It was along this direction that the narrowest line was found in every case. Figure 2 shows a resonance line observed at 540°K.[4] It is only 8.0 oersteds wide. It does not differ from a Lorentzian shape by more than the experimental error. Aside from the very narrow lines at higher temperatures, the most striking feature of the plot in Fig. 1 is the peak which lies between 20° and 65°K. For the case of the steady field along [100], line widths measured at 4.2° and 2.85°K are essentially the same.[5] However, the line widths with the field along other directions are still decreasing with temperature at 2.85°.

Magnetocrystalline anisotropy.—The field required for resonance varied with crystal direction. Values of the constants describing the anisotropy energy surface may be deduced from the fields for resonance measured in an appropriate number of crystal directions. Relations for doing this when first- and second-order terms suffice are collected as a footnote in the paper by Dillon *et al.*[6] If some higher order term in the anisotropy appears, that set of relations is incomplete. Except for data at the very lowest temperatures, K_1/M_s and K_2/M_s were were sufficient to express the observed fields. The coefficient K_1/M_s is plotted in Fig. 3 over the temperature range from 20° to above 500°K. No values of K_2/M_s were obtained in this range which were greater than the error in their determination. At the lowest temperature a much more complex behavior was found.

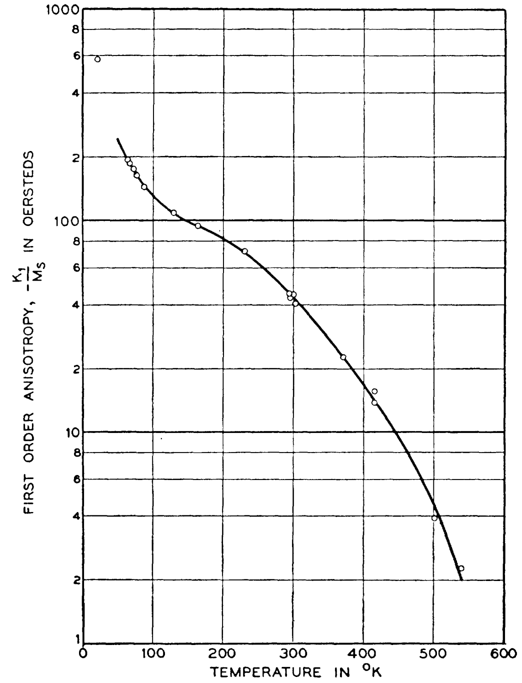

FIG. 3. Variation with temperature of the first-order anisotropy constant K_1/M_s. Values are plotted only for those temperatures at which K_1/M_s described the variation of field for resonance with angle. At 4.2° and below, the coefficients of higher order terms become appreciable.

The crystal still appeared to have cubic symmetry, but the anisotropy surface was rather more convoluted than before. The principal directions are all hard direction at helium temperatures, and the easy directions are near but not exactly coincident with [112] and [221]. This remark applies to directions accessible in a (110) plane. Examination of a crystal mounted to rotate about [111] shows that [123] or a direction very close to it is an even easier direction. The field for resonance in different directions at 4.2° extends over a range of almost exactly 3000 oersteds. Measurements at nearby temperatures show that these values are still changing with temperature. The terms necessary for the expression of this anisotropy and the values of the coefficients will be discussed in a later paper.

Spectroscopic splitting factor.—In the temperature region in which the usual first- and second-order anisotropy terms describe the variation of field for resonance with direction, we may deduce a value of g from the relations in reference 6. The value for g obtained in this way is somewhat arbitrary since it depends upon the form of the terms chosen to express the anisotropy. At room temperature the value $g=2.005\pm0.002$ was obtained at both frequencies for the 0.008-in. sphere, with a slightly lower value for larger spheres. Values of g between 2.002 and 2.009 were obtained for the 0.008-in. sphere in the temperature range from 100° to 540°. Below 100° the values rose with decreasing temperature to 2.040 at 65° and 2.035 at 20.5°. However, this is just the range where higher order terms may be entering the description of the energy surface.

The author wishes to thank J. W. Nielsen for the single crystals, and S. Geller for orienting some of the samples. He is also indebted to A. M. Clogston for helpful discussions and S. Geschwind for many discussions as well as the use of the high-frequency spectrometer.

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Electron Spin Relaxation Times in Gadolinium Ethyl Sulfate

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THE recent proposal by Bloembergen[1] to utilize a paramagnetic salt to amplify or produce microwave power led us to investigate the electron spin relaxation times in dilute gadolinium ethyl sulfate having cerium as an additional impurity. The preliminary results of these investagations are being reported in this letter. The successful operation of a maser incorporating this material is described in the accompanying letter.[2]

The trivalent gadolinium ion is in an ^8S ground state having seven electrons in a half-filled $4f$ shell. The energy levels were investigated in detail by Bleaney, Scovil, and Trenam.[3] The essential features are that the line is split by a fine structure term into seven lines whose spacing varies approximately as $(3\cos^2\theta-1)$ where θ is the angle between the dc magnetic field H_0 and the crystalline field axis. Figure 1 shows the position of four of the lines, the remaining three being omitted for clarity. The inequality of the spacings and the fact that the lines do not cross at 55° can be taken into account by higher order corrections. The paramagnetic resonance of cerium was first investigated by Bogle, Cooke, and Whitley.[4] Its ground state transition is also indicated in Fig. 1.

The crystals investigated were magnetically diluted with isomorphous lanthanum ethyl sulfate in the ratio Gd:La = 1:200 and Ce:La = 1:500. The size of the crystal used was approximately 1 mm×1 mm×0.5 mm. The small size was chosen to avoid violent perturbations on the cavity.

The relaxation times were investigated by the power saturation method.[5] This procedure gives a unique relaxation time for a system which has only two energy levels (i.e., spin $\frac{1}{2}$). In a more complicated system one might not be able to associate a single relaxation time with each pair of levels.[6] However, the microwave power at which χ'' drops by a given fraction is still a measure of the rate at which energy is carried to the lattice via all relaxation processes. In all our experiments we measured the power at which the saturation parameter $S=\chi''(H_1)/\chi''(H_1=0)$ dropped to 0.316 (10 db). In order to calculate the spin-lattice relaxation time T_1 from this measurement, we write for the saturation parameter:[5,7]

$$S=\frac{\chi''(H_1)}{\chi''(H_1=0)}=\frac{1}{1+(W_{M\to M-1}/W_{\mathrm{S.L.}})}$$
$$=\frac{1}{1+\frac{1}{4}(\gamma H_1)^2[S(S+1)-M(M-1)]T_1T_2},$$

where $W_{M\to M-1}$ is the transition probability for $\Delta M=\pm 1$ in an external magnetic field of amplitude H_1, $1/W_{\mathrm{S.L.}}$ is twice the spin lattice relaxation time T_1, γ is the effective gyromagnetic ratio and $T_2=1/\pi\Delta\nu$, $\Delta\nu$ being the width at half maximum power absorption. The experimentally determined T_2 was 8×10^{-9} sec. The line width is due primarily to interactions of the electron spin with the magnetic moments of the neighboring protons, although the electron dipole-dipole interactions are of the same order. It is therefore not surprising that the line is homogeneously broadened as found from its saturation behavior.[8]

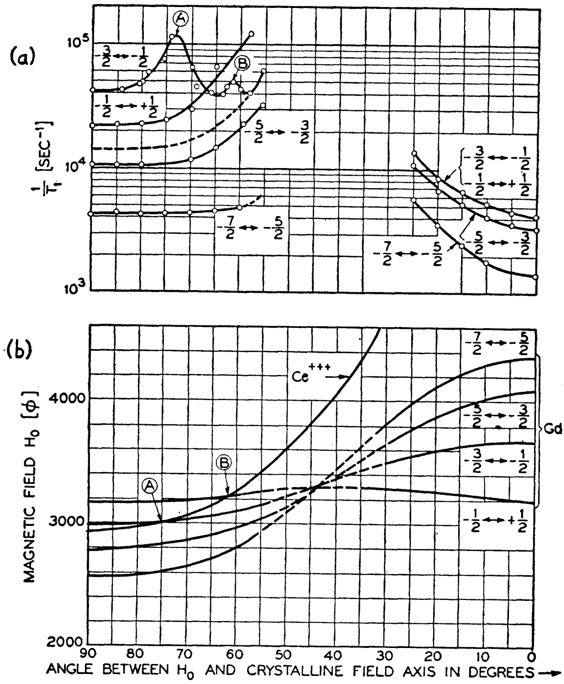

FIG. 1. (a) Inverse relaxation times for the different Gd transitions *vs* angle between H_0 and crystalline axis. Note the reduction in relaxation time when the Gd and Ce transitions overlap. (b) Magnetic field H_0 at which Gd and Ce transitions occur *vs* angle between H_0 and crystalline axis.

The results of the relaxation time measurements at 1.2°K and 9000 Mc/sec are shown in Fig. 1. The most striking feature is exhibited by the $-\frac{3}{2}\to-\frac{1}{2}$ line. When its resonance frequency is equal to that of cerium (see point A, Fig. 1), its relaxation time is reduced by about a factor of 7. This assumes that in the absence of cerium the gadolinium relaxation time would follow the dotted line. A reduction of the relaxation time of Gd by Ce has been reported earlier by Bleaney, Elliott, and Scovil.[9] Their investigations were carried out on a concentrated Ce salt at 14°K. Under those circumstances all Gd levels were affected simultaneously, which is undesirable for the operation of a maser. From those experiments one concludes that the relaxation process proceeds in two steps. First, there is a Gd-Ce spin-spin flip which is energetically most favorable, when the resonance frequencies of the two ions are equal. This process proceeds in a characteristic time essentially given by T_2, which in our case is $\sim10^{-8}$ sec. In the second step the Ce relaxes via its own spin-lattice relaxation time which at 1.2°K was found to be about three orders of magnitude longer than T_2.

Another reduction in the relaxation time is observed when we approach a point at which the Gd transitions overlap (see Fig. 1). In this case the Gd transitions whose resonant frequencies lie nearest to the saturated line take the place of the Ce. It should be pointed out, however, that an unknown impurity with a broad resonance could account for a similar behavior.

The third distinct relaxation process occurs at a point where the Ce transition overlaps a Gd transition differing by $\Delta M=1$ from the saturated line (see point B, Fig. 1). This involves a three-step process. First the saturation is partially passed on from the $-\frac{3}{2}\rightarrow-\frac{1}{2}$ levels to the $-\frac{1}{2}\rightarrow+\frac{1}{2}$ levels via a spin-spin interaction. The $-\frac{1}{2}\rightarrow+\frac{1}{2}$ levels then relaxes via the Ce as discussed earlier.

In the absence of strong interactions between different levels ($\theta=0$ in Fig. 1), the relaxation times are approximately proportional to the inverse transition probabilities as one would expect.

We would like to thank Dr. P. W. Anderson for helpful discussions and Mr. E. A. Gere for his assistance in the experiments.

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Operation of a Solid State Maser

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A MASER of the same type as that proposed by Bloembergen[1] has been successfully operated at 9 kMc/sec. Since the basic theory has been covered in the reference, it will not be reviewed here.

We require a magnetically dilute paramagnetic salt having at least three energy levels whose transitions fall in the microwave range and which may be easily saturated. The ion $\mathrm{Gd}^{+++}|4f^7, {}^8S\rangle$ seems a suitable choice since its eight energy levels give the choice of several modes of maser operation. Of the three salts of Gd^{+++} which have been investigated by paramagnetic resonance[2] the diluted ethyl sulfate appears very desirable. This salt has been investigated in detail by Bleaney *et al.*,[3] Buckmaster,[4] and Feher and Scovil.[5]

If an external magnetic field is applied perpendicular to the magnetic axis, the spin Hamiltonian may be written[3]

$$\mathcal{H}=g\beta H_0\cdot S_z-\tfrac{1}{2}B_2{}^0[S_z{}^2-\tfrac{1}{3}S(S+1)]+\tfrac{1}{4}B_2{}^0[S_+{}^2+S_-{}^2], \quad (1)$$

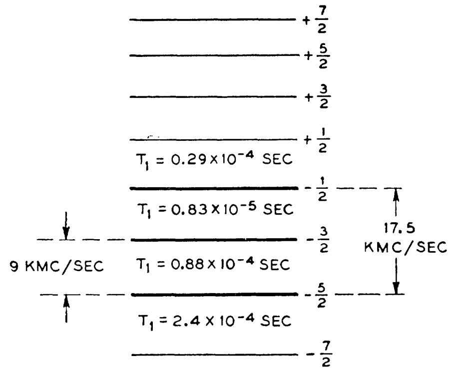

FIG. 1. The energy levels of the ground state of Gd^{+++} in the ethyl sulfate for a large applied magnetic field. The heavy lines identify the maser levels. Spin-lattice relaxation times between levels are shown.

where some small terms have been neglected, $g=1.99$, $B_2{}^0\approx0.02$ cm^{-1}, and the axis of quantization is parallel to H_0. The first term is the usual Zeeman energy and is varied to bring the transitions to the desired operating frequency. The second term disturbs the equality of the level spacings (essential for the device) as shown in Fig. 1. The third term admixes states, thereby permitting $\Delta S_z=\pm2$ transitions which are also essential. The angle between the dc magnetic field and the microwave magnetic field should be zero for the $\Delta S_z=\pm2$ transitions and 90° for the $\Delta S_z=\pm1$ transitions. A convenient compromise of 45° between both microwave fields and H_0 was chosen for the structure employed.

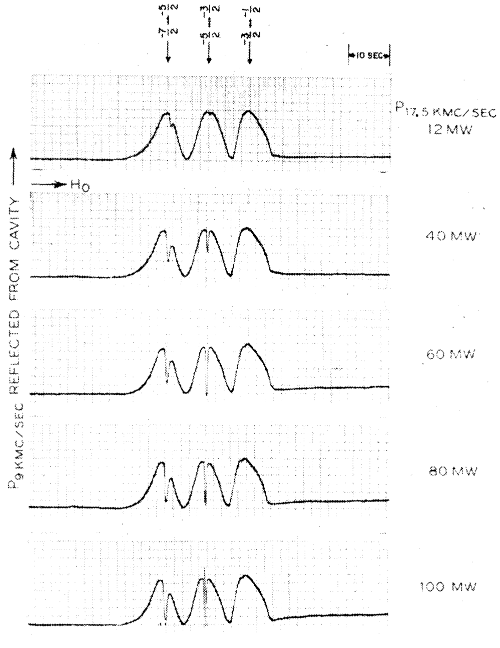

FIG. 2. The power reflected from the 9-kMc/sec cavity as the magnetic field was swept to cover three $\Delta S_z\pm1$ transitions for different 17.5-kMc/sec power levels. The spacing between two lines is about 200 oersteds.