Nuclear Spin Diffusion and Its Thermodynamic Quenching in the Field Gradients of a Type-II Superconductor

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(Received 28 June 1973)

We have observed anomalously rapid relaxation of dipole-dipole energy in mixed-state superconducting vanadium. We show that spin diffusion driven by an inhomogeneous magnetic field uses spin-spin energy as a heat sink. Coupled differential equations are proposed for magnetization and spin-spin energy, and the diffusion coefficient is inferred from our measurements. It is concluded that spin diffusion cannot be a relaxation mechanism for magnetization in the mixed state, as previously assumed.

We have developed and tested experimentally a theory of spin diffusion in a nonuniform magnetic field. A consequence of the theory is that the possibility of Zeeman energy relaxation via spin diffusion in the mixed state is ruled out. A flow of magnetization from nuclei that are relaxed relatively rapidly in the cores of superconducting vortices has been suggested as a source of a deviation from the BCS relaxation rate in type-II superconductors.[1-3] It has been assumed that the diffusion equation, $\partial M/\partial t = D\nabla^2 M$, which describes the transport of magnetization M in a uniform field, is valid in the presence of an inhomogeneous field.

Spin diffusion in a rigid lattice, in the presence of a uniform field,[4] is viewed as the result of mutual spin flips of neighboring spins. These flips are induced by the dipole interaction and lead to a random walk of the nuclear magnetization which tends to suppress any nonuniformities in the magnetization. In a nonuniform field, however, such mutual spin flips no longer exactly conserve Zeeman energy because the interaction energy with the applied field is not identical for neighboring spins. After a mutual spin flip the energy difference, $\delta E = \gamma \delta H$, where γ is the nuclear gyromagnetic ratio and δH is the field difference between neighboring spins, must be taken up by an energy bath with temperature T_d. The transition rate for such a spin flip would no longer equal that of the inverse flip, the ratio of the rates being $\exp(\delta E/kT_d)$ according to the principle of detailed balance.

The question arises, what is the bath and its temperature T_d introduced above? It is not the lattice, which is assumed isolated from the spin system. We argue that it is the dipole-dipole interaction bath and its temperature,[5] following a line of reasoning developed in cross relaxation.[6]

The finite heat capacity of this bath leads to observable anomalies when the dipolar field (a few gauss) is comparable to field variations (such as those in a type-II superconductor) applied to the spin system. Magnetization diffusion is quenched when the dipole reservoir heats up, and, conversely, pre-existing dipolar energy drives a magnetization flow in a nonuniform field. This flow produces dissipation of the dipolar energy which drives it.

An expression for the magnetization current $\vec{j}$ can be obtained by considering the flow of magnetization across an imaginary wall in the solid and associating a transfer of a unit of magnetization with each spin flip of neighboring spins on opposite sides of the wall. Making the high-temperature approximation, $\delta E \ll kT_d$, which is almost always appropriate for nuclear spin systems, we find

$$\vec{j} = -D\nabla M + (DC/T_d)\nabla H, \qquad (1)$$

where C is the Curie constant, and M and H are the magnitudes of $\vec{M}$ and $\vec{H}$, assumed collinear If the spin-lattice interaction can be neglected, the total magnetization is conserved and we have

$$\partial M/\partial t = -\nabla\cdot\vec{j} = D\nabla\cdot[\nabla M - \chi(T_d)\nabla H], \qquad (2)$$

where $\chi(T_d) = C/T_d$ is a magnetic susceptibility. The contribution to $\vec{j}$ which is driven by the field gradient arises in much the same way as the ionic current which flows in the presence of an electric field (potential gradient).[7] The coefficient of ∇H in (1) can be identified as a magnetic conductivity σ_m and is related to D by an analog of the Einstein relation.

We can divide the Zeeman Hamiltonian into a part associated with the average field in the sample, H_{av}, and a part associated with the deviation ΔH from H_{av}. The spin Hamiltonian for a

single species can be written as

$$\mathcal{H} = -\gamma h \sum_i I_{i_z} H_{av} - \gamma h \sum_i I_{i_z} \Delta H_i + \mathcal{H}_d^0, \qquad (3)$$

where the summation is over all nuclear sites, and $\mathcal{H}_d^0$ is the secular part of the dipole interaction.[8] The last two terms in (3) do not commute and there is a flow of energy between the energy systems they represent.[9] The elementary processes involved in the exchange of energy are represented in this model by mutual spin flips with relative transition rates determined by the spin-spin temperature T_d. A thermodynamic analysis shows that equilibrium is reached when $\nabla M = (C/T_d)\nabla H$ with T_d uniform. Spin diffusion will then cease and the magnetization current (1) will be zero.

The rate of change of the dipole energy density E_d arising from the flow of magnetization in the sample is $\vec{j} \cdot \nabla H$. E_d also changes as a result of a tendency, which exists even in a uniform field, of mutual spin flips to wash out any nonuniformities in E_d. Combining these contributions we have

$$\partial E_d/\partial t = \vec{j} \cdot \nabla H + D_d \nabla^2 E_d, \qquad (4)$$

where D_d is the diffusion coefficient of the dipole energy, which can be shown to be of the same order of magnitude as D.[9] E_d and the dipole susceptibility $\chi(T_d)$ are both inversely proportional to T_d: $E_d = -\chi(T_d)H_d^2$, where H_d^2 is the mean square of the fluctuating dipole field associated with $\mathcal{H}_d^0$.[8] Equations (2) and (4) together with relation (1) for $\vec{j}$ describe the spin diffusion process and can be recast as two coupled equations in M and $\chi(T_d)$,

$$\partial M/\partial t = D\nabla \cdot [\nabla M - \chi(T_d)\nabla H], \qquad (5a)$$

$$\partial \chi(T_d)/\partial t = -\vec{j} \cdot \nabla H/H_d^2 + D_d \nabla^2 \chi(T_d). \qquad (5b)$$

The effect of spin-lattice relaxation can be taken into account by adding appropriate relaxation terms to these equations.

Explicit solution of Eqs. (5) is difficult even for simple model situations. In general, however, if the system is initially far from quasiequilibrium[10] and $|\nabla H|$ is sufficiently large, there are two time epochs. In the first, there is a relatively large magnetization current, which produces a rapid local change in $\chi(T_d)$ because of energy dissipation in the field gradient. In the second epoch the system is relatively close to a local equilibrium in which $\nabla M \simeq \chi(T_d)\nabla H$; but since T_d is in general nonuniform, there is a further slow diffusion mediated by the last term in (5b).

For example, suppose that initially M and $\chi(T_d)$ are uniform, while H is not, as in a type-II superconductor; this is the case in practical experiments (see below and Refs. 2 and 3). Then initially the last term in (5b) can be ignored. The rate of change of the current is then

$$\partial \vec{j}/\partial t = -D\{\nabla(\partial M/\partial t) - [\partial \chi(T_d)/\partial t]\nabla H\}$$
$$= D\nabla(\nabla \cdot \vec{j}) - D(\vec{j} \cdot \nabla H)(\nabla H)/H_d^2. \qquad (6)$$

It is expected that the spatial variation of $\vec{j}$ and $\vec{M}$ will be similar in extension to that of H; $\nabla(\nabla \cdot \vec{j})$ and ∇H are, respectively, of the order of magnitude of j/R_0^2 and $\Delta H/R_0$, where R_0 is the nominal radius of a vortex and ΔH is the difference between the field at the vortex center and at a point a distance R_0 from the vortex center. The second term on the right-hand side of (6) is larger than the first by a factor of $(\Delta H)^2/H_d^2$, which in the mixed state is typically greater than 10^3. The first term can, therefore, be neglected and $\vec{j}$ decreases exponentially towards zero with rate constant $D(\nabla H)^2/H_d^2$. This time constant varies spatially since ∇H does. Concurrently, there is an exponential change in M and $\chi(T_d)$, which can be estimated by integrating (5). If initially M is constant and $\chi(T_d)$ is of order M/H as would be the case in studies of Zeeman energy relaxation in the mixed state, then the change in M during the first epoch will be negligible compared to the initial value of M. On the other hand, in our experiment we started with $M = 0$, but $\chi(T_d)$ large (and either positive or negative). The local change of M was not observed, but the average time variation of $\chi(T_d)$ was followed. Initially the current is $\vec{j} = D\chi(T_d)\nabla H$, and the time variation of the dipole susceptibility is given by

$$\partial \chi(T_d)/\partial t = -D[(\nabla H)^2/H_d^2]\chi(T_d). \qquad (7)$$

Thus, $\chi(T_d)$ decays exponentially with the time constant already mentioned.

The second epoch of the time evolution starts when the two terms of (5b) are approximately equal, and we can no longer neglect the second term. If the two terms of (5b) are roughly equal, then the magnitude of $\vec{j}$ can be estimated and is smaller by a factor $(\Delta H)^2/H_d^2$ than either term of (1); thus $\chi(T_d) \simeq (\nabla M \cdot \nabla H)/(\nabla H)^2 \approx \Delta M/\Delta H$, where ΔM is defined similarly to ΔH. Using this fact we estimate j by setting the two terms of (5b) equal and replacing gradients with R_0^{-1}:

$$j \approx [DH_d^2/(\Delta H)^2]\Delta M/R_0, \qquad (8)$$

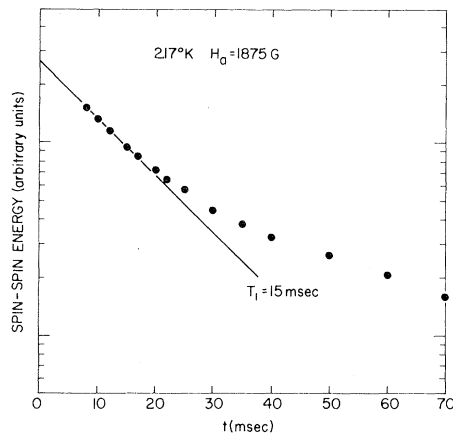which is a factor of $H_d^2/(\Delta H)^2$ smaller than the

FIG. 1. Relaxation of spin–spin energy in the super-conducting state. The initial relaxation time of 15 msec is used to evaluate D.
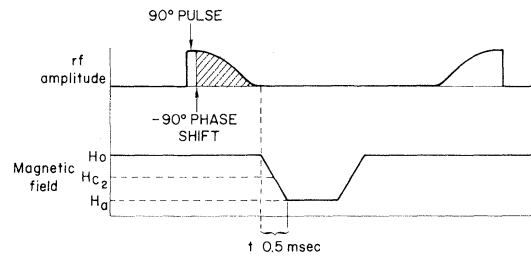

FIG. 2. Basic rf pulse and field cycling procedure. The sample is adiabatically demagnetized by locking the magnetization to the rf field after a 90° pulse and slowly decreasing the rf amplitude. The field is then cycled below H_{c_2} to bring the sample into the supercon-ducting state and then back to resonance for detection of spin–spin energy.

value predicted on the basis of the expression for $\vec{j}$ in a uniform field, $\vec{j} = - D\nabla M$, and is too small to account for the observed relaxation times in the mixed state at low temperatures. Another source must, therefore, be sought to explain the rapid relaxation of Zeeman energy in type-II su-perconductors at low temperatures, and the rath-er convincing experimental basis[3] for assuming the importance of spin diffusion must be re-ex-amined. Possible mechanisms are residual elec-tronic relaxation, impurities, or vortex fluctua-tions.[11]

We were led to the above considerations by a study of the relaxation of dipole-dipole energy rather than of magnetization. We observed an anomalously short relaxation time for this ener-gy as compared to its relaxation time in the nor-mal state (120 msec at 2.17°K) or the relaxation time of Zeeman energy in the superconducting state (1 sec at 2.17°K). A plot of the relaxation of dipole energy in the mixed state is given in Fig. 1 for a vanadium sample described previous-ly.[12]

The principal features of the experimental pro-cedure are illustrated in Fig. 2. We first convert the ordering of the spins in an externally applied field larger than the superconducting upper crit-ical field H_{c_2} to an internal order, in which there is a relatively high degree of alignment of spins in the local dipole fields, by adiabatic demagne-tization in the rotating frame.[6,10] The field is then lowered below H_{c_2} into the mixed state, where the field varies periodically in a two-di-mensional triangular lattice. After a variable time in the mixed state, the field is raised back

to resonance and the sample is adiabatically re-magnetized. The signal which we then detect is proportional to the internal dipole order remain-ing in the sample just before the field was raised. By varying the applied field and the temperature at which the experiment is performed we are able to study spin diffusion in the presence of a wide variety of field gradients.

As we have seen the dipole energy decays with a spatially varying relaxation rate $D(\nabla H)^2/H_d^2$. The initial relaxation rate should be the weighted average of this rate over the area of a unit cell in the vortex lattice. From this experiment and an estimate of the space average of $(\nabla H)^2$ we ob-tain a value 9×10^{-13} cm^2/sec for D, which is $\frac{2}{3}$ the theoretical value.[9] The discrepancy may be due to residual quadrupole interactions.

We have also found at low temperature and ap-plied field, where the field gradients in the mixed state are large enough that the field difference be-tween neighboring spins is comparable to H_d, that the diffusion coefficient, as measured in this way, decreases. This decrease is expected[13] because the frequencies of precession of a spin's neighbors are no longer in resonance with the spin and the rate of mutual spin flip is thereby reduced. This reduction in D is a dynamical ef-fect and is distinct from the thermodynamic quenching discussed in this paper.

Relaxation in insulators containing paramag-netic impurities is mediated by spin diffusion.[5] The importance of thermodynamic quenching of diffusion is limited in this case because diffu-sion perpendicular to ∇H is still allowed. The average field due to an electron spin does not increase, on an angle average, as the distance is decreased, in contrast to the field near a vor-

tex core in a superconductor, which does in-
crease.

We thank R. L. Garwin and J. L. Levine for
many stimulating discussions. We are indebted
to P. M. Marcus for calculating the field profile
for our samples and for valuable discussions.

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Field-Ion Microscope Observations of Indirect Interaction between Adatoms on Metal Surfaces*

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(Received 19 April 1973)

From field-ion microscope kinetic and equilibrium experiments with rhenium adatoms
on W(110) planes it is found that the interaction potential energy between two adatoms
exhibits an oscillatory behavior. The cohesive energy between two adatoms is very small,
only ~0.16 eV at the closest separation. These observations are in general agreement
with the indirect adatom interaction models as proposed and discussed by various inves-
tigators.

When an atom is adsorbed on a metal surface,
the electron gas is perturbed. This perturbation
is long ranged, and the adsorption of one atom
will influence the adsorption of another atom over
large distances where direct interaction of the
two adatoms is negligible. The indirect atomic
interaction was first realized by Koutecky[1] and
subsequently investigated by Grimley,[2] Newns,[3]
and Einstein and Schrieffer.[4] The interatomic
potential resulting from the indirect adatom in-
teraction exhibits oscillatory behavior reminis-
cent of Ruderman-Kittel-Kasuya-Yosida inter-
actions[5] and Friedel oscillations[6] in solids. Both
Grimley[2] and Einstein and Schrieffer[4] find that
the indirect interaction is strong when the virtual
adatomic level is near the Fermi level, and is
weak when the virtual level is far below the Fer-
mi level. The oscillatory period depends also on
the energy of the virtual adatomic level. The lat-
ter authors further find that the interaction at
nearest-neighbor distance is about an order of

magnitude smaller than the adsorption energy of
an adatom with the substrate lattice. They also
succeeded in explaining the superlattice struc-
tures of chemisorbed atoms on solid surfaces as
found by the low-energy electron-diffraction tech-
nique using the indirect adatom interaction. The
indirect interaction is thus fundamental to the
understanding of solid surfaces. It is desirable
to have independent direct experimental evidence
to confirm the theoretical predictions as well as
to substantiate the novel interpretation of the
superlattice structures. However, it is impor-
tant to realize that whatever experiments one per-
forms, a quantitative agreement with the theo-
ries cannot be expected and is not very meaning-
ful because of the experimental difficulties in-
volved in realizing the idealized theoretical mod-
els. One should instead focus attention on ob-
serving the general features as predicted by the
models.

Experimental evidence of the Friedel oscilla-