Nuclear Spin Relaxation in Superconducting Mixed-State Vanadium

WARNER FITE, II,* AND ALFRED G. REDFIELD
IBM Watson Laboratory, Columbia University, New York, New York
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Nuclear spin relaxation was studied by polarizing nuclear spins in 10 kG, quickly lowering the field to the mixed state, and after variable time applying 6 kG and observing a rapid-passage signal. Samples were wires and foils of resistance ratio up to 90, and were fairly reversible. In the normal state at 5.4°K, the relaxation rate at zero field is about one-third that at high field in these samples, the change in rate occurring at fields greater than 30 G. This behavior is attributed to electric quadrupole interactions due to residual imperfections in the lattice. In the zero-field (Meissner) superconducting state, T_1 becomes long at low temperatures, consistent with a gap of order $3.5kT_c$; but just below T_c, T_1 appears to be greater than in the normal state, in contrast to its behavior in other superconductors such as aluminum. This may be due to trapped flux; the possibility of strain-enhanced electric quadrupole relaxation was also considered but estimated to be negligible. In the mixed state, just above H_{c1}, where about half the sample is farther than a coherence length from a vortex, nonexponential decays are observed. Below 1°K the long component of the decay is spin-diffusion-limited, apparently, and the spin-diffusion coefficient is inferred and compared with theory. At these low flux densities the decay can be made nearly exponential by applying a few-gauss 100-Hz field during the time the sample is in the mixed state, presumably moving the vortex structure in and out and making a spin relax at the space-average rate. The space-average relaxation rate changes nearly linearly with flux density, from its normal-state value at H_{c2} to its zero-field superconducting value, at most temperatures. The resolution was not sufficient to establish significant impurity-dependent effects.

I. INTRODUCTION

MEASUREMENT of nuclear spin relaxation time in superconductors by the field cycling technique[1–3] has the advantage that bulk samples of known purity can be used, but this technique is difficult for vanadium because of its fairly short[4] T_1 and high critical field.[5–7] Nevertheless, we undertook to overcome these difficulties because the band structure and relaxation mechanisms in vanadium are different from those in other metals already studied,[8] and, later, because vanadium is one of the two elementary type-II superconductors.[6,7]

For the most part, our data[9] confirm what is expected from earlier measurements and the accepted picture of the mixed state.[10–15] Spins far from vortices relax as they would in a type-I material like Al, while spins within a coherence length of a vortex center relax at a rate comparable to that in normal material. One feature of this technique which may be unique is that these two kinds of behavior can be seen at the same time in a single sample at a suitable field, showing directly that the sample is inhomogenous.

The only important feature of our data for which we have no simple explanation is the lack of observation of a drop in T_1, as the temperature is decreased below T_c. Such an increase in relaxation rate is seen in all other superconductors except V_3X compounds,[14] and is thought to result from the pile-up in the density of states near the edge of the energy gap.[1] This anomaly in our vanadium measurements could be due to trapped flux in our samples, together with a smeared out critical temperature; or electric quadrupole relaxation by conduction electrons; or experimental error. None of these three explanations seems probable, and this may be an anomaly characteristic of a *d*-band superconductor.

Measurements on the field distribution in type-II vanadium will be described in the following paper.[16]

II. EXPERIMENTAL METHOD

A. Samples

Vanadium from three sources was studied; we designate the samples in order of increasing purity (or at

* Also at Physics Department, Columbia University. Present address: General Telephone and Electronics Laboratories, Bayside, New York.

[1] L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1594 (1959).
[2] Y. Masuda and A. G. Redfield, Phys. Rev. **125**, 159 (1962).
[3] A. G. Anderson and A. G. Redfield, Phys. Rev. **116**, 1504 (1959).
[4] J. Butterworth, Phys. Rev. Letters **5**, 305 (1960).
[5] R. Radebaugh and P. H. Keesom, Phys. Rev. **149**, 209 (1966).
[6] R. Radebaugh and P. H. Keesom, Phys. Rev. **149**, 217 (1966).
[7] R. B. Martin and A. C. Rose-Innes, Phys. Letters **19**, 467 (1965).
[8] Y. Yafet and V. Jaccarino, Phys. Rev. **133**, A1630 (1954).
[9] Preliminary descriptions of this work were published in W. Fite, II, and A. G. Redfield, Phys. Rev. Letters **17**, 381 (1966); and in the Proceedings of the 10th International Conference on Low Temperature Physics, Moscow, 1966 (unpublished).
[10] P. G. de Gennes, *Superconductivity of Metals and Alloys* (W. A. Benjamin, Inc., New York, 1966).
[11] Nuclear resonance in type-II superconductors has been reviewed by P. de Gennes in the Proceedings of the 14th Colloque Ampere edited by R. Blinc (North-Holland Publishing Company, Amsterdam, to be published). This article describes unpublished theoretical work by C. Caroli, M. Cyrot, J. Matricon, and Lj. Dobrosavljevic.
[12] C. Caroli, P. G. de Gennes, and J. Matricon, Phys. Letters **9**, 307 (1964).
[13] C. Caroli and J. Matricon, Phys. Kondens. Materie **3**, 380 (1965).
[14] B. G. Silbernagel, M. Weger, W. G. Clark, and J. E. Wernick, Phys. Rev. Letters **17**, 384 (1966); Phys. Rev. **153**, 535 (1967).
[15] Y. Masuda and K. Asayama, J. Phys. Soc. Japan **20**, 1290 (1965); **21**, 1459 (1966).
[16] A. Redfield, Phys. Rev. **162**, 367 (1967).

least resistance ratio) as M, A, B; corresponding resistance ratios (300°K/5.5°K) were 15, 35, 90. Critical temperatures for samples M and A were (5.225±0.02)°K and (5.28±0.02)°K, respectively; T_c was not measured for sample B. These T_c values are consistent with the systematics of T_c versus resistance ratio noted by Radebaugh and Keesom,[5] who conclude that pure V has $T_c=(5.414\pm0.01)$°K. These authors studied a sample having resistance ratio 140; they concluded that the mean free path in this sample was about 5 times the coherence length, estimated to be 450 Å for pure vanadium. Thus, sample B is "clean" (mean free path=3 coherence lengths), sample A is neither clean nor dirty (both lengths about the same), and sample M is fairly dirty.

Sample M was supplied as 0.4 mm wire drawn from triple-pass zone-refined rod by Materials Research Corporation. It was annealed in a vacuum of about 5×10^{-9}-mm mercury by running current through it; the temperature (~1400°C) was that at which sublimation was appreciable. The wire was cut with scissors into short (~1-mm) pieces after annealing; this could have introduced some cold work but not nearly as much as was present initially. We also tried to purge O_2 from another piece of this wire by exposing the wire to 0.1 atm of H_2 while heating it, and subsequently outgassing the absorbed hydrogen. There was no change in resistance ratio. Reaction of oxygen in the vanadium with hydrogen may be favored thermodynamically, but evidently this process is too slow at these temperatures.

Starting material for sample A was kindly given to us by Dr. George Alers of the Ford Scientific Laboratory, and was iodide vanadium[17] which was left over starting material from the single crystal studied by Radebaugh and Keesom. It was swaged into 0.5-mm diameter wire by Materials Research Corporation, then cut by us into short (3–6-mm) pieces. These pieces, together with a longer piece of uncut wire, were annealed and outgassed for several hours at 1000°C in a starting vacuum of 10^{-8}-mm Hg. The resistance ratio of the uncut wire was then measured.

Sample B was made from material supplied through the courtesy of T. A. Sullivan of the Boulder City, Nevada, Laboratory of the U.S. Bureau of Mines. It was rolled into foil approximately 0.1 mm thick, cut into pieces about 4×6 mm, and annealed like sample B, together with a long foil for resistance-ratio measurements.

Magnetization measurements on samples A and B are described in detail in the following paper.[16] The flux trapped in the samples when the field is reduced rapidly to zero was measured in all three samples at 4.2°K and about 1.5°K, and was always about 10% of H_{c1}. Specifically, at 4.2°K the trapped flux in both samples M and A was 40 G ($=4\pi$ times the magnetization per unit volume) at 4.2°.

[17] O. N. Carslon and C. V. Owen, J. Electrochem. Soc. **108**, 88 (1961).

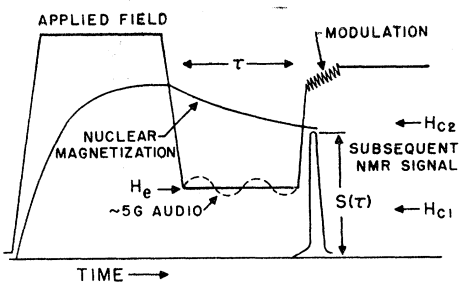

FIG. 1. Field sequence used to measure T_1. A resonant radio-frequency field was applied at the same time as the modulation, through a transmitter coil perpendicular to the main field, to observe the resonance. A 100-Hz audio-frequency field (dashed line) was sometimes applied along the main field, in order to move the fluxoid structure about as discussed in the text.

B. Electronics

The apparatus developed for this experiment was a refinement of apparatus described earlier[2,3]; details are described elsewhere.[18] We briefly review the principle of the method in Fig. 1, for completeness. A field which is as large as possible (10 kG) was applied for a time much longer than T_1, to produce an equilibrium nuclear magnetization; then the field was switched below H_{c2} and the spins relaxed toward their equilibrium magnetization in that field (H_e) with a rate (or rates) characteristic of the mixed state (or the Meissner state, if $H_e=0$). Then the field was switched on to a field where the resonance could be observed with fast passage as described earlier, without undue noise and baseline shift resulting from mixed state or surface sheath superconductivity. A field of about twice H_{c2} seems satisfactory; the lower the observation field the better, since it takes less time to turn on a smaller field. The subsequent signal $S(\tau)$ was recorded as a function of the dwell time τ at the low field H_e.

A superconducting magnet was used to generate the field because of its small size. The resulting small amount of energy stored meant that the field could be turned on faster for a given voltage applied to the coil. The coil used produced a maximum field of more than 10 kG at 15 A; it was a Westinghouse Nb-Zr coil with a coil form split to avoid eddy-current delay of the field variation; the persistent shunt usually supplied on these magnets was cut out and the magnet was supplied by 5 wires, 0.25 mm in diam., run from the top of the Dewar. Of course, the coil contained no shorted copper stabilizing loops such as are used for higher fields. The magnet was compensated for high homogeneity; unfortunately this increases its inductance and may not have been necessary in view of the small volume (0.1 cc) occupied by the sample. The inductance was approximately 200 mH, the inside diameter was 2.5 cm, and the outside diameter was 7 cm.

[18] W. Fite, thesis, Columbia University, 1966 (unpublished). Available from University Microfilms, Ann Arbor, Michigan.

Commercial power supplies, especially those using silicon-controlled-rectifier primary supplies, are usually unsatisfactory for rapid precisely controlled switching of a highly inductive load; one which we tested required nearly a second to recover when the magnet was connected. Much effort was expended to develop a transistorized power supply for this purpose; the circuit will be published elsewhere.[19] The turn-on rate is limited by the voltage which the power supply can apply to the magnet; for the transistors used, this voltage is about 100 V, and in later modifications 60 V. Thus, the 10-kg field could be switched on or off in about 50 msec; correspondingly less time was needed for lower fields.

When the field is cycled to zero, the subsequent signal disappears immediately (i.e., for $\tau=0$) because the nuclear spin system undergoes a nonadiabatic demagnetization resulting from the rapid changes in local field as vortices pass rapidly through the sample. We tried reducing the rate of change of the field when the field was less than roughly H_{c2} by modification of the power supply.[18] The resulting increase in the signal was small, however.

Because of magnetic hysteresis in its own wire, a superconducting solenoid heats when cycled and goes normal if cycled too often. In practice this was not too serious, and we could cycle more than three times per minute.

The silver receiver coil was wound on the inside of a hole in a piece of plastic, which in turn was fastened to a support rod connected to a stainless-steel tube which could be turned from the top of the Dewar. Leads from this coil went directly to a preamplifier and parallel tuning condenser. The transmitter coil consisted of two 10 or 20 turn coils of wire taped with glass tape to the outside of a third miniature unsilvered glass Dewar (described later), which was inside the magnet and contained the receiver coil; the receiver coil was set for crossed coil balance by turning it from above. Glass tape, glass wool, and corrugated copper foil were used liberally to prevent the main helium Dewar, magnet, transmitter coil, miniature Dewar, and receiver coil from rattling with respect to each other. Vibration was especially severe just after the main field was switched on.

The residual rf leakage to the receiver was nulled with a phase-shifted attenuated signal from the transmitter; the resulting small signal was amplified, rf phase-detected, and then lock-in-detected at 1 kHz. The sweep-through resonance was so fast that the signal lasted only about 10 msec, and the selectivity of the narrow-band amplifier of the lock-in amplifier had to be reduced to permit it to reproduce the signal.

Sweep and modulation coils were wound tightly on the superconducting coil to reduce modulation-induced vibration. In later runs, the 1-kHz modulation was generated by the superconducting coil itself, by injecting a 1-kHz voltage in series with the current regulator's voltage reference.

C. Cryogenics

Except for runs between 2 and 4.2°K the receiver coil was placed inside a miniature glass Dewar vessel. This was needed as an oven to get to the sample's critical temperature of 5.3°, and at low temperatures to isolate the sample from large temperature variations of the main bath which occurred whenever the magnet was cycled, because of the magnet's hysteresis which we already mentioned. This Dewar was like that described elsewhere[2] except that it was about 1 cm inside diameter throughout its length so that the receiver coil assembly could be inserted from above.

Below 1.3°K, this Dewar was used as a single-shot He^3 cryostat. Temperature was measured using an oil manometer. The heat leak was large though tolerable, and was possibly due to heat leakage down the receiver coil support from the top, inadequately intercepted at the ring-seal contact with the He^4 bath.

Between 1.3 and 2.2°K the miniature Dewar was filled with liquid He^4 by forcing gaseous helium at atmospheric pressure into the top; then the Dewar was pumped to the desired pressure, which was maintained by bleeding gaseous helium to the pump, and throttling the latter.

For the few runs between 2.2 and 4.2°K, the miniature Dewar was omitted and an open tube inserted to support the transmitter coil.

Above 4.2° the miniature Dewar was used as an oven and a few microns of He exchange gas were admitted. In earlier runs the ring-seal assembly was omitted and the inner and outer tubes of the miniature Dewar went all the way to the top. The pressure on the inside was somewhat less than 1 atm, and the temperature on the outside was 4.2°K. In these runs above 4.2°K, a temperature-sensing resistor was mounted as close to the receiver coil as possible. It was incorporated in a servo loop connected to a heater resistor about 4 cm above the sample coil, to regulate the temperature. Silver wires running vertically were used to aid thermal contact. Typically, about 10 mW was dissipated by the heater.

Critical temperatures were estimated from the onset of strong unbalance of the rf bridge. This may tend to measure the critical temperature of the part of the sample having the highest T_c. Critical temperatures measured with slowly rising temperature agreed within 0.02°K with those measured with slowly falling temperature, so the sample and sense resistor are apparently in equilibrium. The resistor was assumed to obey the formula of Clement and Quinnell[20]; it was calibrated below 4.2°K and extrapolated above. The magnetocaloric effect, which must be considered in a field

[19] A. G. Redfield, W. Fite, and H. Bleich (to be published).

[20] J. R. Clement and E. H. Quinnel, Rev. Sci. Instr. **23**, 213 (1952).

cycling experiment, is assumed to be negligible and is certainly so close to T_c.

Resistance ratios were measured using a crude four-terminal method and a microvoltmeter. The sample holder was moved in and out of a storage Dewar, and a well-defined plateau in the resistivity versus height was observed just before the sample went superconducting. This method works because of the comparative impurity of these samples.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. General

As usual in this type of experiment, the subsequent signal $S(\tau)$ is measured as a function of τ, particular care being required to get as good a value as possible of $S(\infty)$, the signal for very long τ. $S(\infty)$ is nonzero even if H_e is zero because if T_1 is short, the spin system repolarizes itself during the time between when the field starts to come on and the time when resonance is reached (about 50 msec). The $S(\tau)-S(\infty)$ is plotted on semilog paper as a function of τ, frequently yielding what appears to be a straight line whose slope gives T_1.

At low temperatures, and for $H_e \lesssim 0.5H_{c2}$, nonexponential decays were observed. Sample data are shown in Fig. 2. At these fields, more than half the spins may be more than a coherence distance from a vortex. At such a distance the local T_1 is expected to be about the same as in type-I material, and is therefore long because kT is small compared to the gap energy. Close to a vortex, the local T_1 is expected to be comparable to that in normal metals because localized excitations are thought to exist which have no gap (or only a very small gap) in their energy spectrum.[10,13]

It is possible to measure the range of these localized excitations by comparing the size of the slow-decay component of signal, due to spins far from vortices,

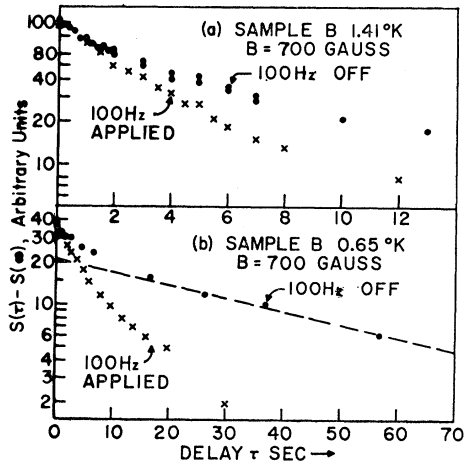

FIG. 2. Sample plots of signal variation versus τ, with and without a 100-Hz field of a few gauss applied along H_e. Nonexponential decay is seen only for $T \lesssim 2°$K and $B \lesssim 1500$ G.

with the total signal. As expected, the range is of the order of the coherence length.

The possibility that the observed nonexponential decay might be due to macroscopic variations in the flux density is fairly well ruled out by the field-distribution studies described in the following paper, and to a lesser extent by a technique suggested by those experiments (Fig. 1). We applied a 100-Hz ac field along the main field direction during the time that the spins were relaxing. It is reasonable[16] (though not certain) that such a field will impel vortices to move in and out of the sample. In particular, if the sample's response to the applied field approximates its thermal equilibrium response, a few parts per thousand change in H_e will result in a few parts per thousand change in B (which is presumed equal to $\phi_0=hc/2e$ times the number of vortices per cm^2). The lateral dimensions of the samples are 0.5 mm or more, and therefore they are several thousands of vortex diameters wide. Thus a change in vortex density of a few parts per thousand means that over most of the sample the vortex structure moves in and out a distance of several vortex diameters, and a given spin therefore samples a fairly representative distribution of the relaxation rates for various distances from vortices. As expected, the relaxation becomes shorter and more nearly exponential.

The inverse of the time constant of the exponential decay induced with the help of the 100-Hz ac field should be the space average, $\langle T_1^{-1}\rangle$, of the relaxation rate. Experimentally it agrees fairly well with the initial slope of $S(\tau)-S(\infty)$ plotted on semilog paper versus τ; this initial slope can easily be shown theoretically to equal $\langle T_1^{-1}\rangle$ also.

That nuclear spin flips were not being induced by direct interaction with the large and possibly erratic field changes resulting from vortex motion could be checked by noting that $S(\infty)$ did not change when the 100-Hz field was applied. That part of $S(\infty)$ which comes from the fact that H_e is nonzero would be wiped out by such transitions, because the transition probability would be the same in both directions, unlike relaxation transition probabilities which differ by the Boltzmann factor.

In the data summaries which follow, T_1 or $\langle T_1^{-1}\rangle$ is given as a function of the applied field H_e. Sample B was in the form of nine foils, stacked with plastic tape and aluminum foil between, whose volume was about twice that of the vanadium. The field was applied perpendicular to the surface. Thus, for sample B, $H_e \simeq B$ to within a few percent, as discussed in the following article in more detail. Later runs on sample A were done using 16 pieces of wire aligned perpendicular to H_e. Approximating these as isolated infinite cylinders, we have $B=H_e+2\pi M=H+4\pi M$ from classical magnetostatics. Earlier runs on sample A used unaligned wire; for these B is inhomogeneous, and B is between $H_e+2\pi M$ and $H_e+4\pi M$, closer to the former on the average. For most of the points taken, $2\pi M$ is

small compared to H_e, so $B \cong H_e$ is an appropriate approximation in view of the low accuracy of our T_1 data.

B. Normal State

At high fields (greater than H_{c2}, and also greater than about 100 G), in the normal state, our measurements of T_1 are consistent with the result $T_1T=0.788$ sec°K obtained by Butterworth[4] at higher temperatures. Our measurements were made down to 0.65°K. Relaxation is thought[8] to be largely via the orbital interaction between the moving charge of the electron and the nuclear magnetic moment.

In the normal state, T_1 is field-dependent because when the external field splitting $\hbar\gamma H_e$ becomes comparable with internal field splittings, the character of the nuclear spin Hamiltonian changes.[3] In a perfect crystal the internal field splitting would be the nuclear dipole-dipole interaction, equal to $\hbar\gamma H_e$ where $H_e \cong 5$ G, for vanadium. In our samples, which presumably contain residual strains due to impurities, the internal field is probably mainly the electric quadrupole splitting resulting from these strains.

While the normal-state field dependence and its source are not tremendously interesting in themselves, they are relevant to the superconducting-state measurements because the field dependence observed in the normal state is likely to be superimposed on the local T_1 in the superconducting state. Variations in T_1 in the superconducting state can thus be caused by variation in field alone, as well as variations in the energy gap, order parameter, etc.

A few measurements of T_1 versus H_e were made just above T_c in samples M and A. In both cases the ratio of high to low field T_1 is about 3.3, slightly greater than the ratio 3 expected[3] if the electric quadrupole splitting is much larger than the dipole-dipole interaction as we believe. If relaxation is via electric quadrupole interaction rather than magnetic dipole interaction, as explored in the Appendix, this ratio is expected to be about 2 (for spin $\frac{3}{2}$).[21]

If the state of the spin system is described by a single spin temperature, T_1^{-1} is expected to be proportional to $(H_e^2+BH_Q^2)/(H_e^2+H_Q^2)$, where $\gamma^2H_Q^2$ is proportional to the mean-square quadrupolar interaction energy, expected to be greater for less pure samples. For sample M, H_Q is about 80 G; for sample A it is roughly 20 G, much greater than the dipolar interaction energy. For both samples B is about 3.3 as mentioned above. From the fact that H_Q is much larger than the dipolar field, we conclude that most spins feel a quadrupole splitting considerably larger than the dipolar splitting, and that therefore the subsequent signal came mostly from the unsplit $m_I=\frac{1}{2} \rightleftarrows m_I=-\frac{1}{2}$ transition (this was not readily verified directly because absolute intensity measurements were rendered difficult by skin effect). This quantity γH_Q is presumably of the order of the quadrupole splitting felt by a typical spin. Probably the spin-temperature assumption is not strictly valid here; Hebel[22] has discussed this problem in detail.

C. Superconducting State Far from Vortices or in Zero Applied Field

Sample M was studied for $H_e=0$ only (and, of course, no additional ac field applied). Except near T_c, the subsequent signal was about $\frac{1}{5}$ as large as would have been expected if only relaxation occurred. The same behavior has been seen in type-I superconductors such as Al,[1,2,23] and is presumed due to nonadiabatic (rapid, irreversible) demagnetization of most of the spin system as a result of rapid motion of domains across the sample. If the field at a point in the sample goes from a value greater than, say, H_Q, to nearly zero in a time shorter than about $(\gamma H_Q)^{-1}$, the local spin order will almost surely be destroyed. That happens because the adiabatic condition of quantum mechanics is then violated. Within about 0.05° of T_c the reduction of signal by this mechanism is less severe presumably because H_{c1} becomes less than H_Q and the internal field decreased below H_Q smoothly.

Zero-field points for sample M are included in Fig. 3 as open squares, as well as a few zero field points taken on sample A (open circles). Except near T_c it is likely that the signals used to obtain these measurements came from regions of trapped flux, with a low but

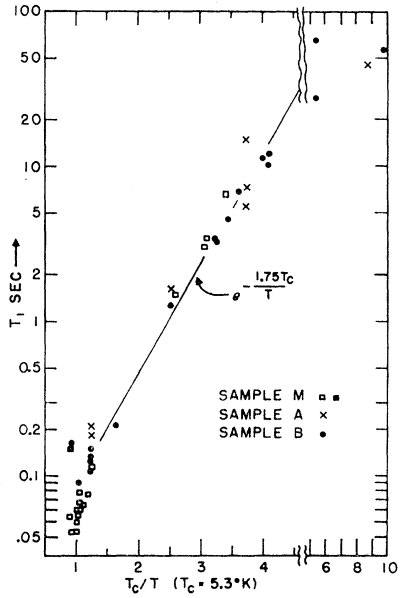

FIG. 3. Relaxation time of spins for from vortices, deduced from zero-field data on sample M, and from long-τ behavior in a field B of order H_{c1} in samples A and B. The open circles and squares were taken with $H_e=0$.

[21] B. C. Johnson and W. I. Goldburg, Phys. Rev. **145**, 380 (1966).

[22] L. C. Hebel, Phys. Rev. **128**, 21 (1962).

[23] D. E. MacLaughin and E. L. Hahn, Phys. Rev. **159**, 359 (1967).

nonzero density of vortices in the mixed state. This seems likely for three reasons: First, in such regions the spin Hamiltonian retains its mostly Zeeman character, if the field is everywhere greater than H_Q, so that the adiabatic condition is fulfilled no matter how rapidly the local field changes, as long as the local trapped field does not point in too different a direction than the polarizing field; second, the 20% of signal retained after cycling is consistent with the trapped flux ($\sim$10% of H_{c1}) typically found after demagnetization; and finally we usually found in sample M that the signals for very short τ were greater than expected from exponential extrapolation back from longer τ, suggesting a nonexponential decay due to a trapped mixed state. We believe, then, that the decay is characteristic of spins far from vortices but probably in a local field of more than 100 G, as would occur if vortices tended to be trapped in clusters where the average flux density ("local B") is several hundred gauss or more.

Most of the data on samples A and B were taken at fields B of the order of $0.2H_{c2}$ or more, because then the loss of signal mentioned above was small or absent, and at fields of 0.2 to $0.3H_{c2}$ a distinct exponential tail was more accurately measurable after the initial rapid decay of signal versus τ. Representative points obtained in this way are included in Fig. 3; because of the low signal-to-noise ratio and the errors inherent in estimating the final slope of a nonexponential decay, the large scatter is not too disturbing.

In the intermediate temperature region, between 4.2 and 1.4°K, the data are in reasonable agreement with the expectation that the relaxation rate varies as $\exp(-\epsilon_0/kT)$, with the gap $2\epsilon_0$ equal to about $3.5kT_c$ as indicated more accurately by other measurements.[5,24] There is no consistent variation of T_1 with purity except possibly at 4.2°K; from measurements on Al containing impurities[25] we would expect none. At 4.2°K it appears that T_1 increases with increasing purity, but the data are far from conclusive on this point.

Near the Critical Temperature

We do not find the dip in T_1 just below T_c which is seen in all other accurate T_1 measurements in superconductors (other than vanadium compounds). It is possible that this reflects some unrecognized property of transition metal and/or type-II superconductors. We briefly discuss all the reasons we can think of to explain this behavior; none is completely convincing.

The effect could be experimental error or noise; but the signal-to-noise ratio is higher just below T_c than at lower temperatures; and there seems little likelihood that the apparent T_1 could be shortened artificially if the field drops cleanly to zero, which we checked.

Anisotropy of the energy gap[2,26] can increase T_1; but to obliterate the T_1 decrease below T_c would require that the anisotropy be a large fraction of the gap itself, which is unlikely and not indicated by any other experiments.

Nuclei with electric quadrupole moments can be relaxed by electric field interaction with the charges of conduction electrons.[27,28] If this were the predominant interaction producing relaxation, the temperature dependence of T_1 would be similar to that indicated by Fig. 3. The matrix element for relaxation is affected, near the gap, by the spin pairing correlations in the BCS wave function and T_1 is predicted to drop just below T_c for all magnetic interactions and to rise for electric interactions.[29] Theoretical estimates of this mechanism show it to be about $\frac{1}{2500}$ as effective in vanadium as the orbital relaxation which is thought to predominate.[27] The estimate is fairly reliable since both electric quadrupole and orbital relaxation depend on the same average $\langle 1/r^3 \rangle$ of the d-band wave function.

Electric quadrupole relaxation could be enhanced by the deformation in the lattice produced by a passing conduction electron, which sets up a field gradient just as an ultrasonic wave does. This mechanism would produce the same temperature dependence of T_1 as the direct electric quadrupole interaction. We present a crude treatment of this mechanism in the Appendix which indicates that it is probably not as important as the direct electric interaction.

Last, and most likely, the decrease in intrinsic T_1 may be counteracted by the presence of large amounts of trapped flux near T_c. Unfortunately, it was not convenient to measure trapped flux with our apparatus above 4.2°K, and we did not do so. Trapped flux will raise T_1 for two reasons: First, T_1 tends to increase as the field is raised above about 50 G because the nuclear spin Hamiltonian changes character, as mentioned in Sec. II B above; second, T_1 tends toward its value for the normal state, and thus tends not to decrease near T_c, for spins close to vortices. The second effect is likely to be unimportant because it requires a trapped flux density comparable to H_{c2}, and offers no explanation for the fairly sharp rise in T_1 below T_c. But unfortunately the first effect is not so plausible either. In regions of trapped flux spins would see fields probably not much greater than H_{c1}. For a region from T_c to 0.1°K less than T_c, H_{c1} is less than about 50 G, and over this region the drop in T_1 might be observed. Several runs were made about 0.05°K below T_c, and T_1 was never less than its normal-state ($\sim$50 msec) value at T_c^+ and zero field. (The trapped field remaining in the magnet when it

[24] P. L. Richards and M. Tinkham, Phys. Rev. **119**, 575 (1960).
[25] Y. Masuda, Phys. Rev. **126**, 1271 (1962).
[26] L. C. Hebel, Phys. Rev. **116**, 79 (1959).
[27] Y. Obata, J. Phys. Soc. Japan **19**, 2348 (1964).
[28] A. H. Mitchell, J. Chem. Phys. **26**, 1714 (1957).
[29] See, for example, Sec. 11.1 of the article by J. Bardeen and J. R. Schrieffer, in *Progress in Low Temperature Physics* edited by C. J. Gorter (North-Holland, Publishing Company, Amsterdam, 1961), Vol. III.

was turned off was measured to be less than 5 G.) We were sure that the sample was below T_c because of the sharp unbalancing of the rf bridge when the sample goes superconducting.

If the transition temperature were smeared by as little as 0.1°K, the sharp dip and rise in T_1, expected to occur over a 0.1°K range in a pure sample, might well be smeared out. According to Fig. 4 of Ref. 5, that would require variations in purity of nearly a factor of 2 for different parts of the sample.

If we accept trapped flux as the explanation, then we expect that T_1 is increased by a factor of over 3 by the "normal" T_1 variation, just below T_c. Since we observe that T_1 quickly rises to very roughly twice its normal state value, we would conclude that the drop in the inherent, isolated spin, relaxation time is about a factor of 1.5. The corresponding factor in aluminum is about 2.

In conclusion, we mention that at an applied field of 100 G, in sample A, there *is* a drop in T_1 just below T_c. That is, at 100 G and 5.3°K, T_1 is about 140 msec; at 5.0°K and the same applied field it is less than 90 msec. This observation tends to support the view that the observed temperature dependence reflects the field dependence found in the normal state, produced by trapped flux. This decrease seems to be absent in sample B; and sample M was not studied except at zero H_e.

Spin Diffusion

At temperatures below 1°K and $B<1000$ G the long tail of the signal versus τ plot ceases to have a decay rate which depends strongly on temperature; for $B\cong$ 800 G the long component of relaxation is about one minute between about 0.65 and 0.9°K, based on a few runs only [Fig. 2(b) and Fig. 3]. The extrapolated T_1 based on a gap model (with gap $3.5kT_c$) is many thousands of seconds at 0.65°K. This shortening of T_1 is not likely to be due to slow diffusion of vortices because that would be thermally activated.

It is possible that this effect could be explained by invoking a small s-band energy gap. Evidence for this gap exists in the heat capacity data of Radebaugh and Keesom; the gap is indicated by their data to be less than $0.1kT_c$ (that is, so small that the heat-capacity contribution is proportional to T) and the apparent (heat-capacity) density of states ρ is $\frac{1}{200}$ the normal value. The hyperfine interaction for s electrons is about ten times the orbital and dipolar interactions for d electrons in vanadium, according to the estimate of Yafet and Jaccarino.[8] The relaxation rate, being proportional to the square of ρ and the square of the hyperfine interaction, might thus be about $\frac{1}{400}$ that in the normal state (compared to $\frac{1}{100}$ experimentally). If this were the predominant mechanism it would be proportional to temperature. The temperature range of our data is too small to identify the mechanism in this way.

The relaxation of spins far from vortices can also take place via spin diffusion of their energy to regions close to vortices. This mechanism was proposed and discussed by Caroli and Matricon[13] and was invoked by Silbernagel *et al.*[14] to explain their T_1 measurements in vanadium compounds. It would be expected to be strongly field-dependent, as we will see, but unfortunately we didn't check this point (at this writing) in sufficient detail to show that this is the mechanism and not the (field-independent?) one mentioned in the previous paragraph. The few observations do fit the spin-diffusion model remarkably well, however.

We present a simplified version of the more exact discussion of Caroli and Matricon. Far from vortices, direct relaxation is negligible and the magnetization obeys a diffusion equation; within a radius r_T of the order of the coherence length the relaxation rate rises rapidly and, in the model, will be taken as infinite. The hexagonal unit cell centered on a vortex is replaced with a circular unit cell of radius $r_c=(\phi_0/\pi B)^{1/2}$, where $\phi_0=hc/2e$ is the flux expected to thread each vortex. The nuclear magnetization M diffuses in the annular region between r_T and r_c; at r_c its gradient is zero and at r_T it equals (after a short time) its equilibrium value ($\cong\chi B$, neglecting variations in local field h which are comparatively small outside r_T). If r_T/r_c is greater than about $\frac{1}{2}$, it is a fair approximation to replace the annular region by a strip of width r_c-r_T. The lowest decay mode of the diffusion equation in such a strip has a time constant $T_1=4(r_T-r_c)^2/\pi^2D$ and this mode contains a fraction $8/\pi^2$ of the total initial (constant) magnetization change in the strip. Thus, the long decay mode has a zero τ intercept which is a fraction $(8/\pi^2)[(r_c^2-r_T^2)/r_c^2]$ of the total

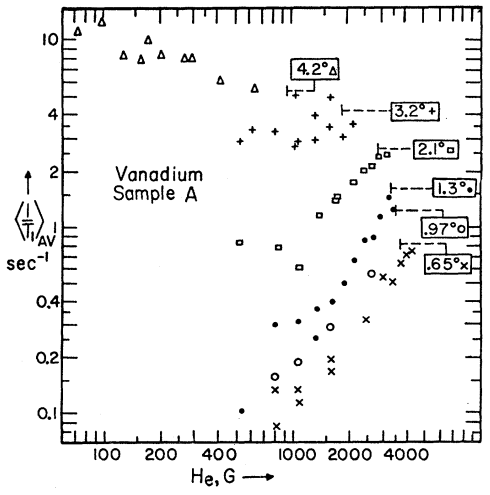

FIG. 4. Space-average relaxation rate for sample A. The horizonal dashed lines attached to the temperature specifying boxes give T_1^{-1} for the normal state as deduced from Butterworth's measurements. The left-hand ends of these dotted lines give H_{c2} at that particular temperature. H_e is the applied field. Runs at 4.2°, 2.1°, and 1.3°K are on randomly oriented wires; the other runs are on wires with axes perpendicular to H_e.

zero τ signal. This intercept ratio is the intercept of the dashed line in Fig. 2(b) divided by the actual signal at zero time.

In Fig. 2(b), the intercept ratio is 0.42 and r_c is 965 Å, and we deduce $r_T=670$ Å, slightly larger than the estimated[6] coherence length (450 Å for pure V). From the long-time T_1 of 45 sec, we calculate a spin-diffusion coefficient D of 7.7×10^{-14} cm²/sec. In another run on sample A aligned perpendicular to the applied field of 1070 G, B was estimated (from measurements described in the following paper) to be 855 G, the intercept ratio was 0.45, and the long time T_1 was 55 sec. From these numbers we get $r_c=875$ Å, $r_T=550$ Å, and $D=4.6\times10^{-14}$ cm²/sec. The diffusion coefficient was estimated theoretically to be 6.5×10^{-14}. Both theory and experiment have an accuracy of only $\pm20\%$ or worse, so the agreement is satisfactory.

The theoretical estimate of D is too technical to give here, but the physical assumptions are simple.[30] We know that there is a quadrupole interaction of the order of 50 kc for most of the spins. This interaction changes the energy difference between adjacent nuclear m_I levels, except the pair $m_I=\pm\frac{1}{2}$. The strain which produces the quadrupole interaction is likely to be sufficiently different for neighboring spins that all the $\Delta m_I=1$ frequencies of a given spin differ by more than a few kilocycles from all those of a neighboring spin, except the unsplit $\frac{1}{2}\rightleftarrows-\frac{1}{2}$ frequencies. Therefore, we assume that only the $\pm\frac{1}{2}$ transitions are effective in spatially transferring energy; these occur every millisecond or so. A second assumption is that the entire system of eight spin levels is in local thermal equilibrium with the $\pm\frac{1}{2}$ levels, e.g., the ratios of populations for adjacent m_I values are locally equal. This is plausible for moderate quadrupole splitting since four-spin processes can transfer population from the $\pm\frac{1}{2}$ levels to the other levels. If these processes occur every second or so, local equilibrium will be maintained during a 1-min decay. These assumptions reduce D by a factor of 27 relative to a perfect crystal with no quadrupole splittings. Possible quenching of diffusion because of magnetic field gradients is negligible since the local field difference between adjacent spins is less than a gauss, small compared to the dipolar interaction.

Two low B runs were made on sample A at 0.97°K; the long time T_1's were 65 sec for $B=480$ G and 27 sec for $B=855$ G; intercept ratios were 0.5 and 0.45, respectively. Assuming $D=6\times10^{-14}$ cm²/sec, we conclude that $r_T=690$ Å at $B=480$ G and 585 Å at 855 G. This field dependence gives positive but meager evidence that spin diffusion is taking place.

Probably further theoretical and experimental work would be worthwhile; precise measurement of r_T versus B and T might yield information on the spatial variations of the fermion excitations within a vortex, and identify the relaxation mechanisms more certainly.

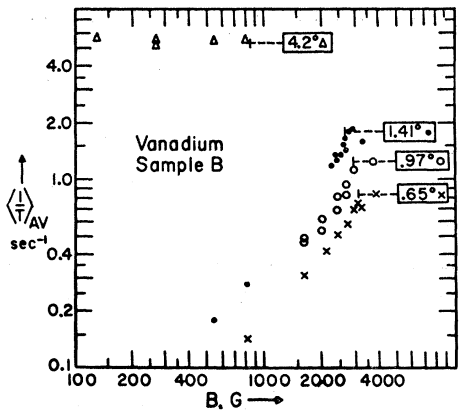

FIG. 5. Space-average relaxation rate for sample B. The normal-state relaxation rate and H_{c2} are indicated as in Fig. 4.

D. Space-Average Relaxation Rate

A survey of the temperature and magnetic field dependance of $\langle T_1^{-1}\rangle$ for samples A and B was made and is summarized in Figs. 4 and 5. The points plotted are the slope of $\ln[S(\tau)-S(\infty)]$, where $S(\tau)$ is the subsequent signal after dwelling at H_a for time τ. Either the initial slope in the absence of any longitudinal 100-cps magnetic field, or the slope of the more or less straight line obtained in the presence of a few gauss of 100-cps field is plotted. The latter method is less affected by noise when the decay is nonexponential; on the other hand, it is possible to shorten artificially the decay by applying too large a 100-Hz field, presumably because of high-frequency components of transverse field felt by a spin as partly pinned vortices move past it. These high-frequency components induce nuclear transitions in both directions with equal probabilities and thus tend to destroy completely the nuclear magnetization. To minimize these effects, we used the smallest possible 100-Hz field needed to give a nearly exponential decay; and in a few cases we checked that $S(\infty)$ was unchanged by the 100-Hz field. The latter precaution is not very meaningful because at the fields where the 100-Hz field was needed, H_a was so small that the expected change in $S(\infty)$ would be only a few times noise.

The data can be summarized by saying that $\langle T_1^{-1}\rangle$ decreases monotonically, and nearly linearly, with the

[30] The calculation is based on the paper of A. Redfield [Phys. Rev. 116, 315 (1959)] assuming $g(\omega)$ Gaussian and truncating I_x and I_y in spin-spin Hamiltonian (I_z is not truncated). Some minor further approximations are made to simplify the calculations, which will be published elsewhere (by A. Redfield). The The method is equivalent to the perturbation approximation of I. J. Lowe and S. Gade [Phys. Rev. 156, 817 (1967)]. Unfortunately the calculation may be completely invalid because the local magnetic field felt by a spin due to its neighbors changes with a correlation time comparable to or longer than the average time between spin flips involving $|m_I|\pm\frac{1}{2}$ levels, and the time for two spins in their $|m_I|=\frac{1}{2}$ levels to flip may just be limited by the time it takes for them to reach the same local field due to flips of their near neighbors. Local field motion is slowed down because of quadrupole quenching of spin flips of neighbors.

flux density B, from its normal state value T_{1N} at H_{c2} to its zero-field value given in Fig. 3.

At low T ($<2°$K), where these two rates differ greatly, this means that $\langle T_1^{-1}\rangle=(B/H_{c2})fT_{1N}^{-1}$, where f is a function which varies between one (at H_{c2}) and 0.6 or more (at $B\cong 0$). Here relaxation outside the coherence length (450 Å for pure vanadium) is small or negligible, and the only contribution to the space average of T_1^{-1} comes from the region inside a coherence length. At low B (low fluxoid density), it is very generally expected that T_1^{-1} is proportional to B, as was shown explicitly for dirty superconductors.[31] We studied the low-field behavior of samples A and B and verified this expectation.

We also searched for interesting behavior of $\langle T_1^{-1}\rangle$ near H_{c2} at low T, but found only the onset of the linear decrease with B, and no sign of a stronger singularity. Any singularity might be washed out by the breadth of the transition at H_{c2}, presumably because of sample purity variation. At low T, the breadth of the transition inferred from magnetization measurements is about 3% of H_{c2} in sample B, and two or three times greater in sample A (see following article).[16]

At high temperatures, sample A appears to follow the behavior predicted by Cyrot[31] and by Eppel, Pesch, and Tewordt[32] for dirty superconductors. That is, T_1^{-1} increases below H_{c2}, for T greater than about $0.6T_c$. Detailed comparison with Cyrot's theory is not possible because this sample is neither "clean" nor "dirty"; its electronic mean free path is about equal to the 450 Å coherence length deduced by Keesom and Radebaugh for pure vanadium.

The same change in slope of T_1^{-1} versus B is also expected theoretically[31] in a clean sample, for some temperature around $T_c/2$. There is no evidence for this in the case of sample B, which is fairly clean. This is the only experimentally discernible difference between the T_1 data for samples A and B.

ACKNOWLEDGMENTS

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APPENDIX

We will make a crude estimate of the strain enhancement of the interaction between the conduction-electron charge and the nuclear quadrupole moment. Yafet[33] calculated this enhancement independently; he kindly pointed out that an earlier estimate of it by one of us was too large.

Consider first the direct interaction, due to the electrostatic potential contributed by the quadrupole moment $\phi_n\sim eQ/r^3$, where e is the electron charge, Q the nuclear quadrupole moment, and r the distance. It produces a scattering matrix element $e^2Q\langle r^{-3}\rangle_d$ for d electrons (unit cell normalization), where $\langle r^{-3}\rangle_d$ is the average of r^{-3} for a d electron, which is estimated to be 10.3 Å^{-3}, nearly the same as for a d orbital. The scattering probability for this process is temperature-independent exactly at the Fermi surface, but the number of electrons permitted to scatter by the Pauli exclusion principle is proportional to kT. Some large constant fraction of these scatterings also flip the nucleus, giving a nuclear flip rate proportional to T. (Semiclassically, the precessing nucleus provides a time-dependent perturbation which changes the electron energy; this energy must come from a nuclear flip.)

We now apply the same sort of reasoning to estimate the strain-enhanced effect. We estimate the strain produced by a static nuclear quadrupole moment; the same fraction of the resulting deformation potential scattering produces a spin flip as in the direct case.

If the quadrupole moment were bare it would produce a field at the closest neighboring nucleus at a distance a_0 (2.6 Å) of $E_N\sim 3eQ/a_0^4$, the gradient of ϕ_N at a_0. The force on this nucleus in the real metal can be written $F=\lambda eE_N$, where eE_N is the force on a unit charge and λ is a number which gives the enhancement of the strain-quadrupolar interaction in the real metal relative to a point charge (unit charge e per atom) model. The number λ includes such effects as conduction-electron shielding, core-electron shielding, and Pauli exclusion interaction between cores. It is estimated[34] to be about 10 for Cu, and we will assume the same for V.

We will consider only the perturbation produced by displacement of nearest neighbors—justified by the crudeness of our estimate— and treat these neighbors in an Einstein approximation, bound to their unperturbed sites by Hooke's law with force constant k. Thus the displacement is $\delta x=F/k$, and $\omega_D^2=k/M$, where M is the nuclear mass and ω_D is the Debye frequency. ω_D is of order c_s/a_0, where c_s is the velocity of sound.

We write the matrix element for scattering as a deformation potential times the fractional strain:

$$V_s'=\phi_d\delta x/a_0.$$

The deformation potential ϕ_d could be deduced from the high-temperature electrical resistivity, which is about ten times that of simple metals. This difference is mainly due to the higher effective mass of the d electrons, and so we guess that ϕ_0 is about that for other metals, one eV or so, for displacement of a single

[31] M. Cyrot, J. Phys. (Paris) **27**, 283 (1966).
[32] D. Eppel, W. Pesch, and L. Tewordt, Z. Physik **197**, 46 (1966).
[33] Y. Yafet (private communication).
[34] P. Sagalyn, A. Paskin, and R. Harrison, Phys. Rev. **124**, 428 (1961).

atom. Here we have all eight nearest neighbors displaced by roughly this amount, and their perturbations add at the unit cell containing the quadrupole moment under consideration, so we guess ϕ_0 is 10 eV or less.

Combining all the relations above we get

$$V_s'/V_s = 3\phi_0\lambda/a_0^2 M\omega_D^2\langle r^{-3}\rangle_d a_0^3 = 3\phi_0\lambda/Mc_s^2 a_0^3\langle r^{-3}\rangle_d.$$

Using the guesses for $\langle r^{-3}\rangle_d$, λ, and ϕ_0 given above, this ratio is about 1/50, showing that the enhancement may conceivably be a few percent but that it is unlikely to make electric relaxation competitive with orbital relaxation. That would require that the ratio V_s'/V_s be about 50, and that either λ or ϕ_d be very much larger than estimated.

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Local-Field Mapping in Mixed-State Superconducting Vanadium by Nuclear Magnetic Resonance

ALFRED G. REDFIELD
IBM Watson Laboratory, Columbia University, New York, New York

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A 10-kG field was applied to polarize the spins; it was then quickly reduced below H_{c2}, and remained there for about 0.1 sec, during which time a transverse ac probe field of frequency ν_p was applied. Then the large dc field was reapplied and a rapid-passage resonance signal observed in order to measure the effect of the probe field, the decrease in this subsequent signal reflecting the NMR absorption. Except near H_{c2} the probe field only burns a small hole in the nuclear magnetization, and it was also necessary to move the vortex structure about by applying a 100-Hz field of a few gauss during the time that the sample was in the mixed state. Detailed studies are reported for a multiple foil sample of vanadium with main field perpendicular to the surface; aluminum foil was interleaved, and the flux density B was measured using the Al^{27} NMR by exactly the same field-cycling resonance as applied to the vanadium. The magnetization was measured ballistically in the same magnet and field cycle. For flux density around $\frac{1}{2}H_{c2}$ the line shape almost uniquely implies a triangular vortex lattice. At high probe power, the effect of the probe field is still confined to the same definite frequency range as at low power, as would be the case for a completely ordered vortex lattice; this implies order over several vortex-lattice spacings. Accurate measurements are presented of the field at a vortex center and at the saddle point halfway between two vortices, and of the average flux density B, as a function of H, in a fairly clean sample at 1.4°K. These parameters determine an accurate field map. Near H_{c2} the field at a vortex center equals H, with a deviation of second (or greater) order in $H-H_{c2}$. The linewidth is greater, for a given magnetization, than would be expected from solutions of the Ginsburg-Landau equations. By extrapolation to zero B, it is concluded that the field at the center of a vortex is 1.2 ± 0.2 times H_{c1}. The data are consistent, at low B, with a superposition model of independent vortices.

I. INTRODUCTION

CONVENTIONAL nuclear resonance studies of the field distribution in type-II superconductors are difficult because of the large resonance linewidths, baseline shift, and noise due to vortex motion, and sample inhomogeneity. Nevertheless, Gossard *et al.*[1] observed a structureless broadening in the NMR of vanadium in V_3Si and V_3Ga and Delrieux and Winter[2] succeeded in observing NMR directly in niobium close to H_{c2}. Much the same kind of information can be obtained using angular correlations.[3]

We have avoided these problems by using field cycling resonance.[4,5] This yields exactly the same information as conventional NMR but has the advantage that the signal can be observed in the normal state with less noise and baseline drift. The cycle is the same as that of Fig. 1 of the previous article,[6] except that τ was fixed at about 0.1 sec, and during that time a transverse rf field $H_p\cos 2\pi\nu_p t$ (which we will call the probe field) was applied perpendicular to the main field H_e.[7]

Typical subsequent signals are shown in Fig. 1, as a function of the probe frequency ν_p. Consider first the case where H_e is greater than H_{c2} (upper right hand points in Fig. 1), so that all but a negligible surface sheath is normal, and the local field inside the sample is everywhere uniform and equal to H_e. The probe field

[1] P. Pincus, A. C. Gossard, V. Jaccarino, and J. H. Wernick, Phys. Letters **13**, 21 (1964).
[2] J. M. Delrieux and J. M. Winter, Solid State Commun. **4**, 545 (1966).
[3] J. Alonso, Bull. Am. Phys. Soc. **12**, 519 (1967).
[4] N. F. Ramsey and R. V. Pound, Phys. Rev. **81**, 278 (1951).
[5] A. G. Redfield, Phys. Rev. **130**, 589 (1963).
[6] W. Fite, II, and A. C. Redfield, Phys. Rev. (preceding article), **162**, 358 (1967), to which the reader is referred for many experimental details and references not included in this article.
[7] The probe field was applied by switching the transmitter coil with a mercury relay to the amplifier described in Ref. 5. The input to this amplifier, normally grounded, was simultaneously switched to a signal generator, which was varied manually. Only a single frequency ν_p was used, unlike Ref. 5.