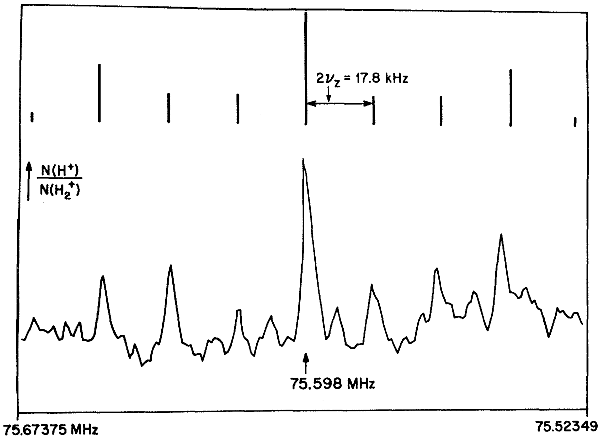

FIG. 3. $\Delta F = \pm 1$ transition, $v = 5$.

more of the above transitions. The results are

$$v = 5 \pm 1, \quad \Delta W_F = 75.598 \pm 0.002 \text{ MHz},$$

$$d = 30.239 \pm 0.001 \text{ MHz};$$

$$v = 6 \pm 1, \quad \Delta W_F = 70.231 \pm 0.002 \text{ MHz},$$

$$d = 28.092 \pm 0.001 \text{ MHz}.$$

The uncertainty in the assignment of vibrational quantum numbers can be removed by utilizing the low-wavelength limits for photodissociation from the various vibrational states, see Fig. 1.

Observation of the $\Delta F = 0, \Delta M_F = \pm 1$ transitions in the intermediate-field region (0.7 Oe) yields a rough value for the rotational moment $\mu_k$. For the state $k = 2$, and with undetermined contributions from vibrational states $4 \leqslant v \leqslant 8$,

$$\mu_k = +1.2 \pm 0.4\ \mu_N.$$

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# ECHO BEHAVIOR IN RUBY*

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Electron spin echoes at 9.25 GHz have been observed in a dilute ruby crystal immersed in liquid helium in a magnetic field of 3.3 kG applied along the optic axis. The echoes are associated with transitions between the $m = \pm\frac{1}{2}$ levels of the $^4A_2$ ground state of the $Cr^{3+}$ ion in $Al_2O_3$,[1] and show a marked modulation[2-4] as the separation between the two excitation pulses is increased. The electron spin echoes disappear when the magnetic field is rotated away from the optic axis by as little as three degrees just as the photon echoes disappeared in the initial photon-echo experiments in ruby.[5] The Hamiltonian describing the system of the $Cr^{3+}$ ion and its Al neighbors, with the magnetic field applied along the optic axis of the crystal, is considered to have the form

$$\mathcal{H} = g\beta H S_z + D[S_z^2 - \tfrac{1}{3}S(S+1)] + \sum_i\{-\hbar\gamma H I_{zi} + Q^i[I_{zi}^2 - \tfrac{1}{3}I(I+1)]\} + S_z\sum_i[(A_i + B_z^i)I_{zi} + B_t^i I_{ti}],$$

where the summation is over the 13 nearest Al neighbors and the constants have been determined by the ENDOR experiment of Laurance, McIrvine, and Lambe.[6] From the above Hamiltonian we obtain an equivalent Hamiltonian which describes the $Cr^{3+}$ ion as a simple two-level system, and we find that a density matrix calculation similar to that of Rowan, Hahn, and Mims[4] (except for the inclusion of a nuclear electric quadrupole term which is treated by perturbation theory) leads to the good agreement of theory and experiment as indicated in Fig. 1. If we assume that the constants $A_i$ and $B_{z,t}{}^i$ arise from the isotropic Fermi contact and the dipole-dipole interactions, respectively, a density-matrix calculation then shows that the echo should be reduced by several orders of magnitude when the magnetic field is rotated away from the optic axis.

The previously mentioned observations and several others[6,7] can be explained by a relatively simple model which takes into account the time-dependent magnetic field[2-4] at the $Cr^{3+}$ ion sites due to the precession of the neighboring Al nuclei. This is easily accomplished by noting that (1) the Al nuclei provide an incoherent quasiperiodic fluctuating field at the $Cr^{3+}$ sites whose intensity and time dependence depend on the magnitude and orientation of the applied magnetic field, and (2) the periodic nature of the fluctuating field reduces dephasing effects so that echoes are obtained when conditions are such that the magnitude of the fluctuating field is not too large.

When the pulse separation is equal to the period of precession of a particular Al neighbor, the time dependence of the magnetic field due to that precessing nucleus at the $Cr^{3+}$ site is the same after each of the excitation pulses, and that neighbor makes no contribution toward dephasing the echo. In the classic case, an echo is produced because the second excitation pulse negates (changes sign of) the relative phase of the precessing $Cr^{3+}$ dipoles which then rephase at the same rate at which they had dephased.[8] This situation obviously obtains in a time-independent magnetic field, but the only necessary requirement is that the time dependence of the magnetic field be the same after each excitation pulse. When the pulse separation is not equal to any of the periods of precession of the Al nuclei, one expects the greatest dephasing of the echo, dependent on the degree to which the time behavior of the local magnetic field at the $Cr^{3+}$ sites differs after each of the excitation pulses.

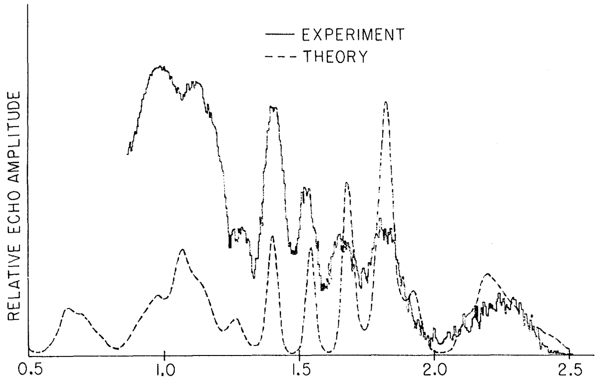

FIG. 1. Comparison of theory and experiment for the amplitude of the electron spin echoes in ruby versus the excitation pulse separation. The two excitation pulses were somewhat wider than 60 nsec while the theoretical curve was calculated assuming infinitely short excitation pulses. Receiver saturation prevented the observation of echoes with pulses much closer together than 1 $\mu$sec. Echoes have also been seen as far out as 6 $\mu$sec with reasonable agreement to our theoretical calculations.

In ruby there are effectively 13 neighbors which give rise to the ESR linewidth; however, when the magnetic field is along the optic axis, 12 of these neighbors can be grouped into four sets of three magnetically equivalent nuclei. The remaining nucleus is located directly above or below the $Cr^{3+}$ ion and does not contribute an oscillating component along the presession axis. The reduction in the number of inequivalent neighbors reduces the destructive interference one would otherwise expect and allows much larger echo amplitudes. The $Cr^{3+}$ ion is sensitive only to that component of the oscillation of the local field which is parallel to the ion's effective precession axis because of the high precession frequency of the ion; the effective precession axis of the $Cr^{3+}$ ion for a particular eigenstate is parallel to $\langle\vec{S}\rangle$, the expectation value of $\vec{S}$ for that state. For high applied fields the magnetic field at each Al neighbor only makes a small angle with the applied field, and for this model the Al nuclear dipoles are regarded as precessing about $\vec{H}$, the applied magnetic field. When a large magnetic field is applied along the optic axis of ruby, the nuclei will therefore precess about the direction of the optic axis with the result that the projection of $\vec{I}$ on $\langle\vec{S}\rangle$ will be constant in time, and the large $A\vec{I}\cdot\vec{S}$ interaction will not be effective in dephasing the echo.

Tilting the magnetic field with respect to the optic axis causes the nucleus above or below the $Cr^{3+}$ ion to contribute to the echo modulation and causes all the nuclei to become inequivalent. These two effects lead to a smearing

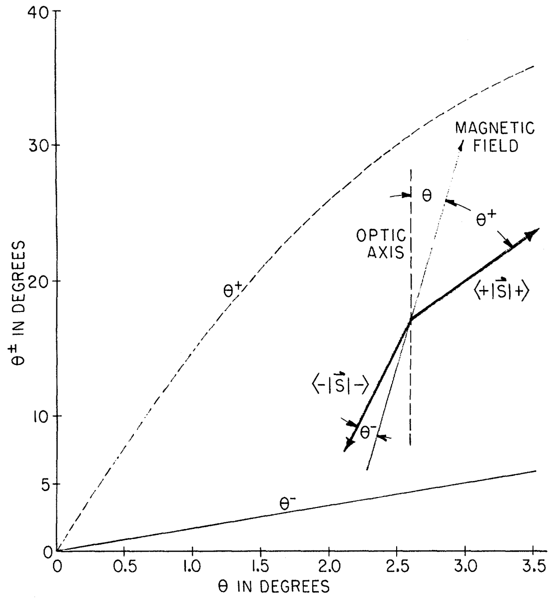

FIG. 2. Angles between the applied magnetic field and $\langle\vec S\rangle$ for the ± states versus the angle between the applied magnetic field and the optic axis. The ± states are the energy eigenstates which evolve from the $m=\pm\frac{1}{2}$ states in the $\mathrm{Cr}^{3+}$ ion as the angle $\theta$ between the optic axis and the applied field, initially zero, is increased.

and reduction of the sharp peaks observed in the on-axis modulation. The most important effect of rotating the magnetic field away from the optic axis, however, is that the direction of $\langle\vec S\rangle$ is no longer along $\vec H$ (because of the trigonal crystalline field at the $\mathrm{Cr}^{3+}$ site), and consequently the nuclei precessing about $\vec H$ will produce a much larger fluctuating field at the $\mathrm{Cr}^{3+}$ site since the projection of $\vec I$ on $\langle\vec S\rangle$ is no longer constant. This large fluctuating field considerably increases the depth of modulation due to each precessing nucleus and thereby causes the echo to effectively disappear. The effectiveness of a small rotation of the magnetic field is considerably enhanced over what one might at first expect. In free space the expectation value of $\vec S$ associated with any energy level would always follow the field $\vec H$. In the case of the $m=\pm\frac{1}{2}$ levels of ruby, we not only find that $\langle\vec S\rangle$ does not follow $\vec H$ but that at 3.3 kG a rotation of $\vec H$ through an angle $\theta$ gives rise to a rotation of $\langle\vec S\rangle$ away from $\vec H$ by an angle even greater than $\theta$ as is shown in Fig. 2.

The magnetic field dependence of the photon echo is now qualitatively understandable in much the same way as the electron spin echo, assuming that most of the dephasing is caused by the interaction of $\mathrm{Cr}^{3+}$ ions with their Al neighbors. Turning the magnetic field away from the optic axis makes the $A\vec{I}\cdot\vec{S}$ interaction effective in dephasing the echo. At 2 and 4 kG the enhancement of the magnetic-field rotation is extremely large because of the level crossings in the ${}^4A_2$ ground state, and one would expect the photon echo to be especially sensitive at these fields as is observed experimentally.[7] Also at lower fields one would expect the photon echo to relax more quickly since the dipolar field of the $\mathrm{Cr}^{3+}$ ion makes a sizable contribution to the local field at the Al sites and thereby causes the Al nuclei to precess about a direction which is not parallel to $\langle\vec S\rangle$.

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