ERBIUM

The curves for erbium are shown in Fig. 16. The characteristics are much like gadolinium, with the possibility of an inflection at low pressure and no other distinctive features.

THULIUM

The thulium isotherms are shown in Fig. 17. The 296°K isotherm shows a minimum near 60–80 kbars and a maximum at 150–160 kbars. The 77°K isotherm has a minimum at 190–200 kbars.

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Electric Field Effects in Spin Echoes

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A new effect has been observed in electron-spin echo experiments in which an electric field was applied for part of the spin-echo cycle of events. It is found in crystals for which the paramagnetic ion is at a site lacking inversion symmetry, and it is due to the linear shift of the Larmor frequency in the applied electric field. It provides a method for measuring these shifts, and may be used even when the shift is several orders of magnitude smaller than the linewidth. The characteristics of the apparatus used in making these observations are briefly described, and some problems arising in the application of this effect to the measurement of electric field shifts are discussed.

A NUMBER of experiments have been described recently in which an electric field was applied during a spin resonance experiment, and a shift was observed in the resonance frequency.[1–4] First-order shifts proportional to the applied field may be found if the atom or ion responsible for the resonance is in a crystal-field site which lacks inversion symmetry. These shifts are small and are usually only observed at high electric field intensities. In the work reported here an electric field was applied in the form of a voltage step occurring during the cycle of events which characterize an electron-spin echo process. Fields of only a few kV/cm caused major changes in the form of the echo-decay envelope. This effect provides a means of measuring electric-field shifts in paramagnetic resonance with relatively low fields and in broad lines. The magnitude of the shift which can be detected in this way is limited by the width of the individual spin packets which constitute the line, as in the case of the double-resonance (ENDOR) experiments.[5]

The oscilloscope photograph in Fig. 1(a) shows the echo-decay envelope for Ce^{3+} ions in a $CaWO_4$ lattice at 4.2°K and with the Zeeman field along the *a* axis. The photograph was obtained by superimposing a large number of echo traces corresponding to a series of values of the time τ between the two microwave pulses. The oscilloscope was triggered in each case at the end of the second microwave pulse. Similar photographs have been reproduced elsewhere.[6,7] Figure 1(b) shows the envelope obtained when the experiment is modified by applying an electric field of 450 volts/cm parallel to the *c* axis immediately after the second microwave pulse and maintaining it until after the echo [see Fig. 3(a)]. In Fig. 1(c) the vertical scale has been magnified to show the null points in the later portions of the envelope more clearly. An electric field applied before the first microwave pulse and maintained until just before the second pulse gave the same result, but no effect at all occurred if the electric field was applied throughout the whole time between the first pulse and the echo.[8]

The role of the electric field in these phenomena may be clarified by giving a summary of the sequence of events in a conventional spin-echo experiment. In any such experiment it is essential that the resonance line should be inhomogeneous, i.e., it should be made up of a large number of spectral components or "spin packets," each with its own independent history of interactions with the applied fields. Ideally a "90° pulse" is followed after an interval τ by a "180° pulse," and during these pulses of microwave power all spin packets are similarly

[1] G. W. Ludwig and H. H. Woodbury, Phys. Rev. Letters **7**, 240 (1961).
[2] J. O. Artman and J. C. Murphy, in *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962* (Academic Press Inc., New York, 1963).
[3] E. B. Royce and N. Bloembergen, in *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962* (Academic Press Inc., New York, 1963); Phys. Rev. **131**, 1912 (1963).
[4] Electric field effects in nuclear resonance are described by J. Armstrong, N. Bloembergen, and D. Gill, Phys. Rev. Letters **7**, 11 (1961); P. S. Pershan and N. Bloembergen, *ibid.* **7**, 165 (1961).
[5] G. Feher, Phys. Rev. **114**, 1912 (1959).
[6] J. A. Cowen and D. E. Kaplan, Phys. Rev. **124**, 1098 (1961).
[7] W. B. Mims, K. Nassau, and J. D. McGee, Phys. Rev. **123**, 2059 (1961).
[8] In a stimulated echo experiment an electric field applied between microwave pulses one and two, or between microwave pulse three and the echo gave the same effects as in a two-pulse echo experiment. An electric field applied between microwave pulses two and three had no effect.

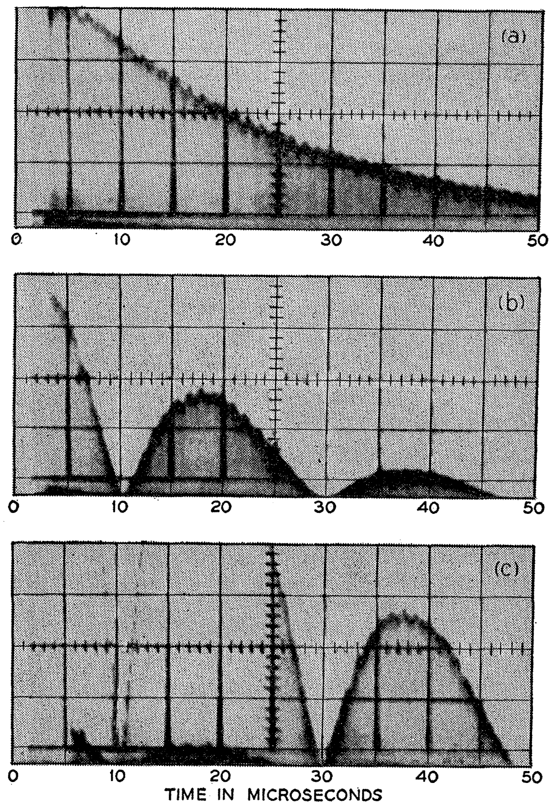

FIG. 1. Echo-decay envelopes for (Ca,Ce)WO_4, 3.3×10^{17} spins/cc, 4.2°K, Zeeman field along the a axis. (a) No electric field. (b) Electric field of 450 V/cm applied along the c axis during the time from the second microwave pulse to the spin echo. (c) As for (b) but with 12 dB additional gain in the vertical direction. The effect of the electric field can be found by dividing ordinates of (b) by ordinates of (a).

affected by the alternating field. The sequence of events can most easily be described in a coordinate system rotating about the Zeeman field (the z axis) with an angular velocity ω equal to the microwave frequency. In this rotating system the microwave field is represented by a vector H_1 along the x axis, and the Zeeman field is canceled out but for a small residual component δH proportional to the difference between the Larmor frequency of a particular spin packet and the microwave frequency. During the time intervals when no microwave power is applied each spin packet precesses about its own δH, and when microwave power is applied precession takes place about the resultant of H_1 and δH. If $H_1 \gg \delta H$ this resultant, or "effective field" lies almost along the x axis and has approximately the same magnitude for all spin packets, thus causing them all to precess in the same way during the microwave pulse. In the initial state of thermal equilibrium the resultant equilibrium due to all the spin packets lies along the z axis [Fig. 2(a)]. The first pulse turns this magnetization by 90° into a direction along the y axis [Fig. 2(b)]. After the pulse the spin packets precess at different rates about the z axis, each being represented by a different vector lying on a disk in the xy plane, and the resultant magnetization decays to zero [Fig. 2(c)]. The second pulse turns this disk over about the x axis with the effect of setting the faster precessing spin packets behind, and vice versa [Fig. 2(d)]. During the second interval τ the faster spin packets then catch up, and the slower ones fall back until there is once more a resultant precessing magnetization and a signal is emitted into the cavity [Fig. 2(e)]. In practice the conditions often deviate from those assumed here. The pulses may be timed to cause precession by angles other than 90° and 180°, and the over-all resonance line may be too wide for the condition $H_1 \gg \delta H$ to be realized. This case can be treated by considering more general rotations about the true effective-field axis, and it can be shown that the size and shape of individual echo pulses are quite different from those predicted under the simpler conditions.[9] In most circumstances, however, this change in size and shape is independent of the interval τ. All echo signals are affected in the same way, and experiments aimed at studying the echo envelope give the same results as they do in the ideal 90°, 180° case.

Let us now consider the effect of applying electric fields. In $CaWO_4$ the Ce^{3+} ion substitutes for Ca^{2+}. It occupies two types of lattice sites, both lacking inversion symmetry, one site being the inversion image of the other. These sites are normally equivalent to one another in magnetic resonance, but they are distinguished from one another when an electric field is

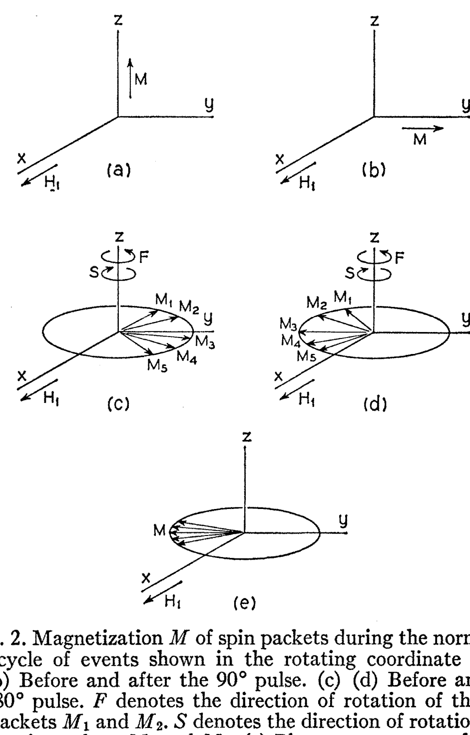

FIG. 2. Magnetization M of spin packets during the normal spin echo cycle of events shown in the rotating coordinate system. (a) (b) Before and after the 90° pulse. (c) (d) Before and after the 180° pulse. F denotes the direction of rotation of the faster spin packets M_1 and M_2. S denotes the direction of rotation of the slower spin packets M_4 and M_5. (e) Phase convergence of all spin packets at the time of the echo.

[9] A. L. Bloom, Phys. Rev. **98**, 1105 (1955).

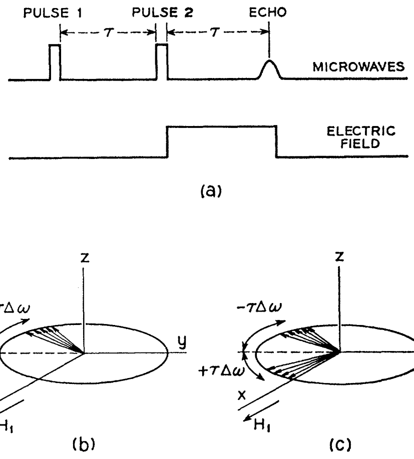

FIG. 3. (a) Timing of the electric field and the microwave pulses. Other possible arrangements are mentioned in the text. (b) Phase convergence of spin packets at the time of the echo if all frequencies are shifted by $\Delta\omega$ after pulse two [compare Fig. 1(e)]. (c) Phase convergence of spin packets for an "inversion image" crystal. Magnetization responsible for the echo is proportional to $\cos\tau\Delta\omega$.

applied. If the g value is increased for an ion at one site, it is reduced by the same amount for an ion at the other. Thus, for a given Zeeman field each spin packet is split into two components, one $\Delta\omega$ above and one $\Delta\omega$ below the original Larmor frequency. Suppose that the electric field is applied immediately after the second microwave pulse [Fig. 3(a)], thus splitting the spin packets shown in Fig. 2(d) into two groups. As in a conventional spin-echo experiment, the spin packets in each of the two groups come in phase after a time τ, since the relative frequencies within each group are not changed, but the resultant magnetization of one group leads by $\tau\Delta\omega$ and that of the other group lags by the same amount [Fig. 3(c)]. Since both groups contain the same number of spins these two magnetizations cancel if $\tau\Delta\omega$ is an odd multiple of $\frac{1}{2}\pi$. The echo signals are proportional to the absolute magnitude of the precessing magnetization and the envelope is proportional to $|\cos\tau\Delta\omega|$. Similar arguments may be used if the electric field is applied between pulses one and two. The two components into which each spin packet is split by the action of the electric field will differ in phase by $2\tau\Delta\omega$ just before the 180° pulse. This phase difference is not affected by the 180° pulse which merely interchanges the two components so that the component which was lagging now leads, and vice versa. After the 180° pulse the phase difference remains constant and is observed as an interference effect in the echo. It may be noted that if the electric field is applied for the whole cycle of events there can be no effect. A component which gains $\tau\Delta\omega$ in the first interval is behind by $\tau\Delta\omega$ after the 180° pulse and is just able to regain this phase loss by the time of the echo. In fact, provided that the frequency shift is small compared with the linewidth, the electric field merely rearranges the spin packets so as to produce a new inhomogeneous line, different microscopically, but the same in its macroscopic behavior as the old one.

The null points in Fig. 1 occur when $\tau\Delta\omega=10$, 30, 50 μsec and indicate upward and downward shifts of 25 kc/sec each. Measurements were also made with the electric field along the c axis and the magnetic field in various orientations. The results have been expressed as g shifts and are shown in Figs. 4 and 5. In Fig. 4 the magnetic field rotates in a plane perpendicular to the c axis. The form of the curve may be interpreted in terms of a modification of the g tensor which occurs when the electric field is applied. The ground state of Ce^{3+} in $CaWO_4$ is a Kramers doublet with $g_{\parallel}=2.92$ and[10] $g_{\perp}=1.43$. The electric field along the c axis changes the g tensor in accordance with the symmetry S_4 of the site of the paramagnetic ion. There should be no change in $g_{\parallel}$. The value of g now depends on the azimuthal angle which the plane containing the c axis and the magnetic field makes with the a or b tetragonal crystal axis. Along the principal axes of the new g tensor $g_{\perp}$ is changed to $g_{\perp}+\delta g_1$ and $g_{\perp}+\delta g_2$. At an angle ϕ to one of these axes $(g_{\perp}+\delta g_{\perp})^2=(g_{\perp}+\delta g_1)^2\cos^2\phi+(g_{\perp}+\delta g_2)^2\sin^2\phi$. To the first order of small quantities $\delta g_{\perp}=\delta g_1\cos^2\phi+\delta g_2\sin^2\phi$. At all angles ϕ, $\delta g_{\perp}$ will have the same magnitude but opposite sign for a pair of inversion image sites. This condition is met by setting $\delta g_1=-\delta g_2$ and interchanging δg_1 and δg_2 when comparing a site

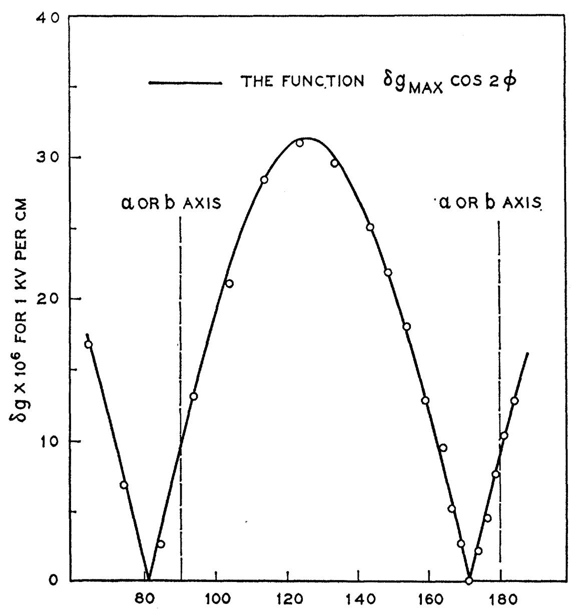

FIG. 4. The g shift for Ce^{3+} ions in a $CaWO_4$ lattice when an electric field is applied along the c axis. The magnetic field is rotated in the plane of the a and b axes. The results may be fitted by a function $|\delta g_{\perp}|=|\delta g_{max}\cos2\phi|$ with $\delta g_{max}=3.15\times10^{-5}$ at an electric field strength of 1 kV/cm, and with $\varphi=0$ at 54.5° to the a axis. A zero electric-field effect is found at 9.5° to the a axis, where $\delta g_{\perp}$ changes sign.

[10] C. F. Hempstead (private communication).

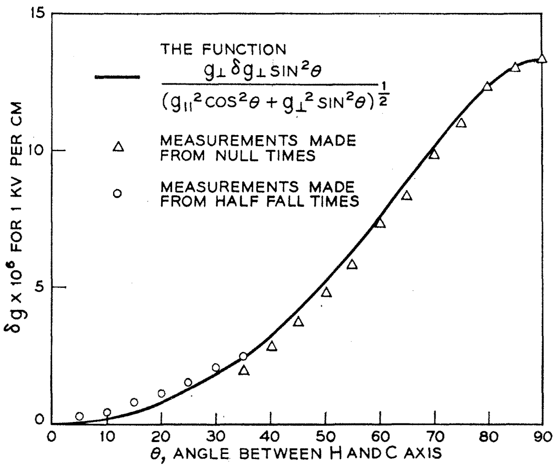

FIG. 5. The g shift for Ce^{3+} ions in a $CaWO_4$-host lattice when an electric field is applied along the c axis. Shifts are shown as a function of the angle θ between the Zeeman field and the c axis. Measurements from 90° to 35° were obtained by finding the null points in the echo envelope and applying Eq. (1). There was considerable inhomogeneity in the shift at smaller angles, and the measurements from 35° to 5° were obtained by finding half-fall points and applying Eq. (2). The results may be fitted by a function.

$$\frac{g_\perp \delta g_\perp \sin^2\theta}{(g_{\parallel}^2 \cos^2\theta + g_\perp^2 \sin^2\theta)^{1/2}}$$

with $g_{\parallel}=2.92$, $g_\perp=1.43$, and $\delta g_\perp = 1.33\times10^{-5}$ (g values for Ce^{3+} ions in $CaWO_4$, $\delta g_\perp$ for electric field of 1 kV/cm). At $\theta=90°$ the magnetic field made an angle of 4° with the a axis.

with its inversion image. For each type of site we then have $\delta g_\perp = \pm\delta g_{\max}\cos 2\phi$. Since the method yields only the absolute magnitude $|\delta g|$ of the shifts, the experimental curve is cusp shaped at points 90° apart where δg changes sign. The results can be fitted by setting $\delta g_{\max} = 3.15\times10^{-5}$ for an electric field along the c axis of 1 kV/cm, and by taking a principal axis of the modified g tensor at 54.5° to the a axis. (If the sample were to be taken out and replaced upside down, this angle would become $-54.5°$, and maxima in $|\delta g|$ would occur at $\phi=35.5°$, 125.5°, etc.) The g shifts observed when the magnetic field is rotated in a plane containing the c axis are illustrated by Fig. 5. In this plane, with the magnetic field at an angle θ to the c axis we have

$$(g+\delta g)^2 = g_{\parallel}^2 \cos^2\theta + (g_\perp + \delta g_\perp)^2 \sin^2\theta.$$

To the first order of small quantities δg this reduces to

$$\delta g = \frac{g_\perp \delta g_\perp \sin^2\theta}{(g_{\parallel}^2 \cos^2\theta + g_\perp^2 \sin^2\theta)^{1/2}}.$$

The curve in Fig. 5 may be fitted by setting $\delta g_\perp = 1.33\times10^{-5}$ for a field of 1 kV/cm. The angle ϕ between the plane of the magnetic field and the ac plane was determined to be 4°. This is not far from the angle giving zero $\delta g_\perp$ (Fig. 4), and as a consequence there is considerable inhomogeneity in the shift. This made it necessary to measure half-fall points instead of null points as a means of determining the shift at the smaller angles θ.

The accuracy with which the shifts can be measured depends on the adequacy of the contact between the electrodes and the crystal, on the homogeneity of the field, on the measurement of the voltage pulse, and on the time measurements as discussed later on. In general, this is good to within 5%. Because of the sharpness of the zeroes in Fig. 5 and the ease with which measurements can be made within a few degrees of the zero, the accuracy of the angular measurement is largely independent of the factors affecting the measurement of δg, and it is determined by the accuracy with which the crystal is aligned in the cavity. For the results given here the error is $\pm2°$.

The experimental shifts ranged from $\frac{1}{2}\%$ of the over-all linewidth to much smaller values. Since these results were comparatively easy to obtain, and the method appears to be one which is generally applicable, it may be of some interest to mention briefly the apparatus with which these measurements were made, and to discuss some of the problems which arise in determining the times from which the frequency shifts are derived. It will be assumed wherever relevant that the host lattice is like $CaWO_4$ in having inversion-image sites. The more general case of an ion in a site without inversion symmetry, but with no inversion-image site can be studied by the same techniques at some additional inconvenience. For example, if the microwave pulses are coherent with each other, the echo signal can be made to interfere with an appropriate cw signal.[11] An alternative solution would be to include two samples in the cavity and apply the electric field to only one of them, or to make a sample equivalent for a particular orientation of electric field to an inversion image sample by cutting a single crystal in two and mounting the portions back to back.

EXPERIMENTAL TECHNIQUE

The result shown in Fig. 1 was obtained with microwave pulses 0.2 μsec long, and a field strength in the cavity of about 1 G.[12] The echo pulses were detected by a superheterodyne system with a bandwidth of 10 Mc/sec. The microwave frequency was 9.4 Gc/sec. A system of this kind does not provide as much bandwidth and time resolution as might be obtained, but it is a convenient compromise and it is fairly easy to set up using components already available in a laboratory engaged in microwave-resonance spectrometry. It appears to be adequate for many electric-effect measure-

[11] In many spin-echo experiments it does not matter whether the two microwave pulses are coherent with one another or not, and it is often convenient to obtain them by pulsing a magnetron oscillator. If this is done, it will not be possible to detect phase changes in the echo signal by comparing it with an external signal source, but the other method suggested here may be used.

[12] The microwave pulses were generated by a Varian V63 klystron.

ments. An apparatus operating with shorter microwave pulses would, of course, make it possible to improve the accuracy of time measurements, and might offer significant advantages in cases where the phase-memory times for the spin echo are short and the frequency shifts large.[13]

The electric field was obtained as a voltage step wave, variable up to 3 kV by driving two Amperex 7534 tubes in parallel from cutoff to full conduction. These tubes working into a 5000-Ω load gave a step nearly equal to the $B+$ voltage of 0–3 kV. The times for the front edge and the back edge of the step were 0.1 μsec and 0.25 μsec, respectively. The calcium tungstate sample was cut to a uniform thickness of $2\frac{1}{4}$ mm and electrodes were provided by gluing aluminum foil to the appropriate faces. It was mounted on the side of a TE_{110} cavity and contact was made by means of a phosphor bronze wire passing through the base of the cavity (Fig. 6). In order to facilitate the measurement of electric field shifts at various magnetic field orientations, the side of the cavity holding the paramagnetic sample was constructed in such a way as to incorporate a small rotatable platform. With this arrangement it was not difficult to maintain a Q of 1000—the highest value which could be tolerated in view of the 10-Mc/sec bandwidth of the pulsing and detection apparatus.

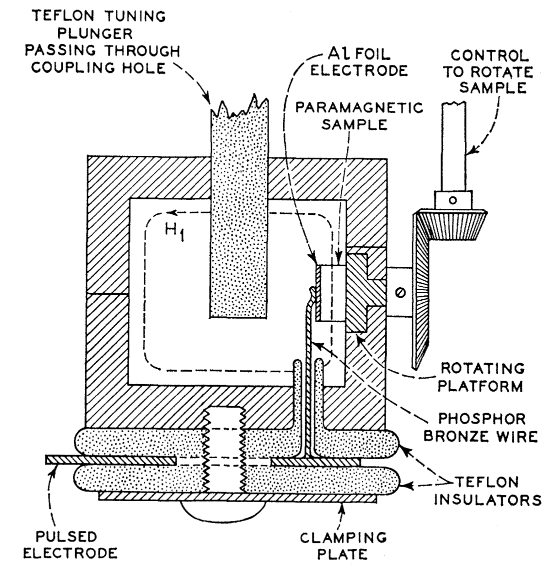

FIG. 6. Microwave cavity and sample. Electrodes consist of aluminum foil attached to sample. The sample can be rotated about an axis perpendicular to the axis of rotation of the externally applied magnetic field.

TIME MEASUREMENTS

The frequency shift can conveniently be determined by varying τ until a null point is found, and substituting the measured time τ_n in the equation

$$\Delta\omega = (2n+1)/4\tau_n , \tag{1}$$

where n is the number of nulls occurring since the beginning of the envelope.[14] Occasionally, it may be more convenient to find the time $\tau_{\frac{1}{2}}$ at which the application of the electric field halves the amplitude of the spin echo. In this case,

$$\Delta\omega = 1/6\tau_{\frac{1}{2}} . \tag{2}$$

There are instances, however, where (1) gives inconsistent results for successive nulls, and fails to agree with (2). There may even by no clear null at all, the echo envelope falling monotonically into the noise. To account for this it is necessary to consider the possibility that the frequency shift is inhomogeneous. This inhomogeneity can arise from lack of uniformity in the crystal thickness or the use of electrodes with large fringing field effects in the paramagnetic material, and it is to a certain extent unavoidable in any simple and practical arrangement. There is also a possibility that the electric field shift may be fundamentally inhomogeneous on account of microscopic irregularities in the crystal-field environment at each site. Both kinds of inhomogeneity may be described by substituting a function $g(\Delta\omega)$ giving the distribution of frequency shifts, in place of the unique frequency shift $\Delta\omega$ assumed up to the present. The precessing magnetization at the time of the echo is then given by

$$M(\tau) \propto \int_0^\infty g(\Delta\omega) \cos(\Delta\omega\tau) d(\Delta\omega) ,$$

and the echo decay envelope is thus proportional to the absolute magnitude of the cosine transform of the frequency shift distribution. An inhomogeneity which is small compared with the mean value of the shift will cause the echo envelope to fall off after a few null points have occurred, but will not lead to any serious difficulties in making the measurements. This may be illustrated by considering as a simple example the frequency shift distribution

$$g(\Delta\omega) = \exp\{-(\Delta\omega - \Delta\omega_0)^2/2a^2\} , \quad a \ll \Delta\omega_0 , \tag{3}$$

and its cosine transform which is proportional to

$$\cos(\Delta\omega_0\tau) \exp\{-a^2\tau^2/2\} .$$

A result of this kind corresponding to a fairly homogeneous frequency shift was found when electric and magnetic fields were set near orientations giving the maximum frequency shift (e.g., at the settings used in Fig. 1), and at such settings it was possible to check the adequacy of the electrode arrangement and the homogeneity of the applied electric field by observing the height to which the echo envelope rose after the first

[13] For a system with higher time resolution see D. E. Kaplan, M. E. Browne, and J. A. Cowen, Rev. Sci. Instr. **32**, 1182 (1961).

[14] At the instant when destructive interference occurs the resultant magnetization undergoes phase reversal. The detection system, which responds merely to the absolute magnitude of the precessing magnetization often shows this as a cusp-like dent in the echo waveform.

one or two nulls. The situation was entirely different, even for the same electrode arrangement and the same sample, when measured were made at field orientations for which the shift was small, or near settings for which the shifts of each spin group changed signs. Here, irregularities in orientation, whether due to microscopic variations in the crystal field or to the bending of lines of force in the fringing field, lead to large relative variations in the shift. In such cases, it was usually impossible to observe a null point followed by a rise in the echo envelope, and it was more convenient to measure the half-fall time. Of course, this cannot be interpreted strictly according to Eq. (2), and it gives only an approximate mean value for the shift. The actual distribution of shifts could, if necessary, be obtained by making a Fourier transform of the echo envelope.

Since the determination of frequency shifts depends on time measurements made on an oscilloscope scale, it is important to establish the amount τ_c by which they must be corrected so that they refer to the true time origin. This can be done directly, without computing delays and timing errors in the apparatus, by measuring a particular null or half-fall time at several values of applied voltage V. On the assumption that all frequency shifts are linear in applied field one can write $\tau=\alpha/V$, where τ is the corrected time and α a constant of proportionality. Then, if τ' is the measured time, $\tau=\tau'-\tau_c=\alpha/V$ and the correction τ_c is given by the intercept in a plot of τ' against $1/V$. If the experimental settings are such that the echo envelope rises to almost its full height after several null points, indicating a fairly homogeneous frequency shift, this procedure is unnecessary, and τ_c can be deduced merely by substituting $\tau_n=\tau_n'-\tau_c$ in Eq. (1) for two successive null points. Small timing errors are introduced by the finite rise time of the electric field step,[15] or, if the step partly overlaps microwave pulse two, from the effect of the microwave field in modifying the precession rates from the ideally expected values. These errors can, of course, be measured as outlined above, but it is convenient to keep them as small as possible, and to adjust the apparatus so that they do not have to be redetermined more often than necessary. The best arrangement appears to be to use the steeper of the two sides of the voltage pulse generated by the apparatus in coincidence with microwave pulse two, and to time the step so as to occur in the middle of the microwave pulse. This latter position is easy to find, as a displacement on either side of it will reduce the magnitude of the electric-field effect on the spin-echo signal at any given time τ.

The effect of pulsed electric fields has so far been discussed without reference to spin-spin and spin-lattice interactions in the paramagnetic material. These give the envelope certain characteristic forms,[16,17] and lead eventually to a randomizing of phase relations, thus setting a limit on the values of τ at which measurements can be made. Provided that the spin-spin and spin-lattice interactions are not modified by the application of the electric field,[18] the echo amplitude is proportional to the product of two factors, one due to the electric-field effect [Eq. (3)] and one due to these interactions. The latter factor can then be eliminated from the results by making measurements with and without electric field and taking ratios of the echo signal intensities. From a practical point of view it is of course desirable to choose the conditions of the experiment so that spin-spin and spin-lattice effects are minimized and the phase memory is as long as possible. In the liquid-helium range, spin-lattice relaxation is usually slow enough to have no effect on the phase-memory time.[19] Electron spin-spin interactions can be reduced by using materials with a high magnetic dilution. Concentrations between 10^{17} and 10^{18} spins/cc form a convenient choice, and have, in some cases given phase memory times as long as 100 μsec (permitting the determination of frequency shifts down to a limit of about 1 kc/sec). Interactions with nuclear moments may set a limit at shorter times (typically 3 or 4 μsec for fluorides and hydrated crystals), and, where possible, the host lattice should be chosen with weak nuclear moments, or with no nuclear moments at all.

ACKNOWLEDGMENTS

The author would like to thank W. E. Blumberg and A. Kiel for numerous discussions during the course of this work.

[15] The area included under the step before pulse two, and the area missing from the step after pulse two both combine to reduce the phase shift in the precessing magnetization.

[16] Envelope shapes due to spin-lattice and spin-spin interactions are discussed by J. R. Klauder and P. W. Anderson, Phys. Rev. **125**, 912 (1962).

[17] A periodic modulation of the envelope due to electron-nuclear interaction is discussed by E. L. Hahn, D. E. Kaplan, L. Rowan, and W. B. Mims (unpublished).

[18] No experimental evidence of any interdependence has been found. It seems unlikely that the electric field would change the over-all effect of electron spin-spin interactions for frequency shifts smaller than the linewidth. In the case of the nuclear modulation effect (see Ref. 17), the electric field shift can be incorporated in the calculation by making a small addition to the Zeeman term in the Hamiltonian used after pulse two.

[19] Lattice relaxation may be a limiting factor even when it is an order of magnitude longer than the phase memory. This is an indirect effect. See the discussion of phase memory in (Ca,Er)WO_4 and (Ca,Ce,Er)WO_4 in Ref. 7.

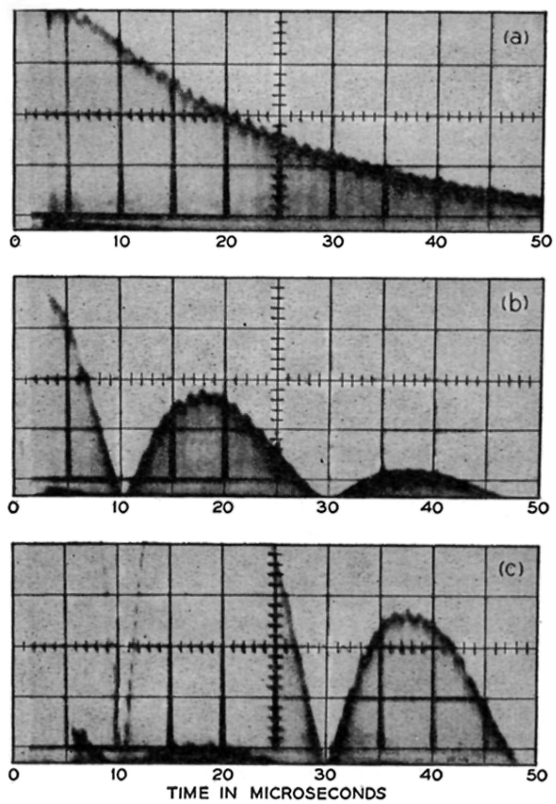

FIG. 1. Echo-decay envelopes for (Ca,Ce)WO_4, 3.3×10^{17} spins/cc, 4.2°K, Zeeman field along the *a* axis. (a) No electric field. (b) Electric field of 450 V/cm applied along the *c* axis during the time from the second microwave pulse to the spin echo. (c) As for (b) but with 12 dB additional gain in the vertical direction. The effect of the electric field can be found by dividing ordinates of (b) by ordinates of (a).