetration depth ($d \ll \lambda$). The foregoing relation may be written

$$\frac{\delta H}{H} \cong \frac{1}{2}\left(\frac{d}{\lambda_0}\right)^2 \left[1 + \xi_0\left(\frac{1}{l} + \frac{1}{2d}\right)\right]^{-1}, \qquad (18)$$

where ξ_0 is the coherence length and l is the mean free path. Taking $\lambda_0 \sim 300$ Å, $\xi_0 \sim 3000$ Å, and $l \sim 300$ Å we estimate rough values for the films in a magnetic field of 8000 G as shown in Table III. In view of the crudeness of the estimate we regard the agreement as satisfactory.

This broadening in the superconducting state decreased as the sample aged. This is to be attributed to a decrease in l during the slow formation of grains in the film. In view of the experiment of Suits[22] we may reasonably conclude that some oxidation occurred in the first few weeks of a sample's life. A powdered sample of vanadium consisting of particles approximately 20 μ in diameter which oxidized over several years' time subsequently showed the resonance for the nonparamagnetic V_2O_5 in addition to the resonance appropriate to metallic vanadium. We may infer from this that whatever small amount of oxidation may have occurred in the films did not produce appreciable amounts of paramagnetic impurities. This is consistent with the lack of field dependence of the normal linewidth.

Table III. Extra linewidth.

Film thickness 2d (angstroms)	$\Delta\nu_S - \Delta\nu_N$ kc, gauss Calculated	Experimental
500	160	75
200	16	35
100	3	2

The line shape and width in the superconducting 200-Å sample are as expected according to the detailed field distribution. Since relatively more of the volume of a film is near its center where the field is lowest, the broadening is primarily on the low-frequency side of the resonance. The high-frequency side is to be associated with metal near the outer surfaces of the film which sees the applied field.

B. NMR Frequency Shift

A number of measurements on the 200- and 100-Å samples at various times in magnetic fields ranging

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[22] J. C. Suits (to be published).

from 3000 to 8000 G give the result for NMR frequency shift: no change greater than the experimental accuracy of ±2 kc/sec was observed for any sample. It is more useful to state the result: $\Delta H/H$ in superconducting vanadium differs by less than ±4% from the value for the normal metal.

Measurements of the resonance line intensities indicated that the resonance in the superconductor represented all of the material of the specimen ±15%.

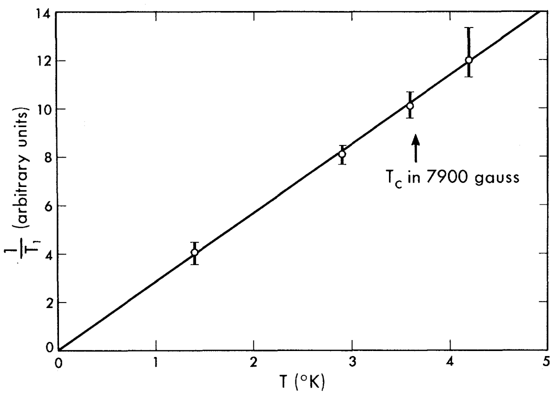

FIG. 4. Spin-lattice relaxation rate vs temperature: in 200-Å vanadium sample, measured in H = 7900 G.

C. Spin-Lattice Relaxation Time

The relaxation time T_1 was measured in the 100- and 200-Å samples by the saturation method. In practice, since sensitivities and gains of the detection system components can and do change for different temperatures, rf levels, etc., a given signal is always measured with respect to a constant artificial calibration signal made under identical conditions.

The absolute magnitude of the relaxation time was determined only so far as to determine that it was in rough agreement with Butterworth's[23] value. The temperature dependence was linear, as in Fig. 4, for both samples. No trace of increased relaxation rate was seen below the transition temperature.

V. DISCUSSION

We can not exclude the possibility that the samples became partially oxidized after a few weeks. It is fair to say, however, that the only known paramagnetic impurity was the 0.02% Fe in the vanadium as it was supplied. The 500- and 200-Å samples showed evidence of being continuous throughout the experiments. After a few weeks the transition temperature of the 100-Å sample dropped to 2.8°K and several individual films of this sample showed no resistive transition at all. Thus the 100-Å sample changed markedly during its life, since its $T_c > 4.2$°K just after it was made. We have no direct evidence that T_c decreased as the result of an increasing concentration of magnetic impurities as observed by Reif and Woolf.[24] Rather the effects of oxidation produce structure changes. During the course of the experiments, however, the 200-Å films showed more stability and are believed to have remained quite homogeneous.

The linewidth is entirely consistent with the assumption of continuous superconducting films of the appropriate thickness. Changes in the normal state width with time are attributable to quadrupole broadening. Changes in the superconducting width are associated with structure and mean free path changes in the films. No filamentary structure was evident in the superconductor.

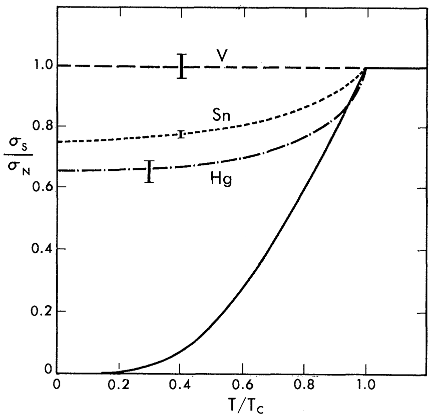

FIG. 5. NMR shift in several superconductors. The experimental accuracies and lowest temperatures of measurement are shown for V, Sn, and Hg. The value for Al (Ref. 7) falls at approximately 0.75 for T = 0. The solid line is Yoshida's curve (Ref. 3).

The line shift appears to be independent of temperature, of sample condition, and of the normal–superconducting transition. Although the orbital contribution may account for as much as three quarters of the observed shift, the core polarization does not appear to be important, and we conclude that the reduction of χ_s in the superconductor is probably less than the reduction for Al, Sn, and Hg. The

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[23] J. Butterworth, Phys. Rev. Letters 5, 305 (1960).

[24] F. Reif and M. A. Woolf, Phys. Rev. Letters 9, 315 (1962).

accuracy of the T_1 measurements still leaves room for a possible 10% increase in relaxation rate in the superconductor just below the transition. Furthermore, the relaxation may be affected by impurities, and, since the relaxation measurements were taken some time after the samples were made we are less certain of the significance of the measurements. A smearing of the energy gap might account for the results.

ACKNOWLEDGMENTS

We wish to thank F. Wright for assistance on some of the experiments, and S. Kiser for his work in adapting the pulse-height analyzer to our apparatus. The pulse-height analyzer was kindly loaned to us by Professor Howard Shugart. We are indebted to M. Klein, V. Jaccarino, R. Hammond, J. Butterworth, and particularly L. Orgel for helpful conversations.

Nuclear Magnetic Resonance and Relaxation in Superconducting Aluminum

R. H. HAMMOND and G. M. KELLY

General Atomic Division of General Dynamics Corporation, John Jay Hopkins Laboratory for Pure and Applied Science, San Diego, California

I. INTRODUCTION

There have been a number of theories[1-8] concerning the change in the Knight shift in a superconductor. In particular, they are concerned with attempting to understand why it is that, in the reported measurements to date,[9-11] the shift does not decrease to zero at $T = 0$°K, as has been predicted by the BCS theory.[1] A feature of two of these theories[4,5] is the strength of the spin-orbit coupling. Aluminum is the superconducting metal with the smallest atomic weight, and thus, it is expected to have a smaller spin-orbit coupling than other superconductors. A feature of another theory[3] is the size of the sample. Aluminum is a convenient metal in this regard because of its strong NMR signal and because of its large coherent length it is possible to study the NMR in a wide range of film thickness. Finally aluminum has no *d* electrons, and we can assume that the paramagnetic susceptibility is entirely due to conduction electrons.

We have recently started some measurements of the Knight shift, nuclear spin–lattice relaxation rate, and resistivity in thin films of aluminum. The preliminary results on one sample are presented here.

II. RESULTS

In Fig. 1 is shown the change of the Knight shift of aluminum in the transition, plotted as the ratio of the NMR shift in normal and superconducting states. These measurements were made at a magnetic field of 3.8 kG. The critical temperature for this field is apparently 0.82°K as judged from the change in Knight shift, and also as judged by the temperature for which the resistance of one film is reduced by $\frac{1}{2}$. The dashed curve is the theoretical result of Yosida[1] based on the BCS theory. Shown also are the apparent values of the Knight shift in other metals at $T = 0$°K. Our result is that the amount of the Knight shift for aluminum at $T = 0$°K is about 75%, as compared to 100% for vanadium,[11] 75% for tin,[10] and 65% for mercury.[9]

An important consideration is: are the results characteristic of a thin film in the superconducting state, or, is part of the sample actually normal. The rest of the paper is concerned with this question.

III. MEASUREMENTS

Sample

The sample was made by the evaporation of one layer of aluminum onto large sheets of Mylar. The estimated thickness of the aluminum was 200 Å. The calculated and measured critical field of 7 kG at

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