Spectral Diffusion in Electron Resonance Lines

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Spectral diffusion in the inhomogeneous paramagnetic resonance lines of Ce^{3+} and Er^{3+} in $CaWO_4$ at concentration $\sim 10^{18}$ spins/cc has been studied by electron spin echo techniques. Measurements show that the spreading of excitation through the line can be approximately described by a diffusion kernel in the form of a Lorentzian function whose width is linear in time. Local field fluctuations due to spin-spin flips and spin-lattice flips appear to be the primary cause of diffusion. In $(Ca,Ce)WO_4$ below 4.2°K the lattice time is long, and spin-spin flips predominate, leading to a diffusion rate which is independent of temperature. In $(Ca,Er)WO_4$ lattice relaxation is more rapid, and the diffusion parameter varies as the lattice time. Nuclei of W^{183} in the host crystal have been observed to give a modulation in the envelope of spin echoes, but the corresponding local fields are smaller than those arising from electron spins at the concentrations studied.

I. INTRODUCTION

In a discussion of paramagnetic resonance of F centers, Portis[1] has drawn attention to certain sources of line broadening which remain steady, or almost steady, in their effects during the time required for an electron spin transition. Such, for instance, are the irregular mechanical strains which are sometimes cited as a cause of anomalous linewidths, or the z components of magnetization of nuclei present in the neighborhood of electron spins. Mechanisms of this kind, where they are dominant, give rise to an "inhomogeneous" line, in which each spectral component, or "spin packet" has an independent history of interactions with the rf field and with the crystal lattice. The properties of such a line are well illustrated by the experiments of Feher[2] on the resonance of donors in silicon. If rf power is applied at one frequency in the line, it excites only a narrow band of spin packets and "burns a hole" which persists for a time comparable with the lattice relaxation time. Any transfer of excitation between the spin packets is exceedingly slow, and it is possible to observe fine structures with a resolution of one thousandth of the linewidth by inducing resonant transitions within the line. The extreme inhomogeneity of this line was also demonstrated in the electron spin echo measurement of Gordon and Bowers.[3] Phase memory times of several hundred microseconds were observed, thus setting a low limit on the fundamental width of the spin packets and on any time variation of the broadening mechanisms. Such extreme isolation between the spectral components of a line does not, however, appear to be typical of many of the materials commonly studied in paramagnetic resonance, and it is often assumed, on the contrary, that, when power is applied to one part of the line, all spin packets are uniformly excited. This need not mean, of course, that the line is homogeneous in a strict sense, but it implies the existence of a spectral diffusing mechanism rapid enough to spread excitation through the line in a time which is short compared with the lattice relaxation time.

We have made an experimental study of spectral diffusion through the inhomogeneous resonance lines of Ce^{3+} and Er^{3+} ions in calcium tungstate crystals at magnetic concentrations of the order of 10^{18} spins/cc and at helium temperatures. In these materials diffusion is moderately slow and we have been able to use the techniques of electron spin echoes. The function governing spectral diffusion can be explored most directly by means of "stimulated echo" experiments,[4] in which three pulses of rf energy are applied at times $t=0$, $t=\tau$, and $t=\tau+T$, and the echo signal appears at $t=2\tau+T$. The first two pulses form an artificial structure of peaks and troughs in the resonance line. In a simple case with two 90° pulses and an rf field greater than the linewidth, the lineshape function is changed from $M_z(\omega)$ to $-M_z(\omega)\cos(\omega-\omega_0)\tau$, where ω_0 is the radio frequency.[5] Spectral diffusion causes a partial filling in of this pattern during the time "T" and whatever remains of it is recalled as a stimulated echo by the third pulse. The periodicity of $1/\tau$, the essential feature of this pattern for diffusion studies, is not restricted to the special conditions mentioned above (Sec. III). In essence this procedure is similar to burning holes and monitoring the rate of filling in, and we have made some measurements of this type (Sec. VI). Spin echo experiments have, however, the advantage of generating "holes" of simple form and of controllable width, and our values for diffusion parameters are based solely on echo measurements. The information can, in principle, be derived from normal two-pulse echoes as well as from stimulated echoes, and we have sometimes found this a more convenient way to follow changes in diffusion behavior (Sec. V), although in practice it is not possible to make two-pulse measurements over such long times, and the early stages of diffusion tend to be the most strongly emphasized. The two-pulse decay envelope reveals in a striking manner the effects of nuclear Larmor precession in the host material.

[1] A. M. Portis, Phys. Rev. **91**, 1070 (1953).
[2] G. Feher, Phys. Rev. **114**, 1219 (1959).
[3] J. P. Gordon and K. D. Bowers, Phys. Rev. Letters **1**, 368 (1958).
[4] E. L. Hahn, Phys. Rev. **80**, 580 (1950).
[5] In all formulas frequencies are given in radian units.

II. MATERIALS AND APPARATUS

Single crystals of calcium tungstate containing cerium, erbium, or both were grown by the Czochralski technique as previously described.[6] The paramagnetic ions were introduced into the crystal lattice by the addition of $NaCeW_2O_8$ and $NaErW_2O_8$ to the melt. Chemical analysis indicates that most of the sodium is lost by evaporation; charge compensation occurs, presumably, by the substitution of two Ce^{3+} or Er^{3+} ions and one vacancy for three Ca^{++} ions. The compositions used can be expressed as $Ca_{(1-3x-3y)}Ce_{2x}Er_{2y}WO_4$ with x and y ranging to 2.7×10^{-4}, corresponding to total paramagnetic ion concentrations of 3.3×10^{17} to 3.4×10^{18} ions/cc. The lowest states of both ions are Kramer's doublets, and for most purposes both give simple two-level systems at helium temperatures. Paramagnetic resonance in these materials has been investigated by Hempstead[7] who finds for Ce^{3+}, $g_{\parallel}=2.92$, $g_{\perp}=1.43$; and for Er^{3+}, $g_{\parallel}=1.2$, $g_{\perp}=8.3$. For Ce^{3+} the proportionality between frequency and field changes gradually from 4.1 Mc/sec per gauss to 2.0 Mc/sec per gauss as the angle between the external field and the crystal axis is varied from 0° to 90°. For Er^{3+} this factor changes from 1.6 Mc/sec per gauss at 0° to 11.6 Mc/sec per gauss at 90°, and has a relatively rapid rate of change near 0° where many of the Er^{3+} measurements were made. W^{183} is the only magnetic nucleus present in significant amounts in the host lattice and has a moment of 0.116 nuclear magneton[8] and a relative abundance of 14%. Its contribution to the linewidth is only 8 mgauss full width, i.e., 16 kc/sec in the Ce^{3+} line at 90°. The linewidths calculated from dipolar interactions of electron spins are fractions of a Mc/sec, e.g., 200 kc/sec full width at half power for 10^{18} Ce^{3+} spins/cc at 90°.[9] Experimental linewidths ranged from 14 Mc/sec to 30 Mc/sec and showed only a slight dependence on concentration, thus suggesting that crystal strains are the major factor in line broadening.[7] Weak satellite lines were seen in many specimens. The isotope Er^{167} ($I=\frac{7}{2}$, relative abundance 23%) accounts for some of these but for others the cause is not definitely known. It is possible that they arise from closely situated ion pairs. We have made no special study of these satellites beyond making a rough measurement of their spin echo decay envelope wherever this was possible. In all satellites decay proceeded at about the same rate as it did in the main lines.

The apparatus was essentially the same as that described earlier in connection with spin-lattice relaxation experiments.[10] Pulses of microwave power at a frequency of 6.7 kMc/sec and of 1 μsec duration were delivered to a resonant cavity from a klystron master oscillator feeding through a grid-controlled traveling wave tube amplifier. The amplifier generated fields in the cavity ~0.1 oe. This was sufficient to give a 90° spin flip during the pulse, and to excite a portion of the inhomogeneous line ~0.5 Mc/sec wide between half power points. The echo experiments were usually concerned with diffusion over intervals short compared with this, and compared with the frequency interval ~0.2 Mc/sec estimated for dipolar broadening. In the "off" position of the amplifier, power leakage was 60 db down, and was found in tests to be one or more orders of magnitude below the cw signal level required to produce any observable effects on the echo lifetimes. The detection apparatus consisted of a superheterodyne system with an over-all response time of 0.25 μsec and contained a paralyzing circuit to prevent overloading of the later amplifying stages by the power pulse. This was provided primarily for relaxation type experiments, and was not usually necessary in echo experiments, where the power pulses were short and the free induction signals (decay time ~0.5 μsec) constituted the main source of unwanted transients following the pulse.

III. SPECTRAL DIFFUSION AND SPIN ECHOES

Spectral diffusion within a nuclear resonance line has been considered in some detail by Herzog and Hahn.[11] Since the physical model described by them has been a useful guide in the choice of experiments and in the interpretation of results, we recapitulate some of its features here. Spins are divided into two groups: spins A which are actually observed, and spins B which provide the local magnetic fields acting on spins A. Reorientation of spins B, due to spin-spin flipping, spin-lattice relaxation, or rf resonance, cause changes in the local fields and shifts in the Larmor frequencies of spins A. A statistical treatment of these shifts is made on the following assumptions: (i) All environments of A spins contain the same numbers of B spins in the same geometric positions. (ii) The instantaneous distribution of local fields is Gaussian and is unchanged, although the local field at a particular site may undergo a sequence of variations. The corresponding frequency distribution function is

$$P(\delta_0)=\frac{1}{\delta_A(2\pi)^{\frac{1}{2}}}\exp(-\delta_0^2/2\delta_A^2), \qquad (1)$$

where $\delta_0=\omega_0-\omega$, the deviation in Larmor frequency caused by the local field. If frequency variations are slow, Eq. (1) also gives the lineshape measured in a resonance experiment. (iii) If at a time $t=0$ we select a group of A spins, all of them seeing the same local field

[6] K. Nassau and L. G. van Uitert, J. Appl. Phys. **31**, 1508 (1960).

[7] Private communication. Paramagnetic resonance of Gd^{3+} and Mn^{2+} in $CaWO_4$ has been reported by C. F. Hempstead and K. D. Bowers, Phys. Rev. **118**, 131 (1960). The narrow linewidths obtained for the $\frac{1}{2}\rightleftarrows\frac{1}{2}$ transitions in these materials suggest that crystal field irregularities are the principal cause of line broadening elsewhere.

[8] M. P. Klein, Bull. Am. Phys. Soc. **6**, 104 (1961).

[9] Estimated from the formula $(\Delta\omega)_{\frac{1}{2}}=n(2\pi^2g^2\beta^2/3\sqrt{3}\hbar)$ for the half-width at half power. The formula has been derived by P. W. Anderson and takes into account the effects of random dilution. See also P. W. Anderson, Phys. Rev. **82**, 342 (1951) and reference 12.

[10] K. D. Bowers and W. B. Mims, Phys. Rev. **115**, 285 (1959).

and all having a Larmor frequency deviation δ_0, then, as time progresses, their frequency deviations will take on a spread of values such that the average $\bar{\delta}$ of the deviation tends to zero according to $\bar{\delta}=\delta_0\exp(-Rt)$. The decay constant R measures the rate at which a particular local field configuration breaks up, and, since all B spins are assumed to have an equivalent perturbing environment, it will be the same everywhere in the crystal.

The spectral diffusion law derived on these assumptions is

$$P(\delta,t;\delta_0)=\frac{1}{\delta_A[2\pi(1-e^{-2Rt})]^{\frac{1}{2}}}\times\exp\left(-\frac{(\delta-\delta_0e^{-Rt})^2}{2\delta_A^2(1-e^{-2Rt})}\right), \quad (2)$$

where $P(\delta,t;\delta_0)$ is the magnetization at a time t and at a frequency δ from the line center, which results from the diffusion of unit magnetization starting at δ_0 at $t=0$. This resembles the familiar Gaussian kernel for spatial diffusion,

$$P(\delta,t;\delta_0)=(2\pi Dt)^{\frac{1}{2}}\exp(-(\delta-\delta_0)^2/4Dt), \quad (3)$$

but provides for an asymptotic approach to the frequency limits set by the resonance linewidth, and takes into account a tendency to diffuse back from the wings towards the center of the line. If diffusion is restricted to frequency intervals much smaller than the linewidth, neither of these two considerations affects the decay of echo amplitudes which follows the same laws as in the familiar case of spatial diffusion. The diffusion parameter is $R\delta_A^2$, the two-pulse echo decay is proportional to $\exp(-\frac{2}{3}R\delta_A^2\tau^3)$, and the three-pulse echo amplitude to $\exp(-\frac{2}{3}R\delta_A^2\tau^3-R\delta_A^2\tau^2T)$. The factor $\exp(-R\delta_A^2\tau^2T)$ in the latter expression describes the decay in time T of a sinusoidal excitation pattern of period $1/\tau$ which is formed out of M_z by the first two pulses.

Although the physical mechanism may be similar it is clear that the identical treatment cannot be applied to a randomly diluted paramagnetic material, in which the spin-A environments are not all similar, but are permanently differentiated according to the distribution of magnetic centers. Magnetically dense neighborhoods give local fields with a wider range of excursions and contribute wings to the frequency distribution function. This will affect the dynamic as well as the static properties of the line and suggests that both the resonance lineshape and the diffusion kernel should be wider in the wings than the Gaussians deduced for a regular spin array. Theoretical analysis has shown that the resonance lineshape should be approximately Lorentzian[9,12] and we have here tentatively adopted a similar form for the diffusion kernel, i.e.,

$$P(\delta,t;\delta_0)=\frac{mt/\pi}{(mt)^2+(\delta-\delta_0)^2}, \quad (4)$$

where m is a diffusion parameter characteristic of the material. The widening of the excited portion is linear in time. No allowance has been made for an asymptotic approach to the resonance lineshape since the diffusion intervals were always relatively small. The decay factors in the spin echo amplitudes corresponding to the diffusion kernel Eq. (4) have been deduced by Klauder,[13] and are $\exp(-m\tau^2)$ for the two-pulse echo and $\exp(-m\tau^2-m\tau T)$ for the three-pulse echo. As will be seen later, there is not always a very close experimental agreement with these functions, but they fit the data much better than the expressions derived from a Gaussian diffusion kernel, and, where discrepancies occur, they are usually such as to indicate an even larger contribution of wide range frequency fluctuations than is implied by the use of the Lorentz kernel. It is in any case doubtful whether the Gaussian kernel, first introduced for diffusion in liquids, gives a correct description of the shifts in Larmor frequencies which arise from local field fluctuations in a solid. The Gaussian process implies a random sequence of small steps of similar magnitude. There appears to be no reason for expecting this, either here or in the concentrated case. Moreover, the problem of relating the spectral diffusion properties of typical electron and nuclear spin systems is not limited to the effects of random dilution. Forces other than dipolar interaction play an important part in determining the shape of an electron resonance line, and the width is often much greater than that calculated from dipolar interactions alone. These additional forces may or may not contribute to the rate of spectral diffusion. The physical situation is a complex one, and, since there is so little data available regarding spectral diffusion, it is probably best to adopt a conservative attitude, treating diffusion measurements on an empirical basis, and regarding Eq. (4) and the echo decay formulas derived from it mainly as convenient standards of comparison.

The mathematical expressions given in the literature of spin echoes are usually derived by assuming that the rf field H_1 is greater than the linewidth, and that all spins are turned through the same angle when an rf pulse is applied. In our experiments the rf fields are much smaller than the linewidth, and are only sufficient to excite a narrow band of spin packets extending for a few hundred kc/sec on either side of the exact resonance frequency. One might expect in such a case that the excited spins would behave as if they constituted a line of half-width $\omega_1=\gamma H_1$ analogous to the "hole" burnt out by the rf pulse. The remainder of the line would then consist of B spins playing their part in the diffusion process undisturbed by the measurements. Although it

[11] B. Herzog and E. L. Hahn, Phys. Rev. **103**, 148 (1956).
[12] C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953).
[13] J. R. Klauder, Bull. Am. Phys. Soc. **6**, 103 (1961).

is not strictly correct, this simple view is often a convenient one, and it avoids consideration of the involved trigonometric expressions which arise in a full analysis for the case of $\omega_1 <$ linewidth. In the following paragraph we take this analysis part of the way in order to show what conditions must be met if the concepts of "hole burning" and of an "effective line" are to give an adequate representation of the facts.

In a system of coordinates rotating about an axis parallel to the Zeeman field with a frequency equal to the signal frequency, it can be shown that each magnetization vector precesses about an effective field which is the resultant of H_1 and of a field δ/γ which represents the discrepancy δ between the frequencies of the signal and of free Larmor precession.[14] If the Zeeman field is along the z axis and the rf field along the rotating x axis, this motion transforms the magnetization in the rotating system $\mathbf{M}=(M_x,M_y,M_z)$ to $[R]\mathbf{M}$, where $[R]$ is the matrix

$$\begin{bmatrix} s_\Psi^2+c_\Psi^2 c_\theta & -c_\Psi s_\theta & s_\Psi c_\Psi(1-c_\theta) \\ c_\Psi s_\theta & c_\theta & -s_\Psi s_\theta \\ s_\Psi c_\Psi(1-c_\theta) & s_\Psi s_\theta & c_\Psi^2+s_\Psi^2 c_\theta \end{bmatrix}.$$

c_Ψ, s_Ψ, c_θ, and s_θ stand for $\cos\Psi$, $\sin\Psi$, $\cos\theta$, and $\sin\theta$, and $\Psi=\tan^{-1}(\omega_1/\delta)$ is the angle between the effective field and the z axis. θ is the angle by which the magnetization turns about the effective field during the pulse time t and is given by $\theta=(\omega_1^2+\delta^2)^{\frac{1}{2}}t$. The z component of $[R]\mathbf{M}$ gives the form of the hole burnt out by a pulse of duration t. Since only a small portion of the resonance line is involved, the initial magnetization $(0,0,M_{z,0})$ may be taken to be the same for all spectral components and the z component $M_{z,t}$ after the pulse is the function

$$\frac{M_{z,t}}{M_{z,0}}=c_\Psi^2+s_\Psi^2 c_\theta$$
$$=1-(\omega_1^2/\omega_1^2+\delta^2)[1-\cos(\omega_1^2+\delta^2)^{\frac{1}{2}}t]. \quad (5)$$

$M_{z,t}$ consists of a Lorentz shaped envelope of half-width ω_1, filled with a periodic pattern. This pattern becomes fine at large values of $\omega_1 t$, and eventually its features will be blurred out either by diffusion or as a result of variations in ω_1 across the sample. Provided that such factors are adequate to smooth out $\cos(\omega_1^2+\delta^2)^{\frac{1}{2}}t$ without also distorting the envelope $\omega_1^2/(\omega_1^2+\delta^2)$, $M_{z,t}$ acquires the form of an ideal "hole" given by

$$(M_{z,t}/M_{z,0})=1-(\omega_1^2/\omega_1^2+\delta^2). \quad (6)$$

In Fig. 1 this is compared with $M_{z,t}$ as derived from Eq. (5). If $\omega_1 t=\pi/2$, $M_{z,t}$ approximately resembles the ideal "hole." At higher values of $\omega_1 t$ undulations become prominent in the wings of $M_{z,t}$, and will, if not smoothed out, modify the experimental observations. Double bumps and other distortions which have been seen in the free induction signals at high power levels can be attributed to the corresponding undulations in the spectrum of $M_{x,t}$ and $M_{y,t}$. The reversals of $M_{z,t}$ which take place as t is varied can be observed by applying a weak rf monitoring signal immediately after each pulse. We have studied these reversals at $\delta=0$ and used them to obtain estimates of ω_1. We could not, however, follow them for more than one or two cycles of ω_1. This suggests either that there was a serious inhomogeneity in H_1 or that spectral diffusion was much faster in the presence of rf power than it was in the echo experiments,[15] and makes it uncertain whether conditions were such as to allow the generation of the ideal hole shape Eq. (6) in our experiments. The effect of operating on the line with a sequence of pulses, as in a spin echo experiment, can be deduced by successive matrix multiplications. During the time τ for which the rf power is off, $[R]$ reduces to

$$[R_0]=\begin{bmatrix} c_\varphi & -s_\varphi & 0 \\ s_\varphi & c_\varphi & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

where c_φ and s_φ stand for $\cos\varphi$ and $\sin\varphi$, and $\varphi=\tau\delta$. Two similar pulses separated by a time τ produce a magnetization $(M_x,M_y,M_g)=[R][R_0][R](0,0,M_{g,0})$. M_g is of especial interest in stimulated echo experiments and is given by

$$\frac{M_z}{M_{z,0}}=c_\varphi s_\Psi^2 c_\Psi^2(1-c_\theta)^2-c_\varphi s_\Psi^2 s_\theta^2$$
$$+2s_\varphi s_\Psi^2 c_\Psi s_\theta(1-c_\theta)+(c_\Psi^2+s_\Psi^2 c_\theta)^2. \quad (7)$$

This function is shown in Fig. 2 for the special case of an interval τ six times the pulse length, and values of $\omega_1 t$ sufficient to give (a) a 90° turn, and (b) a 180° turn to the spins on exact resonance. In our experiments t was 1 microsecond, and τ was usually more than 6 μsec. A small ratio of τ to t was chosen in Fig. 2 in order to give a clear diagram and to emphasize the difference between

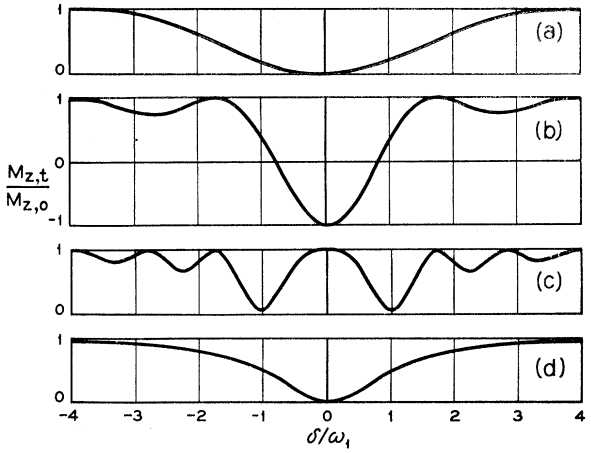

FIG. 1. Calculated effect of applying a single pulse of rf to an inhomogeneous line when $H_1 \ll$ linewidth. Pulse durations are such that spin packets on exact resonance are turned by (a) $\pi/2$, (b) π, (c) 2π. A Lorentzian "hole" (d) is shown for comparison.

[14] I. I. Rabi, N. F. Ramsey, and J. Schwinger, Revs. Modern Phys. **26**, 167 (1954).

the actual pattern of M_z and that which would result from assuming a distribution of spin packets, corresponding to a Lorentz shaped "hole" of half-width ω_1, to be acted on by rf fields sufficient to tilt all spins by exactly 90° [Fig. 2(c)]. The average periodicity of the fine pattern ($\Delta\omega=1/\tau$) is the same in Figs. 2(a) and (c), but in Fig. 2(a) there is a stretching of the period on one side of $\delta=0$ and a compression on the other. This asymmetry arises from the s_φ term in Eq. (7) and becomes unimportant by comparison with $1/\tau$ at higher values of τ. Figure 2(b) illustrates the type of pattern which is produced when $\omega_1 t>\pi/2$. The envelopes of Figs. 2(a) and 2(b) may be compared with the "holes" shown in Fig. 1. Excessive values of $\omega_1 t$ which give rise to double bumps and distortions in the free induction signal lead to similar effects in the echo waveform. The M_z patterns decay by spectral diffusion during the time T following the second pulse. Decay is principally governed by the short $1/\tau$ period, and the decay rate will be more or less independent of the shape of the envelope if $1/\tau$ is several times narrower than ω_1 and the envelope is comparatively smooth, i.e., $\omega_1 t\leq\pi/2$ and $\omega_1\tau>2\pi$. If these conditions do not hold, it is impossible to regard the short period and the envelope as separate, and the decay of stimulated echoes cannot be readily calculated from the diffusion kernel. Experimental checks were made by varying the rf power level and comparing echo decay rates. In general the measurements were insensitive to power levels, but a shortening of the decay time was occasionally observed at low power levels when τ was less than 10 μsec.

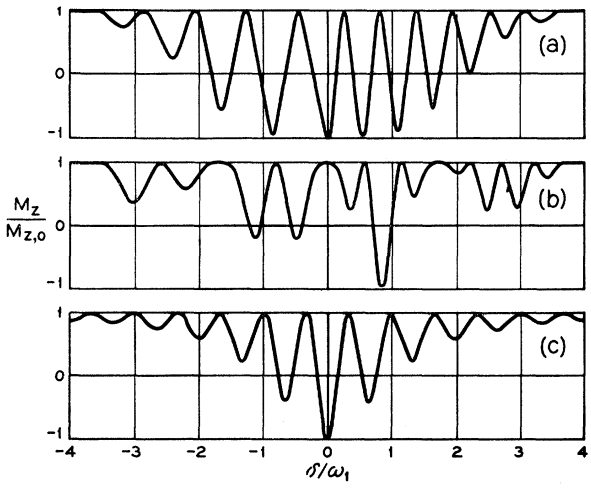

FIG. 2. (a) Calculated effect of applying two pulses of rf to an inhomogeneous line when $H_1\ll$linewidth. Spin packets on exact resonance are turned through $\pi/2$ by each pulse ($\omega_1 t=\pi/2$). The interval τ between pulses is six times the pulse duration ($\omega_1\tau=3\pi$). (b) Spin packets on exact resonance are turned through π by each pulse ($\omega_1 t=\pi$). Otherwise, as in (a). (c) Lorentz-shaped envelope of half-width ω_1 filled with a modulation of period $1/\tau$. A short interval τ has been taken here to give a clear diagram. In practice, τ was normally longer, and many cycles of the modulation were contained within the envelope.

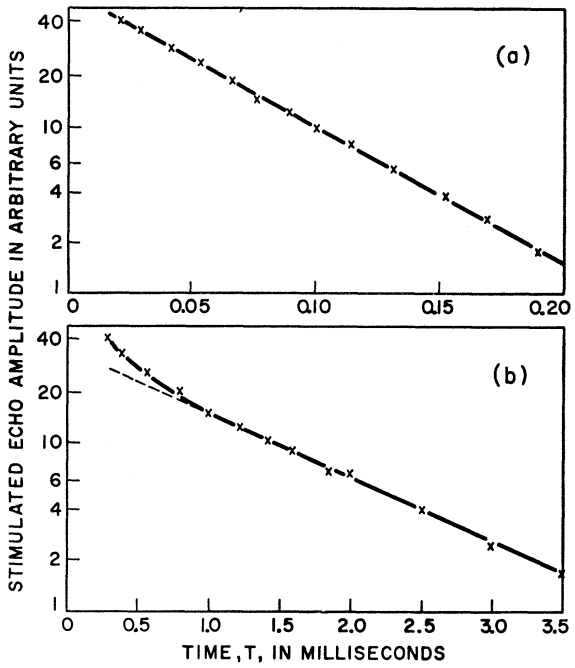

Fig. 3. (a) Stimulated echo amplitude as a function of T for the cerium line in (Ca,Ce,Er)WO_4 at 1.6°K, and with the Zeeman field at 90° to the c axis. (0.83×10^{18} Ce^{3+} ions/cc, 0.99×10^{18} Er^{3+} ions/cc.) $\tau=7$ μsec. (b) A similar plot for a (Ca,Ce)WO_4 sample containing 1.7×10^{18} spins/cc. Zeeman field at 90° to the c axis. $\tau=9$ microseconds. After an initial more rapid fall the decay is given by $\exp[-f(\tau)T]$.

IV. STIMULATED ECHO EXPERIMENTS

The amplitude of the stimulated echo is in general proportional to the product $A(\tau)B(\tau,T)$ in which $A(\tau)$ depends on the loss of phase coherence during the intervals τ, and $B(\tau,T)$ depends on spectral diffusion of M_z during the interval T between pulses II and III. The factor $B(\tau,T)$ can be readily obtained by taking fixed values of τ and measuring the envelope of echoes at T is varied. A typical decay is shown on a semilogarithmic plot in Fig. 3. In some cases the decay was a good exponential for the whole of the observed period [Fig. 3(a)], but in others the exponential portion was preceded by a more rapid fall [Fig. 3(b)]. An exponential dependence on "T" would be in agreement with either the Gaussian or the Lorentzian diffusion kernels discussed in the previous section, and has been shown by Klauder[13] to be a general consequence of assuming that the diffusion of each spectral component is independent of its previous history, and depends only on the time difference and the frequency difference. Since our aim here is to compare the results with some simple, if approximate diffusion law, we have only made measurements on that part of the echo envelope for which $B(\tau,T)$ is of the form $\exp[-f(\tau)T]$ and thus obtained the decay constants $f(\tau)$. These are shown plotted against τ in Fig. 4. The Gaussian diffusion kernel would require a parabola $f(\tau)=k\tau^2$

TABLE I. Diffusion parameters and echo decay times.

Ce^{3+} ions/cc	Er^{3+} ions/cc	Temperature (°K)	Angle with c axis	Linewidth (Mc/sec)	Diffusion parameter m (seconds^{-2})	Two-pulse decay time (microseconds)
3.4×10^{18}	···	4.2	90°	28	6.3×10^{8}	16.5
1.7×10^{18}	···	4.2	90°	24	1.7×10^{8}	35
0.83×10^{18}	···	4.2	90°	18	4.1×10^{7}	63
0.33×10^{18}	···	4.2	90°	18	5.0×10^{6}	90[a]
···	0.99×10^{18}	1.8	0°	30	7.7×10^{8}	14
0.83×10^{18}[b]	0.99×10^{18}	1.6	90°	···	3.1×10^{9}	19
0.33×10^{18}[b]	0.40×10^{18}	1.8	90°	14	9.3×10^{8}	28
0.33×10^{18}[c]	0.40×10^{18}	1.8	0°	23	3.1×10^{8}	28

[a] Rapid decay in first 15 μsec.
[b] Measurements in cerium line.
[c] Measurements in erbium line.

and the Lorentzian kernel (4) a straight line $f(\tau)=m\tau$. The data give a better fit with the latter, although there is a discrepancy near the origin. This discrepancy appears in the curves obtained with most samples and implies a cutoff in the wings of the Lorentz kernel as is physically necessary. However, it is not easy to arrive at a reliable interpretation of the measurements here, since this is also the region in which the simple decay law becomes inapplicable under our experimental conditions. ($\omega_1\tau\sim2\pi$. See Sec. III.)

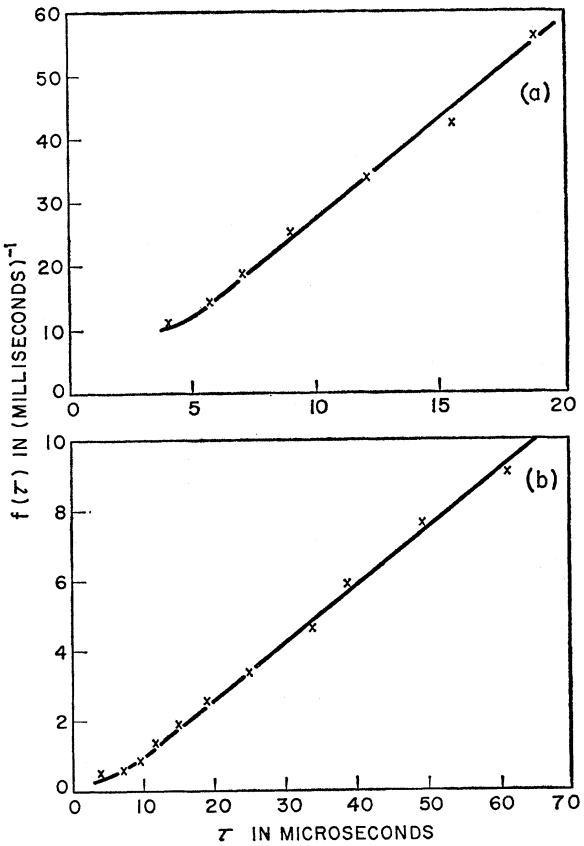

FIG. 4. (a) Decay constants $f(\tau)$ as a function of τ for the conditions specified in Fig. 3(a). (b) A similar plot for the conditions of Fig. 3(b). The diffusion function suggested in Sec. III would require a straight line $f(\tau)=m\tau$. Deviations from this near the origin may be explained by the existence of a cutoff in the wings of the Lorentz diffusion kernel.

Other specimens have given data of the same type as that shown in Figs. 3 and 4, and we use the Lorentzian diffusion function and the diffusion parameter m appearing in it as a basis for the comparison of results. Values of m have been obtained from the slope of curves such as that in Fig. 4 and are tabulated in Table I. Concentration dependence was studied for Ce^{3+} at 90° to the crystal axis and at 4.2°K. m was proportional to (concentration)^2. There was very little variation with temperature for Ce^{3+} in the helium range, but no echoes could be seen at 14°K indicating that a temperature variation must exist above 4.2°K. Er^{3+} showed a very strong temperature dependence in the helium range, and above 2°K the decay times were so short that it was inconvenient to make measurements by the three-pulse method. Some two-pulse measurements were made in this temperature range and are discussed in the next section. This temperature dependence is at first surprising for a process which might be classed with "intermediate" or "cross relaxation" phenomena, but is fully in accordance with the model of Herzog and Hahn. When lattice relaxation is fast, as for Er^{3+} above 2°K, a stage is reached at which spin-lattice flips become more frequent than spin-spin flips. Local field fluctuations then increase with temperature. The total energy in the spin system need not then be exactly conserved. Anderson and Klauder[16] have calculated the diffusion in this case. Using the assumption that the spin-spin interactions are dipolar, and that the spin-lattice relaxation acts as an external agency which flips B spins at random, they obtain just the Lorentzian expression (4) with a value of

$$m=(\Delta\omega)_{\frac{1}{2}}/2T_L, \tag{8}$$

where $(\Delta\omega)_{\frac{1}{2}}$ is the half-width given in footnote 9. They

[15] A relation between rf field intensity and spectral diffusion is predicted by Herzog and Hahn. A form of "discrete" diffusion occurring only in the presence of an rf field has been reported in As-doped silicon [G. Feher and E. A. Gere, Phys. Rev. 114, 1245 (1959)].

[16] P. W. Anderson and J. R. Klauder (to be published).

suggest that in the case of temperature independent diffusion T_L should be replaced by a mean spin-spin flip time T_{flip}. Estimates for this time have been derived by means of Eq. (8) from the diffusion parameters measured for Ce^{3+} and are shown in Table II.

A nice distinction must be made between the familiar role of lattice relaxation, and its part in diffusing energy through a line. Acting directly on the A spins it introduces a factor $\exp(-T/T_L)$ into the decay of stimulated echoes. Indirectly, and by relaxing B spins, it leads to effects such as those observed for Er^{3+}. The factor $\exp(-T/T_L)$ has been ignored in the previous discussion because T/T_L was always one or more orders of magnitude smaller than the echo decay exponents measured for the values of τ chosen in these experiments. The indirect effects can however be large, especially in a multilevel system or in an impure crystal, since they are caused by the relaxation of all spins in the material including those belonging to other intervals or to other magnetic centers. To confirm this, some measurements were made on specimens containing both Ce^{3+} and Er^{3+} ions. Diffusion through the Ce^{3+} line was considerably accelerated by the presence of Er^{3+} even at 1.8°K, and at higher temperatures the diffusion parameters for both lines showed the strong temperature dependence characteristic of Er^{3+}. This did not depend on there being any particular frequency relation between the Ce^{3+} and Er^{3+} intervals, and the lattice relaxation times were found to differ by order of magnitude except at settings where the lines (or their satellites) actually crossed.

V. TWO-PULSE ECHO EXPERIMENTS

Decay envelopes for normal two-pulse echoes can be obtained by varying the time τ between the two pulses and superimposing a large number of traces, the oscilloscope being triggered each time at the end of the second pulse. Some examples are shown in Fig. 5: Echo decay may be due to several causes: to lattice relaxation of the precessing spins, to resonant interactions between them, or to changes in the Larmor frequencies arising from spectral diffusion. Lattice relaxation is slow compcompared with the observed decay traces and can be ignored, at least so far as direct effects on A spins are concerned. Resonant interactions between the precessing A spins also appear to be unimportant here, and the estimates from diffusion data indicate that the true T_2, or spin-spin flip time, lies in the millisecond range (Table II). A direct test for possible effects of resonant interactions was made by comparing echo envelopes obtained at the center and in the wings of a line. No changes were detected, although, presumably, the density of resonating spins is considerably greater in the center of the line. This also accords with observations on satellite lines, and with the results of experiments on mixed (Ca,Ce,Er)WO_4 specimens (Sec. IV) in showing that the echo behavior depends on the total magnetic environment in the crystal, and not merely on the spins

TABLE II. Spin-flip times for (Ca,Ce)WO_4 at 4.2°K and 90° to the c axis deduced by Eq. (8). $(\Delta\omega)_{\frac{1}{2}}$ is the half-width for dipolar broadening computed from the expression in reference 9.

ions/cc	$(\Delta\omega)_{\frac{1}{2}}$ (cps)	m (sec^{-2})	T_{flip} (milliseconds)
3.4×10^{18}	2.14×10^{6}	6.3×10^{8}	1.7
1.7×10^{18}	1.07×10^{6}	1.7×10^{8}	3.2
0.83×10^{18}	0.52×10^{6}	4.1×10^{7}	6.3
0.33×10^{18}	0.21×10^{6}	5.0×10^{6}	21

in one line or in a particular part of a line. The change of Larmor frequencies occurring in spectral diffusion leads to an accumulating loss of phase and gives a decay envelope proportional to $\exp(-\frac{2}{3}K\tau^3)$ for the Gaussian kernel or to $\exp(-m\tau^2)$ for the Lorentzian kernel. In two cases a fairly good fit with the latter was obtained [Figs. 5(a), 6(a)] and the inverse squre of the decay time gave a value near the m derived from stimulated echo experiments. Both these instances occurred when Ce^{3+} echoes in a mixed (Ca,Ce,Er)WO_4 were being observed. For other specimens the decay curves were more like those shown in Figs. 5(b) and 6(b). Although they gave closer agreement with the Lorentzian than with the Gaussian law, they showed a tendency to fall

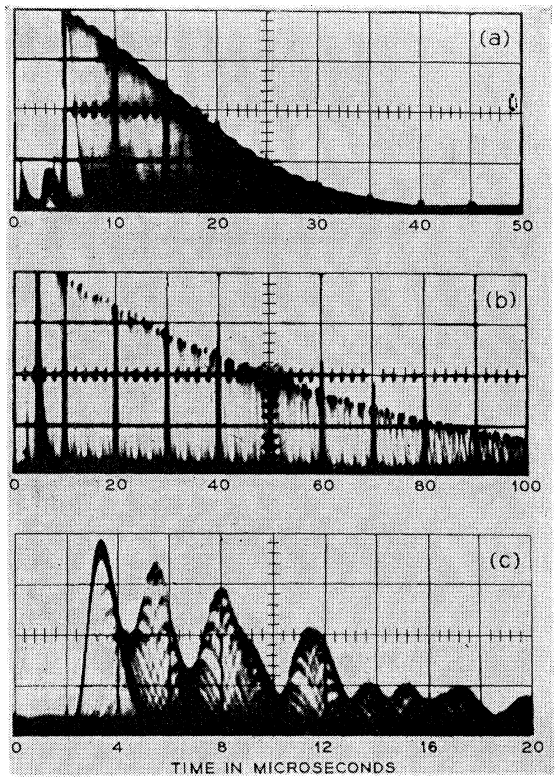

FIG. 5. Envelopes of normal two-pulse echoes. (a) Conditions as in Fig. 3(a). (b) (Ca,Ce)WO_4 specimen at 4.2°K and 90° to the c axis. (0.83×10^{18} Ce^{3+} ions/cc). (c) Echoes in a (Ca,Ce)WO_4 specimen at 4.2°K and 0° to the c axis. (0.83×10^{18} Ce^{3+} ions/cc). Deep modulation of the envelope takes place at the Larmor frequency of W^{183}.

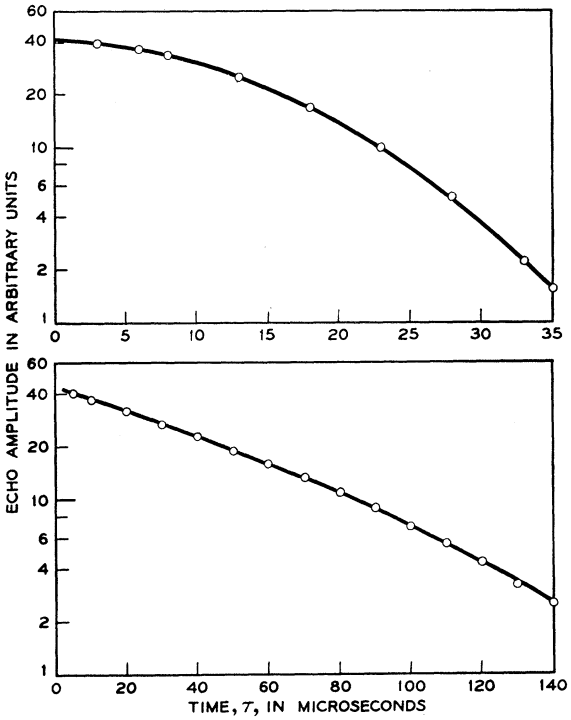

FIG. 6. Semilogarithmic plots of two-pulse echo amplitudes. Measurements were made at three gain settings and combined. (a) Conditions as in Fig. 5(a). A good fit to the $\exp(-m\tau^2)$ decay law which corresponds to a Lorentzian diffusion kernel. (b) Conditions as in Fig. 5(b). The early portion of the curve may possibly be due to the presence in the sample of spin groupings with larger m values than the remainder.

off from the very start as if some of the spins in the specimen were characterized by faster decay parameters than the remainder. The cause of this behavior is not known, although one may speculate as to the possibility of there being fast lattice relaxing impurities in the vicinity of some Ce spins, or clusters of Ce^{3+} ions forming local regions of abnormally high concentration. It seems likely that this behavior in two-pulse experiments is due to the same cause as the rapid initial decay in three-pulse experiments. Specimens giving a good $\exp(-m\tau^2)$ envelope in two-pulse experiments also showed an accurate $\exp[-f(\tau)T]$ decay for stimulated echoes. [See Figs. 3(a), 4(a), 5(a), and 6(a).] In three-pulse experiments it was easy to discount the anomalous portion and to measure only the exponential decay, but it proved to be more difficult to separate an ideal $\exp(-m\tau^2)$ component from the latter part of a two-pulse envelope owing to the rapidity with which the signal disappeared into noise as τ was increased. In Table I we have merely given the times for the initial e:1 decay.

Owing to these difficulties, two-pulse echo experiments could not always be used to derive the m parameter for the diffusion kernel. They are useful, however, when examining a sequence of changes in diffusion behavior. Measurements are simpler, and can be made when the diffusion rates are too rapid to permit a series of stimulated echo observations. Two-pulse experiments afforded the only means by which we were able to follow the variation of diffusion rate with temperature in Er^{3+} and (Ce^{3+},Er^{3+}) specimens from 2° to 3°K, and square of the decay times for an Er^{3+} specimen are shown in Fig. 8 on the same plot as the lattice relaxation times. The similarity in the temperature dependence of the two quantities suggests that diffusion is wholly controlled by spin-lattice flips in this range of lattice times, and that the spin-spin flip time must lie in the millisecond range. Two-pulse experiments were also used to study the relation between diffusion rate and the angle between the Zeeman field and the crystal axis. Two-pulse decay times were approximately four times shorter at 0° ($g=2.92$) than at 90° ($g=1.43$) for Ce^{3+}, the change being gradual over the whole range. Er^{3+} showed a rapid change in the vicinity of 0°, and gave times which were four times shorter at 9° ($g=1.75$) than at 0° ($g=1.2$). It is likely that this large variation in Er^{3+} is partly due to the high angular rate of change of g, which makes spins sensitive to fluctuations in the direction as well as in the absolute magnitude of the local fields.

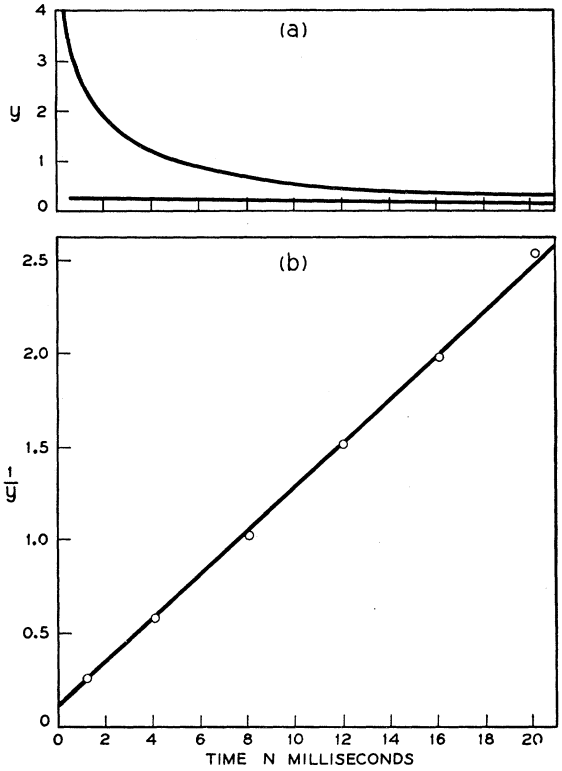

FIG. 7. Relaxation trace due to spectral diffusion of energy to the remainder of the resonance line from spin packets pumped by an rf field. $(Ca,Er)WO_4$ specimen at 1.8°K and 90° to the c axis. (0.40×10^{18} Er^{3+} ions/cc). Pump pulse duration: 0.1 msec. (a) The oscilloscope trace. (b) Plot of reciprocal of vertical displacement, derived from (a) and from a measurement at a higher gain setting. Linearity of reciprocal plot shows that relaxation trace is hyperbolic.

At lower fields (higher g values) a modulation was clearly visible in the echo envelopes for Ce^{3+} [Fig. 5(c)]. The pattern followed a complex sequence of changes as the angle was varied, and it was not always easy to identify a dominant period. Wherever this could be done, the period agreed with the Larmor frequency of W^{183}, and it appears to stem from the motion of the nuclear environment producing a periodic change in the local fields. The relevant interaction is between S_z of an electron spin and x-y components of nuclear magnetization in the neighborhood. A qualitative picture of this can be drawn in classical terms as follows. The application of microwave power and the turning of electron spins are sudden events on the time scale of W^{183} Larmor precession, and at the time when the pulse is applied each electron spin sees the field due to a particular nuclear configuration. This field varies from site to site, and may be rising or falling when the pulse is applied, but it will return to its initial value after one complete nuclear precession cycle, and, if all nuclei were to precess at the same rate, the pattern would repeat indefinitely. Actually the modulation envelope is comparatively irregular and indicates the failure of nuclear synchronism after a few cycles. This may be explained by the proximity of electron spins which give rise to considerable differences in the precession rates of the nuclei, in particular of those nuclei which are nearest and whose contribution to the effect is largest.

VI. RELAXATION TRACES; SPECTRAL DIFFUSION, AND LATTICE TIMES

Pulsed microwave techniques have been used in a number of laboratories to study the phenomena associated with paramagnetic relaxation. In one form of experiment[10,17] a high-power rf pulse is applied to "pump" the resonance line, and its subsequent return to equilibrium is monitored by a weak cw signal and displayed as an oscilloscope trace. If, however, the line is inhomogeneous, the pump may only succeed in burning a hole in the line, and the monitor signal will show the filling in of this hole from the sides. The decay trace is then a "cross relaxation" trace and its form depends on the diffusion function and on the shape of the hole. Let us assume that the pulse burns a hole given by Eq. (6) and that diffusion takes place according to the Lorentz kernel (4). Then a time t' after the end of the pulse the pattern of magnetization in the line, $M_{z,t+t'}$, will be given by

$$\frac{M_{z,t+t'}}{M_{z,0}}=\int_{-\infty}^{+\infty}\left[1-\left(\frac{\omega_1{}^2}{\omega_1{}^2+\delta^2}\right)\right]\left[\frac{mt'/\pi}{(mt')^2+(\delta-\delta')^2}\right]d(\delta)$$
$$=1-\frac{\omega_1(\omega_1+mt')}{(\omega_1+mt')^2+(\delta')^2}. \quad (9)$$

[17] C. F. Davis, M. W. Strandberg, and R. L. Kyhl, Phys. Rev. **111**, 1268 (1958).

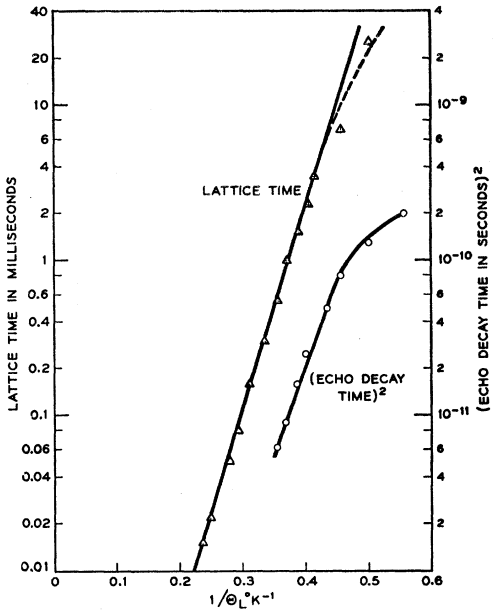

FIG. 8. Temperature dependence of lattice times and echo times in a $(Ca,Er)WO_4$ specimen at 0° to the c axis. (0.99×10^{18} Er^{3+} ions/cc). Relaxation times are proportional to $\exp(-\theta/T_{lat})$ with $\theta=30°K$. Relaxation times at 2°K are difficult to measure with the pulse apparatus because of the slow rate of spectral diffusion. The square of the two-pulse echo decay time is an approximate measure of the diffusion rate, and changes with the lattice time.

If observations are made at the pump freqeuncy, where $\delta'=0$, then

$$\frac{M_{z,t+t'}}{M_{z,0}}=1-\left(1+\frac{mt'}{\omega_1}\right)^{-1}. \quad (10)$$

In our detection system the vertical deflection y on the oscilloscope is proportional to $M_{z,0}-M_z$. At $t'=0$, $M_z=0$, $y=y_0$. The relaxation trace should therefore have the hyperbolic form

$$(y/y_0)=[1+(mt'/\omega_1)]^{-1}. \quad (11)$$

A typical trace and a plot of $1/y$ against t' are shown in Fig. 7. This form of trace has been found in many cases, and it is surprising how close a fit can be obtained by the hyperbolic decay law, in spite of the reasons mentioned in Sec. III for doubting the reliability of Eq. (6) as a description of the initial shape of the hole.[18]

The closeness of the fit obtained by taking only spectral diffusion into account raises the question as to what part, if any, of a relaxation trace, which at first

[18] A similar agreement has been found for some of the "sharing time" traces observed earlier in nickel fluosilicate.[10] Traces such as those shown in Fig. 2 of reference 10 can be obtained from Eq. (8) in this paper by setting $\delta'\neq0$. If an attempt is made to fit the nickel fluosilicate results in this way it turns out that the initial width of the "hole" is many times greater than ω_1. This suggests that diffusion during the pulse was much more rapid in nickel fluosilicate than in most of the tungstate specimens. The temperature dependence of the sharing time which was found in nickel fluosilicate may be similar in origin to the temperature dependence of spectral diffusion in $(Ca,Er)WO_4$.

sight appears to consist of a fast followed by a slow period, can be legitimately ascribed to lattice relaxation. One simple test is to vary the intensity or duration of the pumping pulse and look for changes in the decay rate measured for the slow period. If there are none, this affords indirect evidence that, at the beginning of the slow period, lattice relaxation is competing favorably with further diffusion and is controling the decay rate. The measured time may still be in error but will be closely related to the true spin-lattice time. For the cerium specimen it was not possible to find pumping conditions which would give a stable value for the slow period, and we were not able to measure lattice relaxation time. The maximum pump pulse duration obtainable with the apparatus was 1 msec and during this time excitation was not able to diffuse across more than a fraction of the line. If, after the pulse, an additional interval was allowed for diffusion to set up equilibrium in the line, the over-all excitation became too small to measure. We can, however, estimate very roughly that the cerium lattice times were of the order of a second from an observation that spin echo amplitudes were reduced at recurrence rates of more than a few pulses per second. Erbium was characterized by more rapid spectral diffusion, and above 2°K it was possible to pump the Er^{3+} line sufficiently during the pulse to obtain a decay component independent of pumping conditions. The measured decay times depend exponentially on temperature in the same manner as the relaxation times observed by Finn, Orbach, and Wolf in cerium magnesium nitrate.[19] They are shown on a semilogarithmic scale in Fig. 8.

VII. DISCUSSION

In order to form a clear picture of the spectral diffusion process in an inhomogeneous line it is important to understand the internal structure of the line and to know which of the forces responsible for broadening are static and which are dynamic in character. The linewidth in the calcium tungstate specimens studied here appears to be due primarily to random distortions of the crystal field such as may arise from defects, crystal polytypism,[20] or other microscopic irregularities. This type of broadening is static and will tend to hinder diffusion by reducing the number of spins which are resonant with one another and lengthening the spin-spin flip time. It will also stretch the line over a spectral range which is wider than the frequency excursion of a spin moving under the influence of dipolar forces alone. Transfers of excitation to more distant points in the line then have to be pictured in terms of a relay race in which spins at opposite ends of their individual frequency excursions come into resonance and pass on energy by undergoing mutual flips. This relay process will consist of a random walk with each step $\sim\Delta\omega$ in magnitude and taking a time $\sim T_{\text{flip}}$. Reference to the numerical values in Table II shows that this is likely to be a slow process and may not be able to reach the wings of the line in less than the lattice relaxation time.

In some cases spin-spin interactions of other than the simple dipolar type considered here may constitute a dynamic broadening mechanism leading to an appreciable acceleration in the diffusion rate. Such interactions may contribute in two ways, by shortening the mean spin-spin flip time and by introducing larger shifts of resonant frequency at each flip. Of these, the exchange interactions are potentially the most important because of the large forces usually involved. Suppose, for example, that there is an exchange interaction $J\mathbf{S}_A\cdot\mathbf{S}_B$ between unlike spins A and B and that A forms part of a spin packet excited by the rf field. If for any reason B changes its orientation, A will move by an interval $\sim J$ to a remote point in the spectrum. Interactions of this kind may possibly account for cross relaxation across large frequency intervals such as occurs in ruby.[21] Other types of interaction have been proposed although there is little experimental evidence regarding their magnitude. Finkelstein and Mencher[22] and Bleaney[23] discuss a form of electric quadrupole interaction which can occur between rare earth ions. This interaction energy is greater than the dipolar energy for nearest neighbors in cerium ethyl sulfate.[24] In iron group crystals, where the spins are fairly strongly coupled to the lattice, Suhl has proposed the exchange of virtual phonons as a further source of spin-spin interaction forces.[25]

The line broadening due to nuclei is less than that due to electron spin-spin interactions in the materials and over the range of concentrations studied here, but observations such as that reproduced in Fig. 5(c) suggest that nuclear effects may not be entirely negligible. This I_+S_z type of interaction would not lead to genuine diffusion if it were possible to regard all nuclear frequencies as being the same. The initial pattern of nuclear fields would be repeated each cycle, and the peaks of a modulated echo decay envelope would trace out a curve as if no nuclear effects were present. This is, however, an oversimplified view, and the nuclear frequencies are spread out over a range of values by the very fact of being in the neighbourhood of an electron. The recurring pattern of nuclear local field soon becomes irregular and may eventually be indistinguishable from a sequence of random variations. A low electron spin concentrations it is possible that this becomes the dominant diffusion mechanism, and that nuclear effect determine the echo

[19] C. B. P. Finn, R. Orbach, and W. P. Wolf, Proc. Phys. Soc. (London) **A77**, 261 (1961).

[20] J. O. Artman, J. C. Murphy, J. A. Kohn, and W. D. Townes, Phys. Rev. Letters **4**, 607 (1960). X-ray examination has yielded no evidence for polytypism in the tungstate specimens.

[21] W. B. Mims and J. D. McGee, Phys. Rev. **119**, 1233 (1960). Reference is to the phenomenon discussed under the heading of "general cross relaxation."

[22] R. Finkelstein and A. Mencher, J. Chem. Phys. **21**, 472 (1953).

[23] B. Bleaney, Proc. Phys. Soc. (London) **A77**, 113 (1961).

[24] C. E. Johnson and H. Meyer, Proc. Roy. Soc. (London) **A253**, 199 (1953).

[25] H. Suhl (private communication).

envelope decay as has been suggested by Gordon and Bowers.[3]

Spectral diffusion introduces a number of complications in the measurement of lattice relaxation by microwave resonance methods. Our own particular difficulties, discussed in Sec. VI, arose in part from the limitations of the apparatus. The pump operated directly on only a fraction of the spins and we were not always able to hold it on long enough to allow for adequate diffusion of excitation to the remainder of the line. It is questionable, however, whether a longer pulse, or even the change to a cw method would eliminate the possibility of the results being influenced by diffusion, unless it could be shown by an independent method that the whole line reached a uniform spin temperature before any measurements were made. This cannot often be decided *a priori*. Lattice relaxation would in time bring about diffusion across an interval $\Delta\omega$ corresponding to the magnitude of the local fields, but this interval is frequently much smaller than the linewidth observed in dilute materials. Spin-spin flips may be more important (as shown here by the temperature independence of diffusion in Ce^{3+}), and, in a time of the order of the lattice relaxation time, may spread excitation over a wider interval, but measurements would be needed to ascertain whether this extended to the edge of the line under all experimental conditions. If excitation of the line is still incomplete, even with arbitrarily long pump pulses, the "lattice time" measured by the pulse method will be determined by lattice relaxation in conjunction with some further diffusion. In the cw saturation method incomplete excitation makes it uncertain what is the appropriate value for T_2 and may require some modification, such as that given by Portis,[1] in the simple saturation formula to account for the variation with H_1. For unambiguous measurements of lattice times there appears to be a great advantage in a technique such as that of Wagner *et al.*,[26] which automatically ensures uniform excitation of a resonance line.

ACKNOWLEDGMENTS

The authors would like to acknowledge many helpful discussions with P. W. Anderson and J. R. Klauder during the course of this work. They also wish to thank Mrs. C. A. Lambert for computing the functions shown in Figs. 1 and 2.

[26] J. G. Castle, R. F. Chester, and P. E. Wagner, Phys. Rev. **119**, 953 (1960).

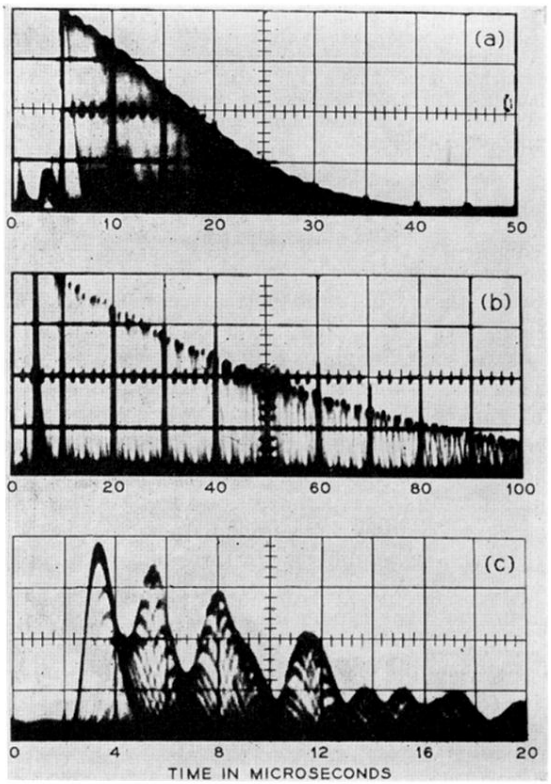

FIG. 5. Envelopes of normal two-pulse echoes. (a) Conditions as in Fig. 3(a). (b) $(Ca,Ce)WO_4$ specimen at 4.2°K and 90° to the c axis. (0.83×10^{18} Ce^{3+} ions/cc). (c) Echoes in a $(Ca,Ce)WO_4$ specimen at 4.2°K and 0° to the c axis. (0.83×10^{18} Ce^{3+} ions/cc). Deep modulation of the envelope takes place at the Larmor frequency of W^{183}.