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Dipole energy dissipation and nuclear spin diffusion in mixed-state superconducting vanadium

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The decay of nuclear spin-spin energy has been studied in the mixed state of vanadium and anomalously rapid relaxation rates are found as compared to the rates for spin-lattice relaxation of Zeeman energy. The experiment was performed by adiabatically demagnetizing the spins in the rotating frame at a field larger than H_{c2} and then cycling the field to bring the sample into the mixed state for a variable time. The residual dipolar energy is detected, once the field is raised, by adiabatically remagnetizing the sample on resonance. I show that the relaxation observed, after the vortices are pinned, is due to a cross relaxation of a spin energy associated with the magnetic field gradients in the mixed state and the dipolar energy which is in semiequilibrium with the quadrupole energy. This process is mediated by a current of magnetization, proportional to the diffusion coefficient D, which is driven by the field gradients and uses dipolar energy as a heat sink. Using a field distribution in the mixed state calculated by Marcus, I find $D=2.8\pm0.9\times10^{-12}$ cm^{2}sec^{-1} from the measurements of the relaxation rate of dipolar energy and of the quadrupole system heat capacity. This measurement of D is the first for a metal or for nuclei with $I > 1/2$ and is twice the value predicted by the moment-moment calculation of Redfield and Yu. In the presence of large field gradients, dynamic quenching of the diffusion coefficient is observed.

I. INTRODUCTION

Nuclear-magnetic-resonance experiments are usually performed in a large uniform field in which the secular part of the spin-spin interaction and the Zeeman interaction commute.[1,2] I report here an investigation of phenomena that appear when these two energy systems are coupled by the presence of large magnetic field gradients, such as those which exist in the mixed state of type-II superconductors.

Previous studies of nuclear magnetic relaxation in superconductors have generally focussed on obtaining the rate of spin-lattice relaxation. The observed relaxation in most cases is due to the interaction of nuclear spins with unpaired electrons and these measurements have yielded much information regarding the density of electronic states in superconducting materials.[3]

Nuclear-magnetic-relaxation experiments have been performed in both type-I and type-II superconductors. The first measurements[4,5] were of the relaxation of dipolar energy, which is the energy of partial alignment of nuclear spins in the dipole fields due to neighboring nuclei. The measurements were carried out in type-I superconducting aluminum in zero external field and were among the earliest confirmations of the BCS theory of superconductivity. A field-cycling technique was used in which the nuclear-spin order is initially induced and finally detected at high fields such that the sample is normal. In these experiments the sample is adiabatically demagnetized and simultaneously brought into the superconducting state, where the spin system is allowed to relax, by lowering the magnetic field to zero.

In the mixed state of type-II superconductors the applied field penetrates the bulk of the sample as a lattice of flux vortices and the relaxation of magnetization has been measured.[6,7] At low temperatures the rate of relaxation is much faster than predicted by BCS theory. The observed relaxation has been attributed to diffusion of magnetization from rapidly relaxing nuclei at the vortex core. Evidence has been given, however, that the diffusion of magnetization is thermodynamically quenched in the field gradients of type-II superconductors and another relaxation mechanism must, therefore, be sought to explain these experiments.[8]

I report here the first measurements of the decay of dipolar energy in a type-II superconductor. The field is cycled to bring the sample into the mixed state but the sample is adiabatically demagnetized and the signal finally detected in a field larger than the upper critical field H_{c2}, where the sample is normal and the field nearly uniform. The experimental procedure will be discussed in Sec. II.

I found anomalously short relaxation times of order 10 msec for dipolar energy in the mixed state of vanadium. In some cases the observed relaxation is two orders of magnitude faster than expected for spin-lattice relaxation based on previous measurements of the relaxation of magnetization in superconducting vanadium.[6] In most instances we find that as either the applied field or temperature are lowered, giving rise to an increase in the average magnitude of the field gradients in the sample, the rate of dipolar relaxation increases.

I have been able to explain these results by assuming that in the presence of large field gradients, the dipole energy reservoir serves as a heat sink for changes of Zeeman energy resulting from nuclear-spin diffusion.[8,9] This is the central concept in the theory of spin diffusion presented by Redfield and Genack in an earlier paper,[9] to which the reader is referred for a full discussion of spin diffusion in the presence of a nonuniform magnetic field. The analysis of spin diffusion was stimulated by this experiment and the consistent interpretation of the data is the first experimental confirmation of the theory. Here I will only give some of the results of the theory and a brief discussion of the physical basis of the decay of dipolar energy which I observe.

On a simple microscopic level spin diffusion is the result of mutual spin flips of neighboring spins. In a uniform magnetic field Bloembergen[10] has shown that random mutual spin flips tend to equalize any variation of magnetization density in the sample. In the presence of a nonuniform field, however, we have shown[9] that since mutual spin flips no longer conserve Zeeman energy, those mutual spin flips which lower the Zeeman energy are favored and a magnetization current density results. The average change in Zeeman energy is taken up by the dipole energy system. The resultant local rate of dipole energy relaxation when the dipole and quadrupole spin systems are in semiequilibrium, is

$$1/\tau = D(\nabla H)^2/(H_d^2 + H_q^2)\ , \tag{1}$$

where D is the diffusion coefficient, $\vec{\nabla} H$ is the magnetic field gradient, H_d^2 is the mean square of the fluctuating dipole field associated with the secular part of the spin-spin interaction,[1] and H_q^2 is an equivalent mean-square field used to express the magnitude of the quadrupole energy. The derivation of Eq. (1) is given in Sec. III.

I emphasize that this experiment is not a study of the relaxation of the spin system brought about by an external degree of freedom, but rather a cross relaxation within the spin system itself. In the presence of the large field gradients in mixed-state vanadium the relaxation of dipolar energy can take place in isolation from the lattice since $1/\tau \gg 1/T_{1d}$, where T_{1d} is the spin-lattice relaxation time of dipolar energy. The initial relaxation rate of dipolar energy due to diffusion is the spatial average of $1/\tau$ over a unit cell of the vortex lattice. Once the quadrupole energy and field variation in the sample are known the diffusion coefficient can be determined from the rate of decay of dipole energy in the superconducting state. In Sec. III I discuss the determination of D from the experimental results. In the presence of large field gradients the diffusion coefficient is observed to decrease due to the dynamical quenching of mutual spin flips when the field difference between spins becomes comparable to H_d.

This determination of the diffusion coefficient is the first which does not depend upon the presence of impurities in the sample and I have thereby overcome a serious limitation in the accuracy of such measurements. In previous experiments[10,11] the relaxation of a nonuniform magnetization created by the presence of paramagnetic impurities was studied in a uniform field. The relaxation of Zeeman energy in the sample as a whole is greatly enhanced in the presence of a small concentration of magnetic impurities even though only a small fraction of the nuclei near the impurity are strongly relaxed by direct interaction with its fluctuating magnetic moment. Bloembergen showed that the observed relaxation is due to a diffusion of magnetization from the nuclei surrounding the impurity. The diffusion coefficient can, therefore, be obtained from the relaxation rate of Zeeman energy. Recently the spin-diffusion coefficient has been obtained using another technique which does not involve the presence of paramagnetic ions. The spin-diffusion coefficient for protons in $Y(C_2H_5SO_4)_3 \cdot 9H_2O$ was determined[12] from measurements of nuclear relaxation in crystallites of varying size which is due to the diffusion of magnetization from the crystallites' surface.

II. EXPERIMENT

A. Experimental considerations

In this experiment I study the decay of dipolar energy in the presence of the inhomogeneous magnetic fields of the mixed state of vanadium. The detection of dipolar energy without any admixture of Zeeman energy, however, can only be accomplished in a uniform magnetic field. For this reason I have used a field-cycling approach in which I prepare and finally detect the dipolar energy in a magnetic field larger than H_{c2}, where the sample is normal and the field inhomogeneity is due solely to the magnet coil. The sample is brought into the superconducting state by lowering the field below H_{c2}.

By the application of resonant rf fields in a uniform magnetic field $\vec{H} = H\hat{z}$, I can reversibly convert Zeeman energy to dipolar energy. A linearly polarized rf field $H_X = 2H_1 \cos\omega t$, which is equivalent to two oppositely rotating, circularly polarized fields, is applied with a coil wrapped around the sample. Only the component rotating in the same sense as the spin precesion can significantly influence the nuclear spins and the evolution of the spin system is most conveniently described in a frame of reference in which the effective component of the rf field is stationary. As is usually done, the rf field can be taken to be in the X direction in the rotating frame and the total effective applied field is $\vec{H}_{eff}=H_1\hat{X}+(H-\omega/\gamma)\hat{Z}\equiv H_1\hat{X}+h\hat{Z}$, where γ is the nuclear gyromagnetic ratio; at resonance $\vec{H}_{eff}=H_1\hat{X}$. In the rotating frame the nuclear moments interact with $\vec{H}_{eff}$ as well as with the local fields, owing to neighboring spins through the secular part of the dipolar interaction which is unchanged by the transformation to the rotating frame. Since the effective spin Hamiltonian is not explicitly time dependence, a spin temperature can be defined in the rotating frame.[2,13] Spin ordering can, therefore, be transferred reversibly between the Zeeman and dipolar systems in the rotating frame, in direct analogy with adiabatic demagnetization in the laboratory frame.[14] This is accomplished in this experiment by applying a 90° pulse and then shifting the phase of the resonant rf so that the magnetization is aligned with $\vec{H}_{eff}=H_1\hat{X}$. A uniform spin temperature is then established in the rotating frame, and the spins are ordered in the vector sum of $\vec{H}_{eff}$ and the secular part of the local field. This ordering is converted to dipolar ordering by reducing H_1 to zero at a rate satisfying the adiabatic condition $T_2 < H_d/(dH_1/dt) < T_1$.

The rather complicated experimental procedure which I will describe was necessitated by the fact that both the static and rf applied fields were not homogeneous in the sample even in the normal phase. The static field was produced in a small superconducting solenoid, which was 5 cm long and 1.5 cm in diameter, and the field variation over the sample was consequently greater than 1 G. The small size of the magnet was necessary in order to cycle the field rapidly. The field is brought into and out of the mixed state in typical times of 0.5 msec by switching ±150 V across the magnet coil.

The sample was composed of a stack of 140-μ-thick insulated vanadium slabs oriented perpendicular to the magnetic field. The material was of high purity, with a value of 80 for the ratio of the resistance at room temperature to that just above the superconducting transition at 5.33 °K. For this sample the penetration depth at the 4-MHz resonant frequency was less than the sample thickness and the rf field was consequently nonuniform. The sample was chosen for study, nonetheless, because the field structure in the vortex state had been extensively studied by Kung[15,16] using the NMR field mapping method developed by Redfield.[17] The knowledge of the field variation in the sample was necessary in order to evaluate the diffusion coefficient.

B. Apparatus

A schematic diagram of the apparatus is shown in Fig. 1. The timing of the various intervals in the experiment is provided by a set of comparators driven by a precision voltage ramp. A crystal oscillator at 4 MHz is the source of all rf fields and provides the triggering of all rf pulses in the experiment. The rf is amplified in two gated channels. The phase in the second channel which provides the decaying rf needed to demagnetize the sample can be shifted by either ±90° relative to the first channel in which all other rf fields are amplified. The high-power gated transmitter which provides further amplification is based on the design of Clark.[18]

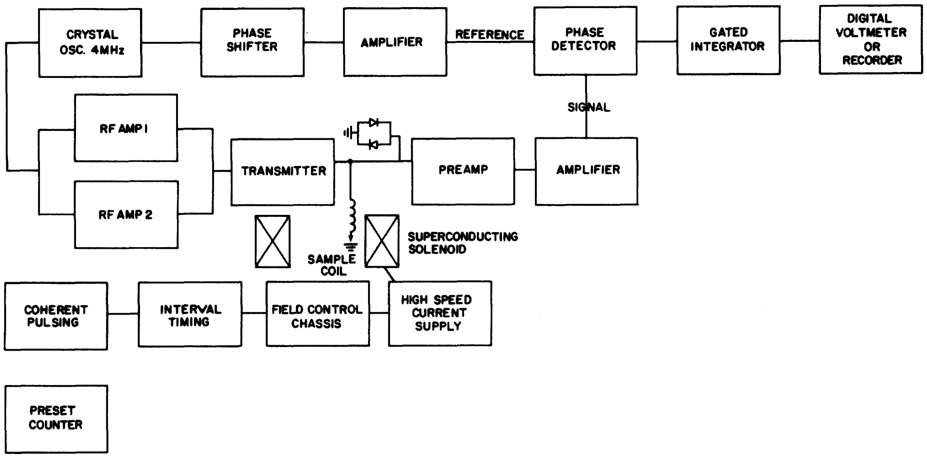

FIG. 1. Schematic diagram of apparatus.

The detection is carried out in a time-shared mode in which the signal is received between a series of transmitter bursts. Since the transmitter is off when the signal is sampled, only a single coil is necessary, and balance problems inherent in cross-coil arrangements are eliminated. The coil is weakly tuned so that the rf will decay quickly when the transmitter is gated off. The receiver and transmitter are pulsed coherently with the rf in order that transients induced are reproducible and can, therefore, be cancelled. Crossed diodes are placed across the receiver input at the end of a quarter-wavelength cable from the coil effectively shorting the cable when the transmitter is on.[19] In this way the preamp is protected when large rf voltages are applied at the coil.

The local oscillator of the phase-sensitive detector is derived from the crystal oscillator and has adjustable phase. The detected signal is introduced to an integrator in one of two gated channels, one of which inverts the signal. The channels are precisely balanced by adjusting a variable resistor in series with one of the gates so that a constant input is cancelled if both channels are gated on for equal times.

The field is produced in a 6.3-mH superconducting solenoid. It is rapidly switched and regulated to within 0.5 G using a switchable current supply based on the design of Redfield *et al.*[20] The sample coil is held snugly in the center of the superconducting solenoid and the entire assembly is immersed in a liquid-helium cryostat.

C. Procedure

The pulse scheme I used is shown in Fig. 2 The rf pulses are alternated between sequences (a) and (b), while the field is cycled as shown in Fig. 2(c) in each sequence. To demagnetize in sequence (a), a 90° pulse is first applied to bring the magnetization into a plane perpendicular to $\vec{H}$. The phase of the rf is then abruptly shifted by $-90°$ so that the spins are locked along the effective field in the rotating frame, $\vec{H}_{eff} = H_1 \hat{X}$, as H_1 is reduced to zero. The dipolar temperature after the demagnetization is $T_d \sim [(H_d^2 + H_q^2)^{1/2}/H]T$, where T is the sample temperature, and H is the resonance field, and corresponds to a few millidegrees in our experiments.

The external field is now lowered to bring the sample into the mixed state for a variable time and subsequently raised back to resonance. Because of flux trapping in the superconducting magnet, the field continues to change slightly even after the current through the solenoid is regulated. The effect this has on dipolar energy relaxation in the superconducting state will be discussed in Sec. III. Because of the magnetic field variation when the field is raised, we allow 15 msec for the field to approach the resonance value. We then apply a 90° pulse in order to destroy any Zeeman energy that might be detected. The magnetization is brought into the plane perpendicular to the field direction and dephases in a time T_2. Since the rf amplitude decreases as the field penetrates the sample, the magnetization in the entire sample cannot be brought simultaneously into the transverse plane. The duration of the pulse which destroys Zeeman energy can, however, be set empirically by finding the pulse length that gives the best single exponential decay for dipolar energy in the normal state. This determination is made at 4.2 °K in a field which is cycled to a value above H_{c2} which is close to field values used in the superconducting

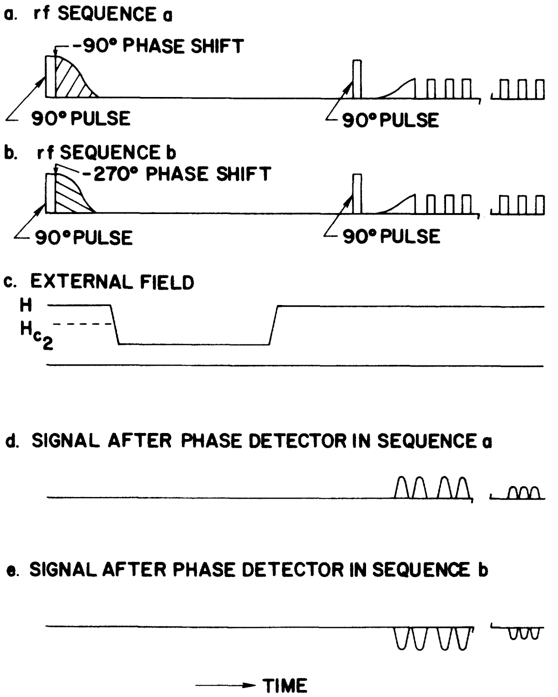

FIG. 2. Experimental procedure and monitored signal before integration are shown. The experiment is performed by alternating the rf pulses between sequences (a) and (b). The field is cycled in both sequences as shown in (c). In sequence (a), a low positive dipolar temperature is induced before the field is cycled by spin locking along the decaying rf field. In sequence (b), a low negative dipolar temperature is induced by shifting the decaying rf by 180° relative to its phase in sequence (a). The detected signal in sequences (a) and (b) is shown in (d) and (e), respectively. The signal shown in (d) is integrated, whereas the signal in (e) is inverted first and then integrated.

experiments at lower temperatures so that similar field transients exist in the normal and superconducting experiments. As I depart from the optimum pulse length setting, the relaxation curve in the normal phase become decidedly nonexponential, indicating that I am observing a mixture of Zeeman and dipolar energy which decay at different rates. In Fig. 3 I show the relaxation of dipolar energy at 4.2 °K measured in the normal phase with optimized 90° pulse length employing the same pulse sequence used for measurements in the superconducting state. On the basis of the observation of this single exponential decay it is established that this apparatus was made sensitive only to dipolar energy. The relaxation rate for dipolar energy measured in the normal state by this method is consistent with the relaxation rate for Zeeman energy in vanadium as will be discussed in Sec. III.

The application of the 90° pulse which destroys the Zeeman energy also effects the dipolar system. The magnitude of the dipolar energy would be reduced in half and the spin reversed in the presence of uniform fields.[21] However, because of the imprecisely defined resonance field in this experiment we find that the detected dipolar energy is changed by a factor of $-\frac{1}{8}$ when this 90° pulse is included in the pulse scheme.

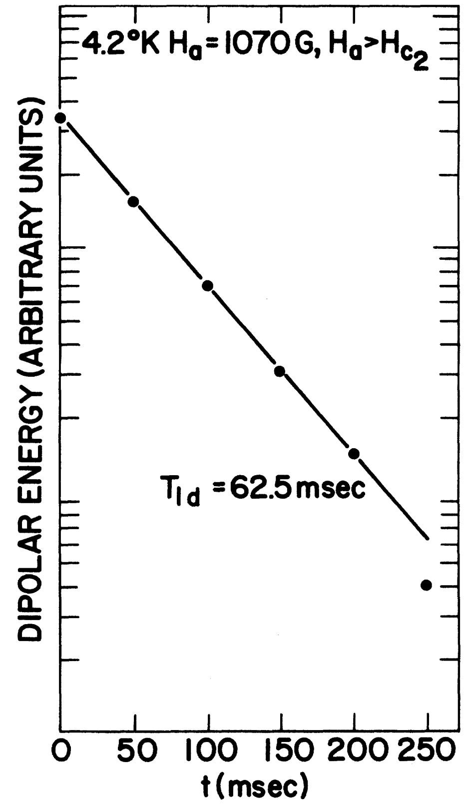

FIG. 3. Relaxation of dipolar energy in the normal state.

Once the precessing magnetization has decayed the sample is remagnetized by adiabatically turning on the rf field at resonance. The rf field is then chopped and the signal is observed between transmitter bursts.

The rf pulses are 8 μsec long and are separated by 28 μsec which is a fraction of T_2 for vanadium. The sidebands in the Fourier transform of the pulse train are, therefore, outside the absorption width of the spins and it can be assumed that the spins effectively respond to a constant rf at the central, resonance frequency.[22,23] Since the spins are in an essentially constant field in the rotating frame the time constant for change of the magnetization will be of order T_1. In this experiment the signal was sampled for 20 msec, whereas without the application of the pulsed rf the signal would decay in about 50 μsec after the remagnetization. As will be discussed below, the phase-sensitive detector is set for the dispersion mode for our pulsed experiment. This phase setting gives a maximum response to the remagnetized dipole energy but makes the detector insensitive to Zeeman energy, since the resonant field is set by adjusting the field to give zero signal in the dispersion mode. During the time that the receiver is gated on the signal is integrated.

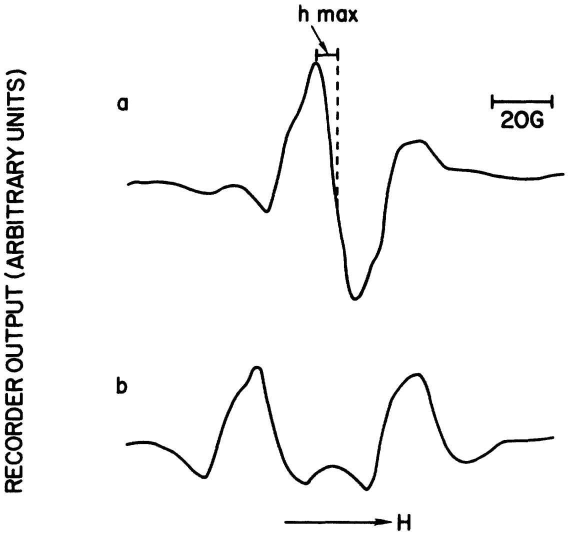

FIG. 4. Signal detected between transmitter bursts in a slow sweep through resonance with the phase of the local oscillator differing by 90° for the curves shown in (a) and (b). The signal near the central resonance corresponds to the dispersion mode in (a) and to the absorption mode in (b). Subsidiary resonances with sidebands of the pulsed rf are observed.

After waiting for a time comparable to T_1 in order to allow for a buildup of magnetization along the field, sequence *b* is initiated. Following an initial 90° pulse the phase of the rf is shifted + 90° so that the field in the rotating frame is aligned opposite to the magnetization. The rf is reduced to zero adiabatically and the final state has a negative dipole temperature equal in magnitude to the temperature obtained after the demagnetization in sequence *a*.

The signal is processed as in sequence *a* except that the detected signal is inverted before it is integrated. In this way the signal due to dipolar energy in the two sequences will add. On the other hand any signal arising from the presence of Zeeman energy will be the same in both sequences and will cancel as will any drift of the electronic apparatus.

In this experiment the sequence is repeated as frequently as 100 times/min. After 1 min the signal-to-noise ratio is about 100 for the shortest dwell times in the superconducting state. The data accumulation stops after a fixed number of transmitter pulses, and the final output voltage from the integrator for dwell time t in the superconducting state $V(t)$ is recorded. The signal is given by $S(t) = V(t) - V_\infty$, where V_∞ is the voltage obtained after an experiment in which I cycle into the superconducting state for a long enough time for equilibrium to be reached. I find that the integrator output obtained by waiting for short times in the superconducting state, but using a sequence in which the sample is not demagnetized before the field is cycled, is equal to V_∞ as expected.

To find the resonance field I pulse the rf continuously and slowly sweep the magnetic field through resonance. Only one channel of the gated integrator is used and a resistor is switched across the output capacitor to give a time constant of 1 sec. In Fig. 4 we show signals for a sweep of 1000 sec which can be characterized by the behavior around the central frequency as the dispersion and absorption modes. The characteristics of the pulse train are the same as discussed above for our relaxation experiments. The secondary resonances that appear are due to sidebands which are separated by the pulse repetition frequency.

The resonance field is at the center of the asymmetric dispersion pattern for the central rf frequency. This corresponds to zero signal and the integrator output is equal to the signal far off resonance. Once the detector reference phase is adjusted for the dispersion mode, the resonance field is found by adjusting the field near resonance for zero signal. The voltage across a shunt in series with the magnet is then measured and the field can be reset throughout the day by adjusting the current through the magnet.

III. RESULTS AND DISCUSSION

A. Normal state

Before considering the relaxation of dipolar energy in the superconducting state, which is my primary interest, it will be useful to consider results obtained for relaxation in the normal state and to evaluate the heat capacity of the nuclear quadrupole system in the sample. Though quadrupole coupling vanishes in a perfect cubic crystal, remanent quadrupole interactions can exist in vanadium which has the bcc structure due to the presence of impurities or dislocations. The quadrupole energy system has an important influence on spin diffusion in the sample because the quadrupole and dipolar energy systems are thermally coupled. These systems may be in semiequilibrium at a single spin temperature if (a) the difference between quadrupole interactions of neighboring spins is not so large as to quench spin diffusion, (b) there is a uniform density of defects in the crystal, and (c) the quadrupole interaction varies rapidly over distances comparable to the diffusion length for a time T_1, $l = (DT_1)^{1/2}$. The average quadrupole energy in the sample may then be written $E_q = -CH_q^2/T_d$, where C is Curie's constant and H_q^2 is an equivalent mean-square field which is assumed uniform in the sample when evaluated over regions of dimensions l. If the quadrupole energy is due primarily to the presence of point defects such as impurities, vacancies, or interstituals, as seems likely for our annealed sample, then a small fraction of the nuclei may contribute the bulk of the quadrupole energy. Diffusion in most of the sample may not then be dynamically quenched owing to quadrupole interactions. Even in regions with large quadrupole interactions, diffusion is not totally quenched since in first order the energies of $m = \pm\frac{1}{2}$ spin levels are unshifted by the quadrupole interaction.

Spin-lattice relaxation in the normal state results from spin scattering of conduction electrons. We will denote the rates of spin-lattice relaxation for the Zeeman, dipole, and quadrupole systems, specifically excluding the effects of thermal mixing of these energy reservoirs, as $1/T_{1K}$, α/T_{1k}, and β/T_{1k}, respectively. Since the Zeeman energy is decoupled from the other energy systems in the presence of a large uniform magnetic field, $1/T_{1k}$ is the relaxation rate for Zeeman energy in high fields. Redfield has shown that in the absence of spatial correlation of the electron wave function α should be 2.[24] This is a consequence of the fact that the dipole interaction is bilinear in spin operators of pairs of nuclei, whereas the Zeeman interaction is linear. As a result dipole energy changes when either of two interacting nuclei are flipped. On the basis of theoretical estimates of electron correlations[25] and a comparison of relaxation observed at high and low magnetic fields in various materials,[26] the increase of α in metals due to correlation effects is expected to be less than 10%. From such experiments performed in vanadium samples with large quadrupole energy, β is found to be 3.3,[6] which is somewhat larger than the maximum value of 3 expected theoretically.

If it is assumed that the quadrupole and dipole energy systems are in semiequilibrium, then the rate of relaxation of internal dipole energy in the presence of large magnetic field is the average rate of relaxation of dipole and quadrupole energy weighted by their respective heat capacities. The ratio of relaxation times of Zeeman and internal energy, which I will denote by Δ is then given by

$$\Delta = T_{1k}/T_{1d} = (\alpha H_d^2 + \beta H_q^2)/(H_d^2 + H_q^2) \ . \tag{2}$$

The value of H_d^2 is obtained from a calculation of the Van Vleck[27] second moment for vanadium: $H_d^2 = \langle \Delta\omega^2 \rangle / 3\gamma^2 = 3.95\ \mathrm{G}^2$.[28] Assuming $\alpha = 2$ and $\beta = 3.3$, I obtain an estimate of H_q^2 from a determination of Δ.

In this experiment the rate of decay of dipolar energy in a large uniform magnetic field is studied. The measurements were performed in the normal state of vanadium at 4.2 °K using the same procedure as in the superconducting experiments except that the field was not cycled below H_{c2}. The relaxation rate for an annealed sample which I have described in Sec. II is 62.5 ± 2 msec. The same ratio was observed from a second sample, which also had a resistance ratio of 80, and was prepared from the first sample by being rolled into a 25-μ foil. This apparent independence of relaxation rate upon significant cold working has previously been noted in aluminum.[26] The relaxation time for Zeeman energy in vanadium at 4.2 °K is determined to be 187 msec from the result $T_1 T = 0.788$ sec °K obtained by Butterworth[29] and verified by Fite and Redfield[6] at low temperatures. The ratio Δ is therefore 3.0, and we obtain from Eq. (2), $H_q^2 = 13\ \mathrm{G}^2$. I should note that the assumption of semiequilibrium between E_d and E_q used in the derivation of Eq. (2) is not fully justified in view of the partial failure of the spin-temperature hypothesis observed in previous experiments in which spin-energy reservoirs are mixed in the presence of low external fields.[26,30] In particular for the case of vanadium I find a value of β which is greater than 3. I have, therefore, checked the consistency of this result with a second calorimetric measurement of H_q^2.

A second determination of H_q^2 is obtained from a measurement of the linewidth of the dispersion signal shown in Fig. 4, obtained by sweeping the field through resonance in a long time compared to the spin-lattice relaxation time and detecting the nuclear magnetization between rf pulses. Since the dispersion is not saturated by the pulsed rf, I can assume that for magnetic field values for which the spins are much closer to resonance with the carrier rf frequency than to any sideband, the magnetization is induced effectively by a single Fourier component of field at the central resonance frequency. In order to compare our results with theory, I will obtain an expression for the magnetization M_x in phase with a rotating rf field of constant amplitude. I follow Redfield's analysis of spin relaxation in the rotating frame[13] and include as well the effect of the heat capacity of the quadrupole system.

In this experiment the absorption is saturated and we can assume, therefore, that a spin temperature can be defined in the rotating frame. Since near resonance H_{eff} is not much larger than H_d or H_q, energy can be exchanged between the various spin systems, and the entire spin system is assumed to be at a single spin temperature in the rotating frame. The magnetization and spin energy in the rotating frame, therefore, satisfy the conditions[31]

$$\frac{M_x}{H_1} = \frac{M_z}{h} = \frac{M}{H_{\mathrm{eff}}} = \frac{-E_z}{H_{\mathrm{eff}}^2} \tag{3a}$$

and

$$\frac{E_z}{H_{\mathrm{eff}}^2} = \frac{E_d}{H_d^2} = \frac{E_q}{H_q^2} = \frac{E}{H_{\mathrm{eff}}^2 + H_d^2 + H_q^2} \ , \tag{3b}$$

where

$$H_{\mathrm{eff}} = (H_1^2 + h^2)^{1/2}, \quad E_z = -MH_{\mathrm{eff}},$$

$$E = E_z + E_d + E_q \ .$$

The effect of the spin-lattice interaction is to relax E_z, E_d, and E_q independently towards equilibrium with the lattice. Cross relaxation between the spin systems then leads to a redistribution of spin energy in accordance with Eqs. (3). Since the correlation time for the electron interaction with spins, τ_c, is much shorter than the rf period, $\tau_c \ll 1/\omega$, the applied magnetic field is nearly constant in an interval τ_c and the effect of spin-lattice relaxation alone upon the magnetization is to relax the magnetization towards its equilibrium value M_0 in the absence of an rf field. This may be expressed by the relations

$$\left(\frac{\partial M_z}{\partial t}\right)_{\mathrm{SLR}} = -\frac{1}{T_{1K}}\,(M_z - M_0) \tag{4a}$$

and

$$\left(\frac{\partial M_x}{\partial t}\right)_{\mathrm{SLR}} = -\frac{M_x}{T_{1K}}\ . \tag{4b}$$

The energies E_d and E_q, as well, are relaxed toward their values in the laboratory frame with a static field by the action of the spin-lattice interaction. Since the spin temperature in the rotating frame is much lower than the lattice temperature and the heat capacity of the Zeeman energy in the laboratory frame is much larger than that of the dipole or quadrupole energy, we can neglect the equilibrium values of E_d and E_q and write

$$\left(\frac{\partial E_d}{\partial t}\right)_{\mathrm{SLR}} = -\frac{\alpha E_d}{T_{1K}} \tag{4c}$$

and

$$\left(\frac{\partial E_q}{\partial t}\right)_{\mathrm{SLR}} = -\frac{-\beta E_q}{T_{1K}}\ . \tag{4d}$$

Combining Eqs. (3) and (4), the equation of motion for the total spin energy in the rotating frame is obtained:

$$\frac{dE}{dt} = -\frac{1}{T_1}\,(E - E_{eq})\ , \tag{5a}$$

where

$$\frac{1}{T_1} = \frac{1}{T_{1K}}\,\frac{h^2 + H_1^2 + \alpha H_d^2 + \beta H_q^2}{h^2 + H_1^2 + H_d^2 + H_q^2} \tag{5b}$$

and

$$E_{\mathrm{eq}} = M_0 h\,\frac{(h^2 + H_1^2 + H_d^2 + H_q^2)}{(h^2 + H_1^2 + \alpha H_d^2 + \beta H_q^2)}\ . \tag{5c}$$

In the absence of an rf field we may set $H_{\mathrm{eff}} = 0$ and Eq. (5b) for the relaxation rate in the rotating frame then reduces to Eq. (2).

The magnetization which is detected is obtained by combining Eqs. (3) and (5c):

$$\begin{aligned} M_x &= \frac{MH_1}{H_{\mathrm{eff}}} \\ &= \frac{H_1}{H_{\mathrm{eff}}}\,\frac{H_{\mathrm{eff}}E_{\mathrm{eq}}}{(H_{\mathrm{eff}}^2 + H_d^2 + H_q^2)^{1/2}} \\ &= \frac{M_0 H_1 h}{(h^2 + H_1^2 + \alpha H_1^2 + \beta H_q^2)}\ . \end{aligned} \tag{6}$$

The magnitude of M_x is a maximum at the fields $h = \pm h_{\max}$, where

$$h_{\max} = (H_1^2 + \alpha H_d^2 + \beta H_q^2)\ . \tag{7}$$

In this experiment H_1 is the amplitude of the Fourier component of the pulse train at the central resonance frequency and has the value $H = 1.5$ G. It is equal to the effective rf field amplitude when the rf is pulsed on, multiplied by the pulse duty factor $\frac{8}{28}$. I find $h_{\max} = 7.7$ G and, consequently, $H_q^2 = 15\ \mathrm{G}^2$, in fair agreement with my first evaluation. Considering the accuracy of the two determinations of the strength of quadrupole coupling I take $H_q^2 = 14 \pm 2\ \mathrm{G}^2$.

B. Superconducting state

Relaxation in the superconducting state is markedly different than in the normal state. In the normal phase the Zeeman and dipole energy systems are uncoupled as long as $H \gg H_d$, H_q, and Δ is, therefore, a constant for a given sample. Using the relaxation rate for Zeeman energy in mixed-state vanadium, measured by Fite and Redfield[6] and by Kung,[16] together with our results for dipole energy relaxations, Δ is found to vary strongly as a function of temperature and applied field. Values of Δ between 10 and several hundred are measured in the mixed state, whereas Δ is 3 in the normal state. These results are explained by noting that, in the presence of the field gradients in the mixed state, the dipolar and Zeeman energy systems are coupled and Eq. (2) for Δ no longer holds. Moreover, since initially the dipole temperature is very low while the temperature associated with the interaction of spins in the inhomogeneous magnetic field is infinite, these coupled spin systems are not in semiequilibrium. What I observe, then, is the cross relaxation of the dipole system, which is in semiequilibrium with the quadrupole system, and the part of the Zeeman-energy system associated with the field gradients.[9]

An example of relaxation of dipolar energy in the superconducting state for our annealed sample is given in Fig. 5. We observe two relaxation regimes, which occur before and after an abrupt change in the slope of the relaxation curve. I will give only a qualitative discussion of relaxation in the first regime, which I believe is due to the motion of vortices that become pinned at the time at which a break occurs in the relaxation curve. This break comes about at a characteristic time for each sample. It is observed after 6 msec for the annealed sample and after 3 msec for the unannealed sample. I find that, though the current through the magnet is switched in 0.5 msec when the field is cycled the magnetic field continues to change for some time. This is due to the expulsion of flux trapped in the superconducting solenoid. After 3 msec the field changes at a rate of 3 KG sec^{-1} and after 6 msec the rate of change is 300 G sec^{-1}. Presumably vortices are pinned more readily in the rolled foil than in the annealed sample. This is confirmed by the observation of increased flux trapping in the unannealed sample as determined from measurements of the field dependence of bulk magnetization in the samples which was measured using a vibrating-sample magnetometer.[32] The degree of vortex pinning can be quite different in the two samples, even though the average quadrupole energy is nearly the same, since the regions of large dislocations at which vortices are pinned may occupy a small fraction of the sample volume.

In studies of Zeeman-energy relaxation in mixed-state vanadium, nonexponential decays are observed.[6] This indicates that the sample is inhomogeneous, and nuclei in different locations, relative to a stable vortex structure, relax at different rates. The decay can be made nearly exponential by applying an audio-frequency magnetic field of a few gauss along the field direction. This imposed field has the effect of moving the vortices about so that all nuclei relax at a space-average rate, which is equal to the initial relaxation rate in the presence of a stable magnetic field. In this study of the decay of dipolar energy the initial relaxation observed once the vortices are pinned is not equal to the relaxation rate observed as vortices are driven through the sample as the field settles. This indicates that different relaxation mechanisms are involved for dipolar energy in the two regimes. The source of relaxation when the vortices are in motion may be a nonadiabatic tilting of the field direction, which is the axis of quantization used in defining the secular dipole Hamiltonian $\mathcal{H}_d^0$. The relaxation might be caused, as well, by the fluctuating field difference between neighboring spins as the vortices move in the sample. The associated interaction commutes with the Zeeman interaction but not with $\mathcal{H}_d^0$. Relaxation due to diffusion in the field gradients should be unimportant in the first regime since the sign and magnitude of the field gradient changes rapidly in the time T_2 and the spins interact in an effectively uniform external field. This effect is much like the motional narrowing of the resonance line width.

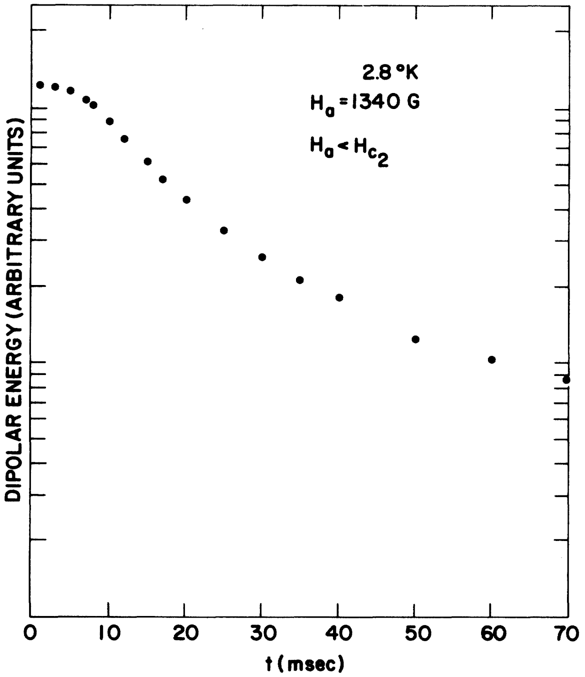

FIG. 5. Decay of dipolar energy as a function of dwell time *t* in the superconducting state. The relaxation rate increases after 6 msec at the point that the vortex lattice becomes stable. From this point relaxation is due primarily to diffusion in the field gradients in the mixed state.

The second regime of relaxation starts once a stable vortex lattice is established. The local field gradients drive a magnetization current which is the vehicle for a cross relaxation between the dipolar energy and the spin energy of interaction with the inhomogeneous magnetic field. We have shown previously[9] that the magnetization current density is given by

$$j = -D[\vec{\nabla} M - (C/T_d)\vec{\nabla} H] \ . \tag{8}$$

When the magnetization is uniform the flow of a magnetization current leads to dissipation of dipolar energy at a rate given by

$$\left(\frac{\partial E_d}{\partial t}\right)_{\mathrm{SD}} = j \cdot \vec{\nabla} H = -D\left(\frac{(\nabla H)^2}{H_d^2}\right)E_d \ . \tag{9}$$

The partial derivative indicates that only the change due to cross-relaxation effects brought about by spin diffusion are considered. The dipole and quadrupole systems, however, are in semiequilibrium and, if we can neglect effects of spin-lattice relaxation and of diffusion of dipolar energy,[9] the total change of dipolar energy is

$$\frac{dE_d}{dt} = \frac{H_d^2}{H_d^2 + H_q^2}\left(\frac{\partial E_d}{\partial t}\right)_{\mathrm{SD}} \ . \tag{10}$$

The rate of change of dipolar energy is then

$$\frac{dE_d}{dt} = -D\left(\frac{(\nabla H)^2}{H_d^2 + H_q^2}\right)E_d \ , \tag{11}$$

leading to a spatially varying relaxation of dipole energy with rate constant $1/\tau = D[(\nabla H)^2/(H_d^2 + H_q^2)]E_d$, as given in Eq. (1). The diffusion coefficient D is not in general a constant. It is dynamically quenched in the presence of large field gradients or quadrupole interactions since energy must be exchanged between the dipolar and the Zeeman and quadrupole system in a mutual spin flip.

The initial relaxation rate of dipolar energy due to diffusion in the field gradients once the vortices are pinned is the space average of $1/\tau$ over a unit cell of area A of the vortex lattice:

$$\frac{1}{T_{1\,\mathrm{diff}}} = \int_A D\left(\frac{(\nabla H)^2}{H_q^2+H_d^2}\right) d\vec{r} \equiv \left\langle \frac{D(\nabla H)^2}{(H_d^2+H_q^2)} \right\rangle . \qquad (12)$$

When the field gradients in the sample are large the diffusion coefficient becomes a function of $|\vec{\nabla} H|$ and Eq. (12) can be recast to define an average diffusion coefficient

$$1/T_{1\,\mathrm{diff}} \equiv D_{\mathrm{av}} \langle (\nabla H)^2 \rangle / (H_d^2 + H_q^2) . \qquad (13)$$

The observed initial relaxation rate in the second regime $1/T_{1\,\mathrm{obs}}$ is due to a combination of the effects of diffusion and spin-lattice relaxation: $1/T_{1\,\mathrm{obs}} = 1/T_{1\,\mathrm{diff}} + 1/T_{1d}$. For the temperatures in this experiment the observed rate of Zeeman-energy relaxation agrees with the BCS prediction for scattering by conduction electrons.[6] The ratio of the rate of relaxation of dipolar energy in semiequilibrium with the quadrupole energy $1/T_{1d}$ to the rate of Zeeman-energy relaxation, including only the effects of the spin-lattice interaction, should be nearly the same as in the normal state. I assume, therefore, that $T_{1d} = \frac{1}{3} T_{1z}$. For a full correction, taking into account the effects of spin-lattice relaxation, T_{1z} should be the space-average relaxation rate. This has not been measured for the cases considered here and I make only a partial correction by using the rate of relaxation far from the vortex center obtained from the slope of the tail of the relaxation curve for Zeeman energy.[16] This introduces only a small error in this estimate of $T_{1\,\mathrm{diff}}$.

The average diffusion coefficient defined in Eq. (13) can be determined from the observed relaxation rate once the field variation in the sample is known. Marcus has obtained values for $\langle(\nabla H)^2\rangle$ for the fields and temperatures we have considered by integrating the Ginsburg-Landau equations using a cylindrical cell approximation for the vortex.[33] The calculated field gradients are scaled so that the total field variation in the sample is in agreement with the measurements of Kung.[16] Extensive measurements were made of the field at the vortex center H_v and at the saddle point of the field distribution H_s. However only a few measurements of the minimum field in the vortex H_m were made for fields and temperatures in this experiment. In those cases we find $(H_s - H_m)/H_v - H_m) = 0.10$ for an applied field H_a of 1340 G at 2.0 and 2.3 K, and $(H_s - H_m)/(H_v - H_m) = 0.06$ when $H_a = 1070$ G at 2.6 K. I have, therefore, assumed that the total field variation in the vortex when $H_a = 1340$ G is 11% larger than the difference in field measured between the vortex center and saddle point. I note that the assumption of a cylindrically symmetric vortex leads to an error in the evaluation of $\langle(\nabla H)^2\rangle$ since it eliminates the distinction between the saddle point and minimum field. Nonetheless, the calculated field difference in the vortex agrees with the measurements of Kung to within 20% for the fields and temperatures we discuss. I expect that the evaluation of $\langle(\nabla H)^2\rangle$ has an accuracy of 25%.

In Table I I present the results of our relaxation measurements as well as some parameters of the mixed state at the fields and temperatures for which $\langle(\nabla H)^2\rangle$ has been evaluated. Most of the data was taken at an applied field H_a of 1340 G at temperatures between 2.0 and 3.1 °K or at 2.6 °K for values of H_a between 1610 and 803 G. In Fig. 6 the deduced cross-relaxation rate $1/T_{1\,\mathrm{diff}}$ is plotted against $\langle(\nabla H)^2\rangle$. I find a marked deviation from a linear fit of $1/T_{1\,\mathrm{diff}}$ to $\langle(\nabla H)^2\rangle$ at large field gradients for which the diffusion coefficient is partially quenched by the field gradients.

In Fig. 7 I give a plot of the average diffusion coefficient defined in Eq. (13) versus $\langle(\nabla H)^2\rangle$. For low fields gradients D_{av} corresponds to the usual diffusion coefficient D_0 for magnetization in a uniform magnetic field. I find $D_0 = 2.8 \pm 0.9 \times 10^{-12}\ \mathrm{cm^2\,sec^{-1}}$. This is larger than a previously quoted result[8] which did not take into account the effect of quadrupole interactions. The deduced value of D_0 is twice the value of $1.4 \times 10^{-12}\ \mathrm{cm^2\,sec^{-1}}$ estimated by Redfield and Yu on the basis of their moment-method calculation.[28] An uncertainty was introduced into this calculation by the assumption of a Gaussian cutoff for the energy absorption from an oscillating nonuniform magnetic field. In view of this uncertainty, these results are roughly consistent with the calculated value for D_0. Apparently diffusion is not significantly quenched by quadrupole interactions in this sample even though $E_q > E_d$. This is quite reasonable since most of the quadrupole energy may be associated with a small fraction of the nuclei which are near point defects.

In the presence of large field gradients the detuning of the resonance frequency of neighboring spins leads to a reduction of mutual spin flips. This results in an increase in T_2 which has been observed in a number of V_3X compounds in the superconducting state.[7] It also leads to a reduction in the diffusion coefficient which is evident

TABLE I. Results for relaxation of dipolar energy in the mixed state of vanadium. Parameters of the vortex state are given. The average diffusion coefficient D_{av} is calculated from the relaxation rate for dipolar energy due to spin diffusion $T_{1\,diff}$ and the mean-square magnetic field gradient in the mixed state $\langle(\nabla H)^2\rangle$.

T (°K)	H_a (G)	$\langle(\nabla H)^2\rangle$ (10^{14} G^{2}cm^{-2})	$T_{1\,obs}$ (msec)	$T_{1\,diff}$ (msec)	D_{av} (10^{-12} cm^2 sec^{-1})
3.1	1340	1.68	25.0	33.3	3.40
3.0	1340	2.8	18.6	22.8	2.85
3.0	1205	6.1	13.5	15.3	1.92
2.9	1340	4.2	14.7	16.6	2.56
2.8	1340	6.1	13.7	15.2	1.95
2.7	1340	9.1	11.7	12.7	1.57
2.6	1610	4.6	19.7	22.3	1.77
2.6	1340	12.1	11.2	11.7	1.27
2.6	1205	19.6	10.6	11.3	0.81
2.6	1070	26.9	8.8	9.3	0.72
2.6	803	38.6	6.6	6.9	0.68
2.5	1340	15.4	8.8	9.2	1.27
2.3	1340	21.8	9.1	9.4	0.87
2.15	1875	4.3	16.4	17.2	2.43
2.15	1340	27.3	7.3	7.46	0.88
2.0	1340	35.3	5.6	5.67	0.90

in Fig. 7. This reduction could be calculated on the basis of treatments used to evaluate[28,34] D_0 by adding the interaction of spins in a constant field gradient to the uniform-field Hamiltonian. Here I will give only an intuitive account of the reduction based on the requirement that the change in Zeeman energy in a mutual spin flip must be taken up by the dipole energy reservoir.[35] It is expected that the probability that energy conserving spin flips of two spins can occur is proportional to the probability that the difference in the z component of the local dipole field at the sites of the spins is equal to the external field difference δH. Assuming a Gaussian shape for the distribution of differences of local field, the rate of mutual spin flips for a given pair of spins is proportional to $\exp[-(\delta H)^2/\epsilon H_d^2]$, where ϵ is of order unity. Of course the diffusion coefficient involves a sum including all neighbors of a given spin.

I find that the average diffusion coefficient D_{av} is reduced almost in half when $\langle(\nabla H)^2\rangle = 9.06 \times 10^{14}$ G^{2}cm^{-2} at $H_a = 1340$ and $T = 2.7$ °K. For this case the largest field difference between

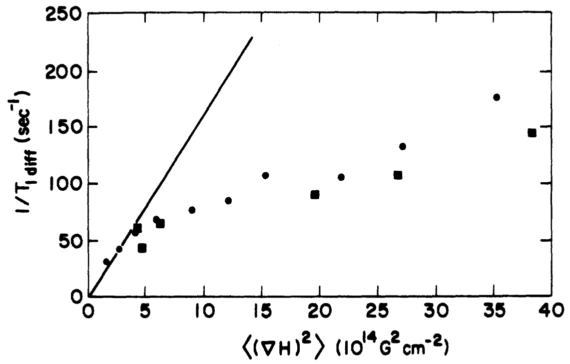

FIG. 6. Relaxation rate due to diffusion plotted against mean–square field gradient in the mixed state. All results at H = 1340 G are indicated with circles, other results are indicated with squares. $1/T_{1\,diff}$ and $\langle(\nabla H)^2\rangle$ are given to accuracies of 5 and 25%, respectively.

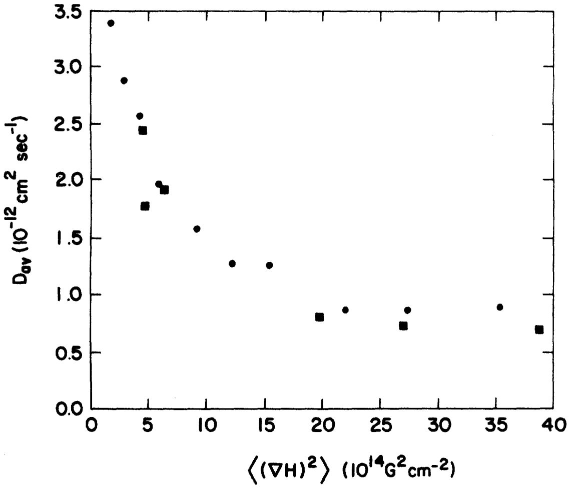

FIG. 7. Average diffusion coefficient D_{av} deduced from Eq. (13) of text. It is given to an accuracy of 35%.

nuclei, which are nearest neighbors and are separated by 2.63 A, is 1.5 G, which is comparable to $H_d = 1.95$ G. For larger field variations in the vortex D_{av} does not drop sharply. This is probably due to the fact that the maximum field gradients in the vortex increase less rapidly than does the total field variation. This is because the fraction of the vortex area with relatively large field gradients is found to increase as the field difference in the vortex increases. It would be interesting to find a functional form of the variation of the diffusion coefficient with the field gradient $D(|\vec{\nabla} H|)$ which would reproduce the deduced values of D_{av} using the relation $D_{av} = \langle [D(|\vec{\nabla} H|)][\nabla H]^2 \rangle / \langle [\nabla H]^2 \rangle$. If $D(|\vec{\nabla} H|)$ is found to have a physically reasonable form, this would provide further confirmation that the dissipation of dipolar energy we observe is due to spin diffusion.

IV. CONCLUSION

I have made the first study of the decay of dipolar energy in the presence of large field gradients and found unexpectedly rapid relaxation as compared to the relaxation of Zeeman energy. These observations stimulated the development of a general theory of spin diffusion in which purely diffusive effects and the new phenomenon of dipole energy dissipation in a spatially varying magnetic field are treated in a unified way.[9] I have shown that the relaxation observed can be attributed to a cross relaxation between the dipolar energy and an energy associated with the spin interaction in the field gradients. In this process, the dipolar energy reservoir serves as a heat sink for changes of Zeeman energy which result from a flow of magnetization which is driven by the field gradients in the sample.

Because of the relationship between diffusive and dissipative phenomena in spin systems, which is a consequence of the fluctuation-dissipation theorem, the diffusion coefficient can be obtained from a measurement of the relaxation rate of dipolar energy in an inhomogeneous field. I have obtained a value for the uniform field diffusion coefficient D_0 for vanadium which is in reasonable agreement with theory, and have given a qualitative explanation of the relaxation measurements for dipolar energy in the presence of large field gradients in which diffusion is partially quenched. The consistent interpretation of the data as a cross relaxation within the spin system, in the absence of another plausible explanation for the rapid decay of dipolar energy, provides support for our theory of spin diffusion.[9]

I should mention, however, that dipolar energy can be selectively relaxed by the fluctuating longitudinal field difference between neighboring spins which is produced by thermally excited flux vortex vibrations. Though the size of this effect is difficult to estimate, particularly since it depends upon the distance between points at which the vortex is pinned, it should be of the same order of magnitude as the relaxation of spin energy by transverse components of the magnetic field which are produced by vibrating vortices. These transverse fields would relax both Zeeman and dipolar energy. However, this effect has not been observed in studies of Zeeman energy relaxation in vanadium and measurements in other materials indicate it would be quite small.[36] I believe, therefore, that relaxation of dipolar energy by vibrating vortices is too slow to explain the rapid relaxation observed.

In the mixed state of vanadium the relaxation rate of dipolar energy due to diffusion is faster than the spin-lattice relaxation rate, $1/T_{1\,\mathrm{diff}} > 1/T_{1d}$, and I was able for the first time to measure the diffusion coefficient in a metal. In previous studies of nuclear-spin diffusion the relaxation of Zeeman energy caused by the diffusion of magnetization from nuclei near impurities was measured.[11] This is a relatively slow process, and measurements of D_0 were made only in ionic crystals which have long spin-lattice relaxation times.

The diffusion coefficient could also be measured by this method by observing the decay of dipolar energy at the surface of superconducting materials or at normal-superconductor interfaces where large field gradients can exist. I note that the diffusion coefficient cannot be obtained from the rate of relaxation of Zeeman energy in type-II superconductors. In that case magnetization current density is thermodynamically quenched because the dipolar energy reservoir is nearly depleted after a cross-relaxation time τ.[8,9]

Though the relaxation rate I observe is modified by the presence of the quadrupole interaction, the relaxation itself is an intrinsic effect of pure materials. In this sample the quadrupole interaction was not large enough to dynamically quench diffusion for most nuclei even though $I = \frac{7}{2}$ for vanadium. Previously measurements of the diffusion coefficient were restricted to nuclei with $I = \frac{1}{2}$, since for nuclei with larger spin large quadrupole interactions near impurities would significantly quench diffusion in the sample. The accuracy of the determination of D_0 is limited in such experiments because of the essential role played by impurities. The dynamic quenching of spin diffusion in the fluctuating field gradients near impurities is difficult to treat quantitatively and the density and distribution of impurities is not precisely known. In the present method for determining *D*, diffusion can be studied in the presence of small enough field gradients that dynamic quenching does not occur. The accuracy of the measurement of *D* is determined by the knowledge of the field gradients in the superconducting state and of the heat capacity of the quadrupole energy system.

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[1] L. C. Hebel, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 15

[2] M. Goldman, *Spin Temperature and Nuclear Magnetic Resonance in Solids* (Clarendon, London, 1970).

[3] D. M. Ginsberg and L. C. Hebel, *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), Vol. 2.

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

[5] Y. Masuda and A. G. Redfield, Phys. Rev. 125, 159 (1962).

[6] W. Fite II and A. G. Redfield, Phys. Rev. 162, 358 (1967).

[7] B. G. Silbernagel, M. Weger, W. G. Clark, and J. H. Wernick, Phys. Rev. 153, 535 (1967).

[8] A. Z. Genack and A. G. Redfield, Phys. Rev. Lett. 31, 1204 (1973).

[9] A. Z. Genack and A. G. Redfield, Phys. Rev. B 12, 78 (1975).

[10] N. Bloembergen, Physica (Utr.) 10, 386 (1949).

[11] G. R. Khutsishvili, Comments Solid State Phys. 5, 23 (1972).

[12] J. V. Gates II and W. H. Potter, Phys. Rev. Lett. 33, 878 (1974).

[13] A. G. Redfield, Phys. Rev. 98, 1787 (1955).

[14] C. P. Slichter and W. C. Holton, Phys. Rev. 122, 1701 (1961).

[15] Albert Kung, Phys. Rev. Lett. 25, 1006 (1970).

[16] Albert Kung, Ph.D. thesis (Columbia University, 1970) (unpublished).

[17] A. G. Redfield, Phys. Rev. 162, 367 (1967).

[18] W. G. Clark, Rev. Sci. Instrum. 35, 316 (1964).

[19] I. J. Lowe and C. E. Tarr, J. Phys. E 1, 320 (1968).

[20] A. G. Redfield, W. Fite, II, and H. E Bleich, Rev. Sci. Instrum. 39, (1968).

[21] H. M. Einbinder, Ph.D. thesis (Columbia University, 1968) (unpublished).

[22] U. Haeberlen and J. S. Waugh, Phys. Rev. 175, 453 (1968).

[23] Such simplifying assumptions are not always valid A. Pines and J. D. Ellet, Jr., Am. Chem. Soc. 95, 4437 (1973).

[24] A. G. Redfield, IBM J. Res. Dev. 1, 19 (1957).

[25] P. A. Wolff, Phys. Rev. 129, 84 (1963).

[26] A. G. Anderson and A. G. Redfield, Phys. Rev. 116, 583 (1959).

[27] J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

[28] A. G. Redfield and W. N. Yu, Phys. Rev. 169, 443 (1968); 177, 1018 (E) (1969).

[29] J. Butterworth, Phys. Rev. Lett. 5, 305 (1960).

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

[31] I. Solomon and J. Ezratty, Phys. Rev. 127, 78 (1962).

[32] A. G. Redfield and C. Moleski, Rev. Sci. Instrum. 43, 760 (1972).

[33] P. M. Marcus, *Low Temperature Physics LT9*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum, New York, 1965), part A, p. 550; P. M. Marcus, *Low Temperature Physics LT10*, edited by N. V. Zavaritsky and I. P. Krylov (Nauka, Moscow, 1967), Vol. IIa, p. 345.

[34] I. J. Lowe and S. Gade, Phys. Rev. 156, 817 (1967).

[35] N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. 114, 445 (1959).

[36] E. Ehrenfreund, I. B. Goldberg, and M. Weger, Solid State Commun. 7, 1333 (1969).