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Theory of nuclear spin diffusion in a spatially varying magnetic field

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Spin diffusion driven by either a magnetization gradient or a field gradient is viewed as a flow of magnetization current. An expression for this current in a nonuniform field is derived. The magnetization current is the vehicle for a cross relaxation between the nuclear dipole-dipole energy and the spin energy of interaction with the inhomogeneous part of the magnetic field. From a measurement of the decay rate of dipole energy in the presence of large field gradients, which are present in type-II superconductors or at normal-superconductor interfaces, the spin-diffusion coefficient can be determined. Coupled differential equations describing magnetization and dipole energy densities are deduced and their solution is discussed.

I. INTRODUCTION

In nuclear-magnetic-resonance experiments the inhomogeneity of an applied magnetic field is ordinarily regarded simply as an obstacle to obtaining a large signal or good resolution. However, a number of new effects emerge in the presence of large magnetic field gradients which can be understood within the context of the spin-temperature hypothesis. They involve the spatial diffusion of magnetization in a field gradient with concomitant dissipation of spin energy. The effects are especially pronounced in the mixed state of type-II superconductors or near an interface with superconducting materials, where field gradients larger than 10^7 G/cm are typical.

We have conducted experiments in the mixed state of vanadium in which we have measured the decay of nuclear dipole-dipole energy, which is an energy associated with the partial alignment of nuclei in the dipole fields due to neighboring spins. We found anomalously rapid relaxation[1] which we attribute to cross relaxation between the dipole-dipole and Zeeman energy reservoirs, which are coupled by the presence of a nonuniform magnetic field. This has led us to develop a general theory of spin diffusion, incorporating purely diffusive effects separately from dissipative effects in a potential gradient, as is traditionally done in the case of ionic diffusion and conductivity.[2]

Spin diffusion was first invoked by Bloembergen[3] to explain the significant influence of a small concentration of paramagnetic impurities on spin-lattice relaxation in ionic crystals. He suggested that only a small number of nuclei in close proximity to an impurity spin are strongly relaxed by direct interaction with its fluctuating magnetic moment. He assumed that the rest of the nuclei relax primarily through a diffusion of magnetization from nuclei surrounding the impurity.

The elementary processes involved in spin diffusion are mutual spin flips of neighboring spins. Such spin flips are induced by the dipole interaction between the spins and correspond to a flow of magnetization across an imaginary surface between the two spins. In a uniform field, spin flips tend to suppress any nonuniformities of magnetization. It has been noted[4] that in an inhomogeneous field magnetization ordinarily flows towards regions of higher field, resulting in a reduced Zeeman energy for the spin system. If we can neglect the effect of spin-lattice relaxation, the reduction in Zeeman energy must be taken up by the dipole energy system since the total spin energy is conserved.

It is difficult to obtain an accurate value for the diffusion coefficient D from relaxation measurements in samples containing paramagnetic impurities since the impurity concentration cannot be precisely determined. In addition the details of magnetization transfer among nuclei which experience the large fluctuating magnetic fields near the impurity have not been worked out quantitatively. Near the magnetic ions, spin diffusion is dynamically quenched when the difference in field due to the magnetic ions at neighboring nucelar sites is comparable to the dipole field due to neighboring nuclei, since then the change of Zeeman energy in a mutual spin flip cannot readily be taken up by the dipole energy system. This quenching of spin diffusion is most often accounted for phenomenologically by assuming the existence of a diffusion barrier around the impurity. Inside the barrier spin diffusion is assumed to be completely suppressed, while beyond the barrier the diffusion coefficient is taken as a constant. For more information about spin diffusion in paramagnetically doped crystals the reader is referred to Refs. 5–7.

We have shown that the value of D can be obtained using a technique that does not depend upon the presence of magnetic impurities. D can be inferred from the rate of decay of dipole energy to diffusion of magnetization in the presence of a nonuniform magnetic field. Thus we were able to obtain a value for D in vanadium by observing the relaxation of dipole energy due to diffusion driven by the field gradients in the mixed state.[1] We found a value for D of 2.8×10^{-12} cm^2/sec, which is twice the value obtained by Redfield and Yu on the basis of a moment-method calculation.[4]

The approach can be applied even to nonsuperconducting substances by observing the decay of dipole energy induced by an externally applied field gradient. Large field gradients in normal metals might be obtained by exploiting the proximity effect, in which superconducting properties, and particularly flux expulsion, are continued into the adjacent normal metal over short distances. If the magnitude of the field gradients are known, an accurate value for D can be obtained.

It has previously been generally assumed that spin diffusion would proceed whenever there is a variation of magnetization density on a microscopic scale. In type-II superconductors the spatially periodic variation of magnetic field and relaxation properties give rise to a magnetization that varies over the dimensions of the vortex lattice spacing. It has been supposed that the diffusion of magnetization from the relatively rapidly relaxing nuclei in the vortex core is the primary mechanism for spin relaxation in such samples at low temperatures.[8,9] However, we give arguments below which tend to show that the diffusion of magnetization is thermodynamically quenched in the field gradients of a type-II superconductor.[1] This occurs because the energy for the diffusion process must be supplied by the dipole-dipole energy reservoir whose heat capacity is very small compared to that for the energy system associated with the nonuniform magnetic field. On the other hand, the diffusion of magnetization driven by large field gradients results in a rapid depletion of the dipole-dipole energy reservoir which we have reported. Some new explanation for the relaxation of magnetization in type-II superconductors must be sought.

One of the special points of interest in dealing with nuclear spins in solids is that they represent a simple yet nontrivial example of thermodynamics. In Sec. II, we show that an understanding of spin diffusion can be obtained by using a heuristic picture as well as from a more formal treatment. In Sec. III spin diffusion is described by two coupled differential equations in the magnetization and dipole energy densities. It is shown that spin diffusion in a nonuniform field is equivalent to a cross relaxation of a part of the Zeeman energy system and the dipolar system. The nature of spin diffusion in a variety of circumstances is explored in Sec. IV. In Sec. V we discuss a new method for obtaining accurate values of D by observing the decay of dipole energy in the presence of large field gradients. In Sec. VI we discuss the application of our results to related systems.

A detailed treatment of the coupling of spin diffusion with the dipolar reservoir, and its possible use to measure the diffusion coefficient, was developed independently while our work was in progress, by Stengers and Jeener.[10]

II. MAGNETIZATION CURRENT

A. Spin interactions

Before attempting to derive an expression for the magnetization current we need to consider briefly the interaction of nuclear spins in a solid. Spins in a rigid lattice interact with an externally applied field $\vec{H}$, which is of the order of several kilogauss in typical NMR experiments, as well as with local fluctuating dipole fields produced by neighboring spins which are of the order of 1 G. If we neglect the quadrupole interaction, which vanishes in a perfect cubic crystal, the spin Hamiltonian is the sum of the Zeeman and secular dipole interactions, $\mathcal{H}=\mathcal{H}_Z+\mathcal{H}_d^0$. The truncated dipole Hamiltonian $\mathcal{H}_d^0$ is that part of the total dipole Hamiltonian which commutes with $\mathcal{H}_Z$, and is the only part which is effective in inducing spin transitions in high fields.[5,11,12]

The spin Hamiltonian for a single nuclear species of gyromagnetic ratio γ can be written

$$\begin{aligned}\mathcal{H}&=\mathcal{H}_Z+\mathcal{H}_d^0\\&=-\gamma\hbar H\sum_j I_{j_z}+\frac{\gamma^2\hbar^2}{4}\sum_{j,k;\,j\neq k}\frac{1-3\cos^2\theta_{jk}}{r_{jk}^3}\\&\quad\times(3I_{j_z}I_{k_z}-\vec{I}_j\cdot\vec{I}_k)\ .\end{aligned}\tag{1}$$

The field $\vec{H}$ is so far assumed homogeneous and is taken to be in the z direction, and $\hbar I_z=\hbar\sum_j I_{j_z}$ is the total z component of spin angular momentum obtained by summing over all lattice sites i. In the expression for the truncated dipole interaction r_{jk} is the distance between nuclei j and k and θ_{jk} is the angle between $\vec{r}_{jk}$ and the z axis.

Since $\mathcal{H}_Z$ and $\mathcal{H}_d^0$ commute with $\mathcal{H}$, the Zeeman energy and dipole energies are separately constants of the motion and the spin system may be described thermodynamically with Zeeman and dipole spin temperatures T_z and T_d.[13-15] The degree of alignment of spins in the external or local field is a Boltzmann distribution described by a density matrix

$$\rho=\frac{\exp(-\mathcal{H}_Z/kT_z-\mathcal{H}_d^0/kT_d)}{\mathrm{Tr}[\exp(-\mathcal{H}_Z/kT_z)\exp(-\mathcal{H}_d^0/kT_d)]}\ .\tag{2}$$

The spin interaction energies are so small that we can almost always make the high-temperature approximation yielding $\rho\simeq(1/Z)(1-\mathcal{H}_Z/kT_z-\mathcal{H}_d^0/kT_d)$, where Z is the partition function. From this density matrix it follows that the magnetization along the field direction obeys Curie's law

$$M = \mathrm{Tr}(\rho\gamma\hbar I_z) = (\gamma^2\hbar^2/ZkT_Z)\mathrm{Tr}(I_z^2)$$
$$= \gamma^2\hbar^2 NI(I+1)H/3kT_Z \quad , \tag{3}$$

where N is the nuclear spin density. The magnetization can thus be written as $M = \chi(T_Z)H$, where the static susceptibility is

$$\chi(T) = \gamma^2\hbar^2 NI(I+1)/3kT = C/T \quad , \tag{4}$$

and C is Curie's constant.

The Zeeman energy density is $-MH = -\chi(T_Z)H^2$. The dipolar energy density, which is $\frac{1}{2}$ the sum over all spins i of the energy $-\vec{u}_i \cdot \vec{h}_i$ which the magnetic moment $\vec{\mu}_i$ of spin i has with respect to the local magnetic field $\vec{h}_i$ due to neighboring nuclear moments, has a similar inverse dependence on the dipolar temperature T_d as a consequence of the high-temperature approximation. Therefore, in what follows it is convenient[5] to represent it as

$$E_d = -\chi(T_d)H_d^2 = -CH_d^2/T_d \quad . \tag{5}$$

H_d is in effect the root-mean-square average of h_i and is a constant of the spin system. For a one-species dipolar system having a Hamiltonian of the form of (1) it is $1/(\sqrt{3}\gamma)$ of the square root of the Van Vleck second moment.[12] The magnetic susceptibility $\chi(T_d)$ is here a purely mathematical function equal to C/T_d, where C is a property of of the sample given by Eq. (4) and T_d is the dipolar temperature.

Because of the interaction of nuclei with nonspin degrees of freedom of the solid, the spin system approaches equilibrium with the lattice with characteristic spin-lattice relaxation times for the Zeeman and dipole-dipole energy systems, which we denote respectively as T_{1Z} and T_{1d}. We often implicitly take these times to be infinite, unless otherwise stated.

We must emphasize that we restrict our discussion to the case $H \gg H_d$. In this case, although the untruncated dipolar Hamiltonian possesses matrix elements which change total M, these are nonsecular and completely negligible, and the truncated Hamiltonian (1) is an excellent approximation which is used below. Thus, we continue to assume that *total* M is invariant, except as affected by spin-lattice relaxation.

What is new here is to consider effects of a moderate field inhomogeneity—not moderate in the usual sense, but small enough that the difference in external field between neighboring spins is small compared to H_d. This means that mutual spin flips are not *dynamically* quenched; e.g., mutual spin flips continue to occur. The field gradients must, on the other hand, be large enough that the spatial variation in H be large compared to H_d over a distance equal to the spin-diffusion length in a spin-lattice relaxation time:

$$H_d/(DT_1)^{1/2} \ll \left|\vec{\nabla}|\vec{\mathrm{H}}|\right| \ll H_d/a \quad , \tag{6}$$

where a is a lattice spacing, $\left|\vec{\nabla}|\vec{\mathrm{H}}|\right|$ is the magnitude of the gradient of the magnitude of $\vec{\mathrm{H}}$, and D is the nuclear-spin-diffusion coefficient. Gradients of this order of magnitude occur in type-II superconductors although either inequality can be violated in them, depending on the sample, field, and temperature. In another paper[16] we will present an experimental study of spin diffusion in a variety of field gradients in the mixed state of superconducting vanadium. For the case of large field gradients, $\nabla H \sim H_d/a$, the diffusion coefficient will be partially quenched but the theory we will develop here will remain essentially valid with the diffusion coefficient becoming a function of field gradient.

In the present case, we assert that the truncated Hamiltonian is still of the form (1) if H is interpreted as the magnitude of $\vec{\mathrm{H}}$, and the I_j are represented in a coordinate system which spatially varies so that its z axis is along the local direction of $\vec{\mathrm{H}}$. Henceforth, we use the symbol H in this sense. The coefficients of the terms in the double sum in the term of (1) would be altered slightly, but only to the second order in $|\vec{\nabla} H|^2 a^2/H^2$.

In this case the two terms in (1) no longer commute, their commutator being proportional to $|\vec{\nabla} H|$, so E_d is no longer conserved by (1) even though the total magnetization is conserved. (Total magnetization is the volume integral of M, which is the magnitude of $\vec{\mathrm{M}}$. In our essentially thermodynamic treatment, $\vec{\mathrm{M}}$ and $\vec{\mathrm{H}}$ are always assumed collinear.) E_d changes locally and these changes of dipolar energy are compensated by changes in Zeeman energy.

We will discuss this problem quantitatively in essentially the same way that diffusion and conduction in a semiconductor or ionic conductor are traditionally treated, to relate diffusion rates and rates of flow of magnetization driven by the gradient of H. The problem is unusual, though, in that the only "lattice" is the dipole-dipole interaction which has low heat capacity (assuming T_1 infinite). Analogous systems would be: an ionic conductor in which the applied field gradient is so large and the lattice heat capacity so small that lattice heating produces appreciable countercurrent due to diffusion, or a half-filled inpurity band at an extremely low temperature where local electron-electron interactions might provide the dominant heat capacity. In these analogs, the electric field must be determined by external conductors and voltage clamps which must not, however, accept or donate charge to the conductor. Probably a realistic electric analog could not be found.

B. Simplified model for spin diffusion

In a rigid-lattice mutual spin flips lead to a random walk of magnetization which brings the spin system to equilibrium. A simple picutre of diffusion in which only spin flips due to nearest neighbors are included, and in which the spin-spin interaction is treated phenomenologically, can be used to obtain the form of the magnetization current density in a nonuniform field. The use of such a simplified model gives a clear picture of the underlying processes involved in spin diffusion.

We introduce the idea of magnetization current and current density. The magnetization current density $\vec{j}$ is defined as the vector whose divergence gives the rate of change of M:

$$\frac{dM}{dt} = -\vec{\nabla}\cdot\vec{j}. \tag{7}$$

In the presence of spin-lattice relaxation, (7) would be augmented in the usual way. The magnetization current across a surface is the surface integral of normal $\vec{j}$ as usual.

We will first consider the case of diffusion in a uniform magnetic field, following Bloembergen's approach.[3] He considered spins $\frac{1}{2}$, which are spaced at intervals a on a linear chain and interact only with nearest neighbors. If μ_z is the z component of the spin magnetic moment, then a mutual spin flip of oppositely aligned spins changes the magnitude of the net magnetic moment on each side of the plane between the two spins by $2\mu_z$.

The rate of spin flips due to interaction with a single neighbor will be denoted as W. It is a fraction of the rate of spin flips assumed over all neighbors, due to the interactions of a spin with the total local field, and has been estimated[6] to be of order $\frac{1}{15}T_2$. When two spins are oppositely aligned, the rate of mutual spin flip is $2W$, since there can be no mutual spin flip in the equally likely circumstance that the interacting spins have the same orientiation.

We will assume the spins at position x have z component of magnetic moment of either plus or minus μ_z with probability $P_\pm(x)$. The contribution to the current of magnetization arising from interactions of the pair of nuclei at positions $x-a$ and x along the chain is the sum of the contributions due to each of the two possible initial states of oppositely aligned spins and can be written as

$$J(x) = 2WP_-(x)P_+(x-a)(2\mu_z) + 2WP_+(x)P_-(x-a)(-2\mu_z) \ . \tag{8}$$

The probabilities $P_\pm(x)$ can be expressed in terms of a single parameter, $p(x) = P_+(x) - P_-(x)$, since we have the relation $P_+(x) + P_-(x) = 1$. We assume $p(x)$ is slowly varying so we can write $p(x-a) = p(x) - a\,\partial p(x)/\partial x$, and if we linearize Eq. (8) we get

$$J(x) = -Wa\frac{\partial p(x)}{\partial x}\mu_z \ . \tag{9}$$

If the chain of spins we considered is taken as a component of a simple cubic lattice, we can express the magnetization density in the field direction as $M(x) = \mu_z p(x)/a^3$, and obtain an expression for the magnetization current density

$$j_x = -Wa^2\frac{\partial M}{\partial x} \ . \tag{10}$$

If we identify the coefficient Wa^2 as the spin-diffusion coefficient D and ignore, for simplicity of notation, its tensor character[17] we can extend (10) to three dimensions; $\vec{j} = -D\vec{\nabla}M$. Since the magnetization is conserved if we neglect the spin-lattice interaction of the diffusion equation follows:

$$\frac{\partial M}{\partial t} = -\vec{\nabla}\circ\vec{j} = D\nabla^2 M \ . \tag{11}$$

We now consider how this must be modified in the presence of a nonuniform field, where mutual spin flips no longer exactly conserve Zeeman energy. There is an increase in the probability $W\!\downarrow$ of spin flips which lower the Zeeman energy relative to the probability $W\!\uparrow$ of spin flips which raise the Zeeman energy. Spin flips are induced by the dipole interaction and the change in Zeeman energy, δE, is taken up by the dipole energy reservoir. The ratio of the rates for the two types of processes should, therefore, be given by the Boltzmann factor

$$W\!\downarrow/W\!\uparrow = e^{\delta E/kT_d} \ . \tag{12}$$

The use of T_d in this equation is discussed at the end of this section.

The energy difference can be expressed as $\delta E = \mu_z a\,\partial H/\partial x$, where a is the distance between neighboring spins, and H is the spatially varying magnetic field. Using the high-temperature approximation we obtain

$$W\!\downarrow \cong W\!\uparrow\left[1 + \mu_z a\left(\frac{\partial H}{\partial x}\right)\Big/kT_d\right] \ . \tag{13}$$

The flow of magnetization across an imaginary surface between two spins at x and $x-a$ is given by an expression similar to Eq. (8):

$$J(x) = 2W\!\uparrow P_+(x-a)P_-(x)(2\mu_z) + 2W\!\downarrow P_-(x-a)P_+(x)(-2\mu_z) \ . \tag{14}$$

Since $W\!\uparrow \simeq W$, (13) and (14) can be combined to yield

$$J(x) = 2WP_+(x-a)P_-(x)(2\mu_z) + 2WP_-(x-a)P_+(x)(-2\mu_z) + W\mu_z^2 a\left(\frac{\partial H}{\partial x}\right)\Big/2kT_d \ . \tag{15}$$

The first two terms on the right-hand side of (15) represent a contribution to the current that would flow in a uniform field. An additional term proportional to the field gradient emerges. The magnetization current density due to this last term can be written as

$$Wa^2\left(\frac{U_z^2}{kT_d}\right)\left(\frac{1}{a^3}\right)\frac{\partial H}{\partial x}=D\left(\frac{N\mu_z^2}{kT_d}\right)\frac{\partial H}{\partial x}$$

$$=D\chi(T_d)\frac{\partial H}{\partial x} \quad . \tag{16}$$

Including all the terms contributing to $\vec{\mathrm{j}}$ in a nonuniform field, and generalizing to three dimensions we find

$$\vec{\mathrm{j}}=-D[\vec{\nabla}M-\chi(T_d)\vec{\nabla}H] \quad . \tag{17}$$

If we identify the coefficient of $\vec{\nabla}H$ as the magnetic conductivity $\sigma_m=D\chi(T_d)$, we obtain the magnetic analog of the ionic charge current; $\vec{\mathrm{j}}_i=-D_i\vec{\nabla}(ne)+\sigma\vec{\mathrm{E}}$, where D_i is the ionic diffusion coefficient, n the ionic density, e the electronic change, and σ the conductivity. The coefficients of the two terms in the expression for the ionic current are related through the Einstein relation $\sigma/D_i=ne^2/kT$, where T is the temperature of the solid. The diffusion coefficient D_i can be obtained either by measuring the time variation of the density n or from a measurement of n and σ utilizing the Einstein relation.[2]

In our case of a magnetic current we have an analogous relation,

$$\sigma_m/D=\chi(T_d)=N\langle\mu_z^2\rangle/kT_d \quad , \tag{18}$$

where $\langle\mu_z^2\rangle$ is in general the average value of the square of the z component of a spin's magnetic moment and is equal to the eigenvalue μ_z^2 above for $I=\frac{1}{2}$.

In analogy with the case of ionic diffusion, the diffusion coefficient might be obtained either from a measurement of D or of σ_m. In our experiments on vanadium it is measured calorimetrically, by observing the increase in T_d as the system is heated up by an applied field gradient.

The key assumption above, beyond the usual connection between D and σ_m, is the use of the dipolar temperature T_d in Eq. (8). It is justified to a greater extent in Sec. IIC, but at this point we may say the following: In this type of problem the Zeeman temperature is not really a statistical temperature but only expresses the ratio of H to M. The dipolar temperature is truly a temperature in the sense, for example, that it can be measured by a thermometer consisting of another, dilute, spin system. An example of this occurs in nuclear-polarization experiments, where the nuclear polarization reaches a value which, interpreted by Curie's law in terms of a spin temperature, yields the electron's dipolar temperature. In the present case, the irrelevance of T_Z can be seen by comparing two cases where the spatial variation of M, $\vec{\nabla}H$, and E_d are the same, but in which an extra uniform field ΔH_0 is added in one case. This would not change the flow of magnetization or the local change of E_d. The latter invariance can be proven by transforming ΔH_0 away by a rotating-frame transformation, which leaves the truncated dipolar interaction and M invariant.

C. Thermodynamic approach

In a nonuniform field, the spin temperature is not necessarily uniform while magnetization flows. It is useful to divide the Zeeman Hamiltonian into a homogeneous part $\mathcal{H}_{Zh}$ associated with the average field in the sample, H_{av}, and an inhomogeneous part $\mathcal{H}_{Zi}$ associated with the deviation ΔH_i from H_{av}. The Hamiltonian can be written in a form which emphasizes the interactions at each nuclear site,

$$\mathcal{H}=\mathcal{H}_{Zh}+\mathcal{H}_{Zj}+\mathcal{H}_d^0$$

$$=\gamma\hbar\, H_{\mathrm{av}} I_z-\gamma\hbar\sum_i \Delta H_i I_{i_z}$$

$$+\frac{\gamma^2\hbar^2}{4}\sum_i\sum_{j\neq i}\frac{1-3\cos^2\theta_{ij}}{r_{ij}^3}(3I_{i_z}I_{j_z}-\vec{\mathrm{I}}_i\cdot\vec{\mathrm{I}}_j)$$

$$=\mathcal{H}_{Zh}+\sum_i\mathcal{H}_{Zi_i}+\sum_i\mathcal{H}_{d_i}^0 \quad . \tag{19}$$

The spin operator I_z commutes with $\mathcal{H}$, and the total magnetization is, therefore, conserved if we neglect the spin-lattice interaction. Further, since $\mathcal{H}_{Zh}$ commutes with $\mathcal{H}$ a single constant homogeneous Zeeman spin temperature T_{Zh} can be defined. The inhomogeneous Zeeman Hamiltonian and dipole Hamiltonian do not commute and there is an exchange of energy between these spin systems. This leads to local variations of spin energy which can be described statistically in terms of spatially varying inhomogeneous Zeeman and dipole temperatures which take values T_{Zi_i} and T_{d_i} at the ith nucleus. The density matrix for the spins can now be written approximately as

$$\rho=\frac{1}{Z}\exp\left(-\frac{\mathcal{H}_{Zh}}{kT_{Zh}}-\sum_i\frac{\mathcal{H}_{Zi_i}}{kT_{Zi_i}}-\sum_i\frac{\mathcal{H}_{d_i}^0}{kT_{d_i}}\right) \quad . \tag{20}$$

The transport of spin energy due to spin diffusion will continue until $\partial\rho/\partial t=(i/\hbar)[\rho,\mathcal{H}]=0$. It is evident from expression 20 for ρ that this condition is only obtained when T_d is uniform and equal to T_{Zi}. At equilibrium the density matrix is

$$\rho=\frac{1}{Z}\exp\left(-\frac{\mathcal{H}_{Zh}}{kT_{Zh}}-\frac{\mathcal{H}_{Zi}+\mathcal{H}_d^0}{kT_d}\right) \quad .$$

We then have

$$\chi(T_{Zi})=\frac{M-M_{\mathrm{av}}}{H-H_{\mathrm{av}}}=\frac{\Delta M}{\Delta H}=\chi(T_d) \quad ,$$

where M_{av} is the average value of the magnetization in the solid.

The condition for equilibrium can be written equally well as a local relation,

$$\vec{\nabla} M = \chi(T_d)\, \vec{\nabla} H . \tag{21}$$

An expression for the magnetization current which is consistent with the above equilibrium condition and reduces to the usual diffusion current in the absence of a field gradient is (17), $\vec{j} = -D[\vec{\nabla} M - \chi(T_d)\vec{\nabla} H]$, which yields the diffusion equation

$$\frac{\partial M}{\partial t} = D\vec{\nabla} \cdot [\vec{\nabla} M - \chi(T_d)\vec{\nabla} H] . \tag{22}$$

We note that the term proportional to $\chi(T_d)$ in the square brackets of Eq. (17) cannot be $\vec{\nabla}[\chi(T_d)H]$ since this would lead to a buildup of magnetization in the case of nonuniform M and H, but uniform $T_{Zh} = T_{Zi} = T_d$, whereas in this case there should be no changes in M since the spin system is at equilibrium at a single temperature.

III. COUPLED DIFFUSION EQUATIONS

The Zeeman energy of the spin system is altered as a result of the redistribution of magnetization in a nonuniform field described in (22). The energy of the spin system must be conserved in mutual spin flips and the local change in Zeeman energy must be taken up by the dipole energy system. The dipole energy reservoir thus serves as a heat sink for spin diffusion.

To complete the description of spin diffusion it is necessary to give an expression for the rate of change of dipolar energy due to the flow of magnetization in a magnetic field gradient. Such an expression is apparent from analogy with ionic diffusion, where the electrical energy density is the charge density times the electrostatic potential and the rate of Joule heating is the current times the field. In our case the potential energy density is $-MH$ and the rate at which energy is absorbed by the dipole energy system is $\vec{j} \cdot \vec{\nabla} H$. The dipole energy density 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

$$\frac{\partial E_d}{\partial t} = \vec{j} \cdot \vec{\nabla} H + D_d \nabla^2 E_d , \tag{23}$$

where D_d is the diffusion coefficient for dipole energy. This coefficient can be shown to be of the same order of magnitude as D using a moment-method calculation.[4]

Equations (5), (22), and (23) provide a complete description of magnetic transport in a inhomogeneous field, ignoring spin-lattice relaxation. It is easy to eliminate (5), though it somewhat obscures the physics of the problem. The result is the two coupled equations

$$\frac{\partial M}{\partial t} = D\vec{\nabla} \cdot [\vec{\nabla} M - \chi(T_d)\vec{\nabla} H] , \tag{24a}$$

$$\frac{\partial \chi(T_d)}{\partial t} = \frac{\vec{j} \cdot \vec{\nabla} H}{H_d^2} + D_d \nabla^2 \chi(T_d) . \tag{24b}$$

In Eq. (24b), $\chi(T_d)$ is not the really significant quantity, but it is a way to express the size of E_d without extra notation. These equations would have to be modified in case N, the density of spins per unit volume, were not uniform.

The effect of spin-lattice relaxation can be taken into account by adding appropriate relaxation terms to these equations. To the right-hand side of Eqs. (24a) and (24b) we would add, respectively, $-[M - M(T_L)]/T_{1Z}$ and $-[\chi(T_d) - \chi(T_L)]/T_{1d}$, where T_L is the lattice temperature. These relaxation terms can be ignored when analyzing spin diffusion for metallic samples in which large field gradients are present at low temperatures since, as we will show presently, cross-relaxation effects due to diffusion occur on a faster time scale than spin-lattice relaxation. Relaxation effects will, however, be considered implicitly since they can be the source of an inhomogeneous magnetization, as in the case of type-II superconductors.

Applications and solutions of the coupled diffusion equations (24) will be considered in Sec. IV. At this point it is useful to write Eq. (24b), which describes the dissipation of dipole energy in a field gradient, explicitly in terms of spin temperatures. Once this is done it will be apparent that spin diffusion can be described as a cross relaxation of spin systems.[18]

The result of spin diffusion is the equilibration of the dipole and inhomogeneous Zeeman spin temperatures. This equilibration is a very slow process since the entire sample must reach a uniform final temperature with $T_d = T_{Zi}$. Because the final value of T_{Zi} is a property of the sample as a whole, it is not useful in describing the dynamics of spin diffusion, which is a local process. Specifically T_{Zi} is not a useful parameter in describing the initial rapid diffusion of a spin system far from equilibrium since spins only sense the energy of their immediate neighbors in a short time interval. This reflects the fact that the rate of spin diffusion is influenced by the spatial derivatives of M and not by the inhomogeneous magnetization density itself. It is useful, therefore, to define the gradient spin temperature T_{Zg}, which describes the gradient of M along the direction of the field gradient;

$$\vec{\nabla} M \cdot \vec{\nabla} H / (\nabla H)^2 = C / T_{Zg} . \tag{25}$$

The gradient temperature has the significance, for example, that the magnetization flow stops locally when T_{Zg} equals the local dipole temperature T_d. In that case Eq. (17) becomes zero.

We may now express (24b) in terms of spin temperatures or, more conveniently, inverse spin temperatures $\beta_{Zg}=1/T_{Zg}$ and $\beta_d=1/T_d$. Dividing through the equation by C we obtain

$$\frac{\partial\beta_d}{\partial t} = -\frac{D(\nabla H)^2}{H_d^2}(\beta_d - \beta_{Zg}) + D_d\nabla^2\beta_d \ . \qquad (26)$$

The first term on the right-hand side of Eq. (26) gives the change of β_d due to a cross relaxation of the dipole and Zeeman energy systems. The cross-relaxation rate for β_d and β_{Zg} is $1/\tau = D(\nabla H)^2/H_d^2$.

In the case that the field gradients are large and the system is far from equilibrium the dipole diffusion term is negligible compared to the cross-relaxation term on the right-hand side of (26). β_d rapidly approaches β_{Zg} and the magnetization current density $\vec{j}$ will be quite small. The equilibration of β_d and β_{Zg}, which tends to be established by the cross-relaxation term, is upset by the slow diffusion of dipole energy. A small magnetization current density will consequently persist until a uniform value for $\beta_d=\beta_{Zg}$ is established in the sample. A more detailed discussion of the various stages of spin diffusion is given in Sec. IV.

IV. SPIN DIFFUSION IN REAL SYSTEMS

Explicit solutions of Eqs. (24) are difficult even for simple model situations. In general, however, the discussion of Sec. III shows that if the system is initially far from quasiequilibrium and $|\vec{\nabla}H|$ is sufficiently large, there are two time epochs. In the first, there is a relatively large, exponentially decaying 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 $\vec{\nabla}M \simeq \chi(T_d)\vec{\nabla}H$, but since T_d is in general nonuniform there is a further slow diffusion mediated by the last term in Eq. (24b).

For example, suppose that initially M and $\chi(T_d)$ are uniform, while there is a large variation of H in the sample, of magnitude ΔH, with $\Delta H \gg H_d$. This is the case in type-II superconductors in many practical experiments, where ΔH is more than an order of magnitude larger than H_d. During the initial stage of spin diffusion $\vec{j} \simeq D\chi(T_d)\vec{\nabla}H$ and we can neglect the dipole diffusion term in Eq. (24b) compared to the cross-relaxation term since

$$\frac{D_d\nabla^2\chi(T_d)}{\vec{j}\cdot\vec{\nabla}H/H_d^2} \approx \frac{D\nabla^2\chi(T_d)}{D\chi(T_d)}\,\frac{H_d^2}{(\nabla H)^2} \approx \frac{H_d^2}{(\Delta H)^2} \ll 1 \ . \qquad (27)$$

The rate of change of the magnetization current density is

$$\begin{aligned}\frac{\partial\vec{j}}{\partial t} &= -D\left(\vec{\nabla}\,\frac{\partial M}{\partial t} - \frac{\partial\chi(T_d)}{\partial t}\,\vec{\nabla}H\right)\\ &= D\vec{\nabla}\cdot(\vec{\nabla}\cdot\vec{j}) - D(\vec{j}\cdot\vec{\nabla}H)\vec{\nabla}H/H_d^2 \ . \end{aligned} \qquad (28)$$

It is expected that the spatial variation of j, $\chi(T_d)$, and M will be similar in extension to that of H; $\vec{\nabla}\cdot\vec{j}$ and $\vec{\nabla}H$ are then, respectively, of order of magnitude j/R_0 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 R_0 from the vortex center. The second term on the right-hand side of Eq. (28) is larger than the first by a factor of order $(\Delta H)^2/H_d^2 \geqslant 10^3$. The first term can, therefore, be neglected and j decreases exponentially toward zero with rate constant $D(\nabla H)^2/H_d^2$. Concurrently there is an exponential decay in M and $\chi(T_d)$ which can be estimated by integrating Eqs. (24a) and (24b).

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. Physically this is because of the relatively small heat capacity of the dipole energy system, which serves as a heat sink for the energy dissipated by the inhomogeneous Zeeman energy system. If we were to consider a sample with a sinusoidal nonuniform field equal to $(\Delta H/2)\sin kx$, the ratio of the heat capacities for equal temperatures of these two spin energy systems would be $8H_d^2/(\Delta H)^2$.

A related example of thermodynamic quenching has been considered by Buishvili[19] for a case in which nuclear spins are relaxed primarily by fluctuating fields due to the dipole-dipole interaction of magnetic ions. This may occur in systems with large ion concentration at low temperatures. The energy of the relaxing nuclei is transferred to the dipole reservoir of the magnetic ions and from there to the lattice. But the small dipole reservoir may become heated, thereby becoming a bottleneck for the flow of nuclear Zeeman energy to the lattice.

Elsewhere[16] we will describe experiments in which the magnetization is not monitored as is usual but rather the average time variation $\chi(T_d)$ is observed. In these experiments we start with $M=0$ but $\chi(T_d)$ large. Initially the current is $\vec{j}=D\chi(T_d)\vec{\nabla}H$, and the time variation of the dipole susceptibility is given by

$$\frac{\partial\chi(T_d)}{\partial t} = -D\,\frac{(\nabla H)^2}{H_d^2}\,\chi(T_d) \ . \qquad (29)$$

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

The second epoch of the time evolution starts when the two terms on the right-hand side of Eq. (24b) are approximately equal and we can no longer neglect the second term. The two terms are unequal and the inequality (27) holds as long as the magnetization current density can be written as $\vec{j} \approx D\chi(T_d)\vec{\nabla}H$. It follows, then, that the two terms are roughly equal when $j = [H_d^2(\Delta H)^2] D\chi(T_d)\nabla H$. Since the difference of the two terms in the expression (17) for $\vec{j}$ is much smaller than the larger term $D\chi(T_d)\vec{\nabla}H$, the two terms must be nearly equal. During the second epoch, therefore, a kind of local equilibrium is approached with $\vec{\nabla}M \simeq \chi(T_d)\vec{\nabla}H$. We have seen that this corresponds to the equalization of T_d and T_{Zg}. Spin diffusion continues with the approximate equalibrium value $\vec{\nabla}M$ keeping step with local changes of dipole temperature as a uniform dipole temperature is established in the sample. At the outset of this second stage of spin diffusion, the magnitude of the magnetization current density may therefore be estimated as $j \approx D[H_d^2/(\nabla H)^2]\vec{\nabla}M$. This is a factor $(\nabla H)^2/H_d^2$ smaller than would be obtained on the basis of the relation $\vec{j} = -D\vec{\nabla}M$, which is appropriate only in a uniform field, but which had been used to estimate the diffusion current in type-II superconductors. The role of spin diffusion in spin-lattice relaxation in type-II superconductors must, therefore, be reconsidered.

On the basis of the foregoing discussion of spin diffusion, a variety of experimentally realizable situations can be characterized. During the first interval of spin diffusion, the spin system is far from equilibrium and we can neglect the dipole energy-diffusion term in Eq. (24b). The expression for $\partial\chi(T_d)/\partial t$ then becomes

$$\frac{\partial\chi(T_d)}{\partial t} = D[\nabla M \cdot \nabla H - \chi(T_d)(\nabla H)^2]/H_d^2 \, . \qquad (30)$$

We will first consider a situation in which the term $D\chi(T_d)(\nabla H)^2/H_d^2$ predominates on the right-hand side of Eq. (30). This term can be made large by first adiabatically demagnetizing in the rotating frame (ADRF) to produce a low dipole-dipole temperature, and then lowering the magnetic field in order to bring the sample into the superconducting state, where there may be large field gradients, as will be discussed in Sec. V. The dipole temperature after ADRF can be made either positive or negative. If it is positive it is clear from (17) and (30) that the magnetization current density will be in the direction of the field gradient and that the dipole temperature will increase. If a negative dipole temperature is produced, $\vec{j}$ will flow opposite the direction of $\vec{\nabla}H$ and a magnetization aligned opposite to ΔH will develop, while T_d will decrease, becoming more negative.

The term $D\vec{\nabla}M \cdot \vec{\nabla}H/H_d^2$ in Eq. (30) may become large in the mixed state of a type-II superconductor. In the magnetization in the superconductor is saturated by large rf pulses,[9] the magnetization will increase more rapidly near the vortex core. A large magnetization gradient along the field-gradient direction is thereby created. The magnetization current will then flow opposite to the direction of $\vec{\nabla}H$, thereby lowering the dipole energy. The opposite sense of flow is produced in a field-cycling experiment in which the nuclei are first aligned in a field larger than H_{c_2} before the field is lowered into the mixed state.[8] The relatively rapid spin-lattice relaxation within the vortex core causes the lowest magnetization to exist within the region of highest field. Spin diffusion will then result in a flow of magnetization towards regions of high field which will drive the dipole temperature negative in most of the sample. It is interesting to note that if the magnetization in a sample is uniform and the dipole energy is zero, there would be no spin diffusion in a nonuniform field since the inhomogeneous Zeeman and dipole systems would be at equilibrium at infinite spin temperature.

V. DETERMINATION OF D

The diffusion coefficient has generally been inferred from measurements of enhanced spin-lattice relaxation of magnetization in paramagnetically doped crystals.[3,20,21] In these experiments a diffusion current is driven by a nonuniform magnetization in a uniform field. Elsewhere[16] we describe the first measurement of D that does not depend upon the nuclear interaction with paramagnetic impurities nor indeed upon the existence of a nonuniform magnetization. We will show here that a value for D can be obtained from measurements of the relaxation rate of dipole energy of samples in the presence of a nonuniform field. Accurate values for D could be obtained for samples in which the field gradients are known. The spin-diffusion coefficient has recently been obtained for protons in $Y(C_2H_5SO_4)_3 \cdot 9H_2O$ using another technique in which paramagnetic impurities are not inherently involved. D is inferred from the rate of nuclear relaxation in crystallites of varying size which is due primarily to the diffusion of magnetization from the crystallite's surface.[22]

We have already mentioned that a large dipole energy in the presence of large field gradients can be created by use of a field-cycling technique. The sample is adiabatically demagnetized in a large homogeneous field and then the field is lowered, thereby bringing the sample into the superconducting state. After a variable time in the superconducting state, the field is raised to resonance. The sample is then adiabatically remagnetized by applying a slowly increasing resonant rf field. The residual alignment of spins in the local dipole fields is converted to an alignment in the applied rf field which can be detected. The signal obtained is proportional to the internal dipole energy remaining in the sample just before the field was raised.

The observed relaxation rate, $1/T_{1\,\mathrm{expt}}$ is the sum of the rate of dipole energy dissipation due to spin diffusion, $1/T_{1\,\mathrm{diff}}$, and the spin-lattice relaxation rate, $1/T_{1\,\mathrm{expt}} = 1/T_{1\,\mathrm{diff}} + 1/T_{1d}$. We will consider here only the initial relaxation rate, since this allows us to make the simplifying assumption that the dipole energy density $E_d(\vec{r})$ is uniform in the sample. The initial decay rate of dipole energy due to diffusion, for the experiment we have described, can be obtained using (29),

$$\frac{1}{T_{1\,\mathrm{diff}}} = \int \frac{\partial E_d(\vec{r})}{\partial t} d\vec{r} \Big/ \int E_d(\vec{r})\, d\vec{r} = \int \frac{D(\nabla H)^2}{H_d^2} d\vec{r} \ . \tag{31}$$

The relaxation rate due to diffusion is the weighted average of $1/\tau = D(\nabla H)^2/H_d^2$. The rate $1/\tau$ varies spatially since $\vec{\nabla} H$ does. The diffusion coefficient itself is also a function of $\vec{\nabla} H$ since neighboring spins are effectively detuned by the field gradients. The rate of mutual spin flips is, therefore, reduced. The decrease in D becomes significant when the field difference between neighboring spins is comparable to the local dipole-dipole fields.

For an accurate determination of D it is helpful if $1/\tau > 1/T_{1d}$. This condition is often satisfied at interfaces involving superconducting materials and in type-II superconductors.[23] For example, below the bulk critical field H_c, type-I superconductors exhibit the Meissner effect, excluding flux from the interior of the sample. Surface currents cause the field to be exponentially damped inside the sample in a distance λ, which is of order 500 Å. A field gradient of order $H_c/\lambda \approx 10^7$ G/cm will, therefore, exist on the surfaces of a sheet of superconducting material aligned parallel to a magnetic field. The decay of dipole energy in a stack of such sheets could be measured using the field-cycling technique in which an rf field is applied only when the applied field is larger than H_c. The rf field is applied in a direction perpendicular to H and parallel to the plane of the sheets.

Even larger field gradients and more rapid cross-relaxation times can be produced in a superconducting surface sheath, which exists in fields larger than the upper critical field for the bulk material but below a field H_{c3}. The superconducting state nucleates at the surface of almost all superconducting materials except for some pure type-I superconductors. For a sheet aligned parallel to an applied field less than H_{c_3}, the fields at the sample's surface and in its interior are equal to the applied field while the field in the surface sheath may be appreciably lower.

The diffusion coefficient can be obtained for normal metals by exploiting the proximity effect in samples composed of alternating normal and superconducting layers. Cooper pairs leak from the superconducting to the normal region up to a typical depth of 10^3 Å and large field gradients are thereby created in the normal material.

In our own experiment we observed spin diffusion driven by the field gradients which exist in the mixed state of vanadium. By varying the applied field and temperature in such experiments a wide range of field gradients can be produced.

VI. APPLICATIONS TO OTHER SYSTEMS

A. Dynamic quenching

It has been stressed that the considerations above are independent of, and complementary to, previous predictions that diffusion will be dynamically quenched when the field difference between neighbors $a|\vec{\nabla} H|$ becomes comparable to H_d. Presumably the theory outlined above would still be applicable but D and D_d would be reduced because over-all energy conservation is required in a mutual spin flip. These diffusion coefficients could be calculated using previous methods[4,21] by including a spatially linearly varying field in the starting Hamiltonian. An experimental study of dynamic quenching is presented in another paper.[16]

B. Electric quadrupole interactions

In the presence of quadrupole interaction the above theory would be modified in that H_d^2 would be replaced by $H_d^2 + H_q^2$, where CH_q^2 is the sum of the traces of the square of the quadrupolar interaction for the N spins in a unit volume. The sum would have to exclude spins with a quadrupolar interaction so large that they would not cross relax with other spins in a relevant time, and this would be delicate since these spins would otherwise contribute heavily to the sum. Thermodynamic quenching would occur when the total spatial variation of H is greater than H_q^2. The large quadrupolar interactions present in the superconducting alloys studied previously[9] may thereby be sufficient to avoid thermodynamic quenching of diffusion, although this seems unlikely particularly since dynamical quenching due to the quadrupole interaction would then significantly limit the rate of spin diffusion.

C. Spectral diffusion

The present theory outlines a precise and tractable treatment of spectral diffusion for the case of spatially slowly varying spectral position. Of course, any theory of spectral diffusion must take account of the requirement of local energy conservation. It is possible that the ideas in this paper may be useful for developing the theory of spectral diffusion in the more difficult case where spectral position is spatially random. The present paper is closely related to ideas long used in the theory of cross relaxation of spectral lines, which are also thermodynamically quenched.[14]

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