tion process populates the two levels equally, and that the actual population is obtained by a balance between spin-lattice relaxation and radiative decay, the spin-lattice relaxation time is about 2×10^{-4} second. Also the crystal may have been heated above the helium bath temperature by the exciting radiation, so the actual relaxation time may be somewhat less. In any case, it seems that there is nearly complete thermalization between the Zeeman levels of the excited state during its relatively long lifetime of several milliseconds.

The great disparity between calculated and observed intensities for a ruby containing 0.05% Cr_2O_3 by weight is shown in Fig. 2(b). This disparity is explained by self-absorption which differs from one component to the next because of the Boltzmann population distribution of the ground-state levels. Thus component α terminates on the ground level $(m = -3/2)$, which is populated by 85% of the atoms and is strongly absorbed. At the other extreme the component δ terminates on the $+3/2$ level, which is 8.3 cm^{-1} above it, and contains only 0.3% of the atoms, so that δ is much less absorbed. While self-absorption is often encountered in gaseous luminescence, it is seldom possible for a gas to be cold enough to have appreciably different populations in individual Zeeman levels.

Quantitatively, we find that an absorption coefficient of about 25 cm^{-1} for the α component produces satisfactory agreement with the observed intensity ratio of γ to α in the 0.05% ruby spectrum. A direct absorption measurement at 77°K, where only half of the atoms are in the $\pm3/2$ state and line widths have increased from 0.25 to 0.32 cm^{-1}, gave $k = 13$ cm^{-1} in good agreement. The

radiative lifetime of the excited state was also measured in the very dilute sample, and in finely divided and dispersed 0.05% ruby, and was found to be 4.3 ± 0.3 milliseconds. This gives an oscillator strength $f = 7.5 \times 10^{-7}$ for the same transition, which then gives $k = 11$ cm^{-1} for 0.05% ruby. This satisfactory agreement indicates that the observed lifetime is indeed predominantly radiative.

It has been possible in the 0.05% ruby to observe for the first time in a solid the trapping of resonance radiation. At 77°K the radiative lifetime is found to vary smoothly from 4.3×10^{-3} second for a fine, dispersed powder to 15×10^{-3} second for a whole boule, a very long lifetime. The observation of trapping confirms the predominantly radiative character of the decay of the excited state, and the strong self-absorption of the resonance radiation. The ratio of lifetimes with and without trapping is only about 4, showing that other modes of decay such as radiation in vibrational sidebands and nonradiative processes also occur.

We are indebted to D. G. Thomas for the use of his spectrograph and magnet, to A. M. Clogston, S. Geschwind, and S. Sugano for helpful discussions, and to G. E. Devlin for extensive experimental assistance.

[1]Geschwind, Collins, and Schawlow, following Letter [Phys. Rev. Letters 3, 545 (1959)].

[2]Brossel, Geschwind, and Schawlow, this issue [Phys. Rev. Letters 3, 548 (1959)].

[3]S. Sugano and Y. Tanabe, J. Phys. Soc. (Japan) 13, 880 (1958).

[4]S. Sugano and I. Tsujikawa, J. Phys. Soc. (Japan) 13, 889 (1958).

OPTICAL DETECTION OF PARAMAGNETIC RESONANCE IN AN EXCITED STATE OF Cr³⁺ IN Al₂O₃

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We have observed paramagnetic resonance in an excited metastable state of Cr³⁺ in Al₂O₃ by a method of optical detection which should have wide applicability to the general problem of studying paramagnetic resonance in excited states of ions in solids. This method makes use of the selective reabsorption in the ground-state Zeeman levels of the fluorescent light from the excited states in solids at very low temperatures.[1] Referring to Fig. 1 of the preceding Letter,[1] at 1.6°K, the lower of the two Zeeman levels of the excited state $\bar{E}(^2E)$ will be much more heavily populated. Let us first assume there is no reabsorption so that the theoretical

intensities for transitions to the Zeeman levels of the $^4A_2$ ground state are as given by Sugano and Tanabe.[2] In this case, when the sample is irradiated with microwave energy of the proper frequency so as to excite ions in the lower Zeeman level of $\bar{E}(^2E)$ to the upper Zeeman level, the ions upon radiating to the ground state emit two σ lines, δ, β of relative intensity 3:2 just as they do in radiating from the lower Zeeman level of the excited state (α, γ). In this case, the total emitted light in σ polarization would remain constant, i.e., it is independent of the relative population of the magnetic sublevels of the excited state. Similarly for the π component. On the other hand, if there is reabsorption of the fluorescent light, components β and δ originating from level b will be less strongly absorbed than α and γ due to the larger Boltzmann populations of the lower Zeeman levels in the ground state at low temperatures. Then, by inducing microwave transitions between the magnetic sublevels of the excited state so as to raise ions from level a to b, we can increase the total light output and thereby detect paramagnetic resonance in the upper state.[3] In contrast to standard optical double resonance techniques in gases, where normally a change in linear or circular polarization is detected along the field direction,[4] this method of utilizing selective reabsorption enables one to observe a change in the light in linear polarization in the much more convenient direction at right angles to the field.

The sample was a $\frac{1}{8}$-in. diameter by $\frac{1}{4}$-in. long cylinder of ruby, containing 0.05% of Cr, whose c axis was perpendicular to the axis of the cylinder. It was placed along the axis of a cylindrical $TE_{0,1,2}$ mode K-band cavity with a hole cut in one end wall for continuous vertical illumination from below by a 200-watt Osram mercury lamp. The ions were continuously excited to the metastable state by absorption of the 5461A and the 4000A light from the mercury lamp and subsequent decay by radiationless transitions to the metastable state. The metastable state $2\bar{A}(^2E)$, 30 cm^{-1} above, is virtually depopulated at 1.6°K, i.e., the thermalization of the metastable states in the radiationless decay is much faster than the radiative lifetime of these states. Slots were cut in the side wall of the cavity to view the fluorescent light which was detected by a photomultiplier preceded by a polaroid, collimating lens, and narrow band interference filter of 70A half-width centered at 6934 A. The microwaves were chopped with a 30-cps square wave and the resulting 30-cps component in the fluorescent light, as one swept the dc magnetic field through the excited state resonance, was recorded using standard lock-in detection techniques. A recorder trace of the increase in σ light is shown in Fig. 1. The line width is 17 gauss and is comparable to the widths observed in the ground-state resonances. We estimate that this signal arises from approximately 10^{10} Cr^{3+} ions in the excited state.

The excited state can be represented by an effective spin Hamiltonian

$$\mathcal{H} = \mu_\beta \vec{H} \cdot \tilde{g} \cdot \vec{S}', \qquad (1)$$

where $\vec{S}'$ is an effective spin of $\frac{1}{2}$. The energy levels of the excited state are given by $W = \pm \frac{1}{2} g \mu_\beta H$, where $g = (g_\parallel^2 \cos^2\theta + g_\perp^2 \sin^2\theta)^{1/2}$. The variation of the dc magnetic field required for resonance, H_{res}, as a function of the angle θ between the c axis and H_{res}, is shown in Fig. 2. $1/H_{res}$ is seen to vary as $\cos\theta$ within the accuracy of our measurements,[5] with the components of the g tensor given by $g_\parallel = (-)2.445 \pm 0.001$ and $|g_\perp| < 0.06$. While the sign of $g_\parallel$ has not actually been measured by using microwaves of circular polarization, theoretical analysis by Clogston[6] indicates that it is negative.

The actual increase in the total fluorescent signal when the Zeeman levels of the excited state were saturated amounted to 2.5% of the total fluorescence. This very large light signal made it possible to measure directly the relaxation time T_1 in the excited state. Figure 3(a) is an oscillogram of a sample of the microwave power, square-wave modulated at 50 cps, incident on the cavity. Figure 3(b) is an oscillogram of the
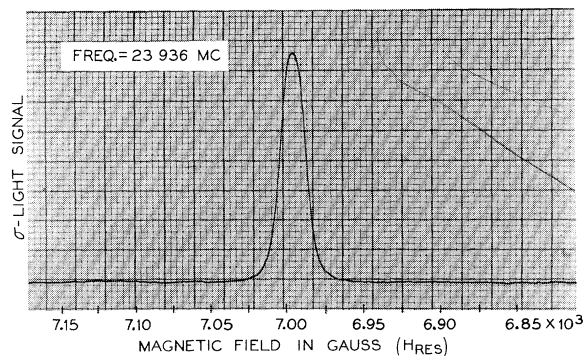

FIG. 1. Recorder trace of increase in σ component of fluorescent light as magnetic field is swept through resonance of excited $\bar{E}(^2E)$ state. This signal corresponds to approximately 10^{10} Cr^{3+} ions in the excited state. H is parallel to the c axis.
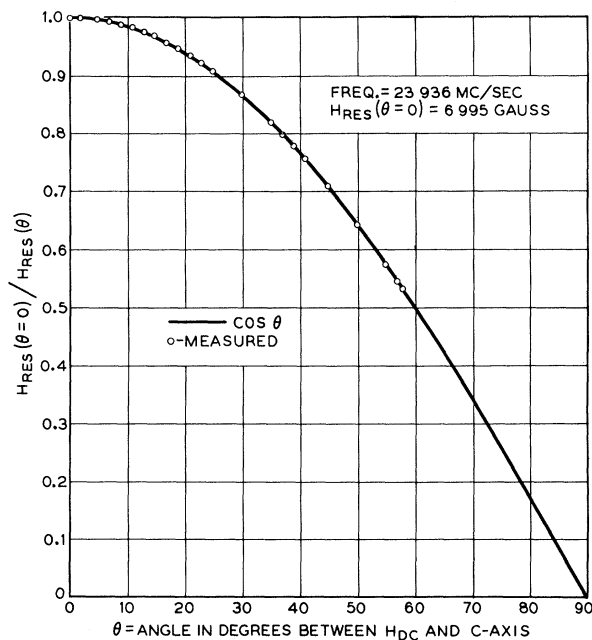
FIG. 2. Variation of magnetic resonance of $\bar{E}(^2E)$ state with angle θ between the applied field and the C axis of the crystal.
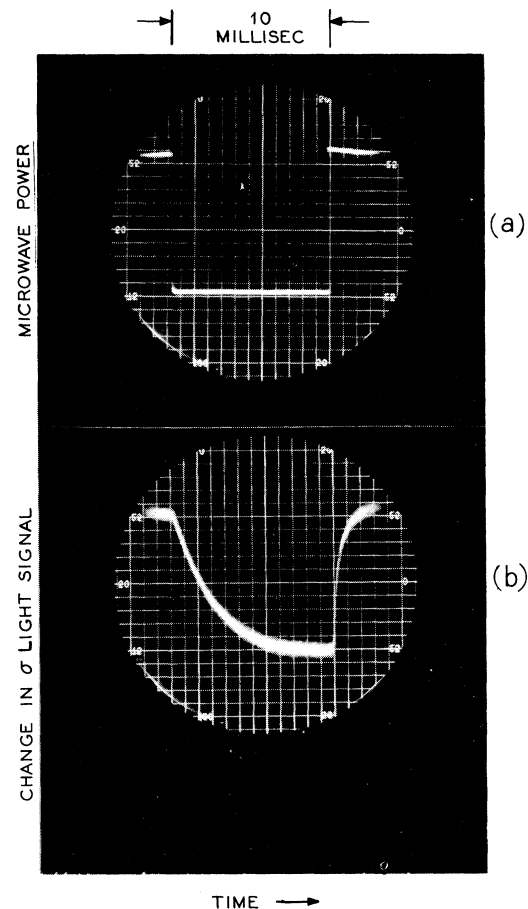

FIG. 3. (a) Oscillogram of microwave power square-wave modulated at 30 cps. The lower portion of the square-wave corresponds to the microwave-power-off part of the cycle. (b) Corresponding change in the σ component of the fluorescent light signal. From the decay of the increased fluorescent light signal when the microwave power is turned off, T_1 for the excited state ions is found to be 2.3 milliseconds.

corresponding light signal. From the decay of the light signal with microwave power off, we determine T_1 to be 2.3 milliseconds. T_1 need not necessarily be a spin-lattice relaxation time; it is, however, the time taken for the magnetic sublevels of the excited state to thermalize when saturated, irrespective of the process, i.e., direct spin-lattice, cross-relaxation to ground-state spins, or even radiative relaxation. It is this latter radiative lifetime τ which sets an upper limit on the nonradiative T_1 which can be observed. Since τ is known to be about 8×10^{-3} sec, the value of T_1 of 2.3×10^{-3} sec can be assumed to be mainly connected with nonradiative thermalization. Further evidence for this is the speedup in T_1 to $\sim 1.6 \times 10^{-3}$ sec at certain angles θ where the energy separation of the excited state approaches the Zeeman separation of some of the ground-state levels.

From a study of the saturation of the light signal with microwave power, the value of microwave power where $(\vec{\mu} \cdot \vec{H}_{rf}/\hbar)^2 T_1 T_2 \sim 1$ was determined. Since we know T_1 and T_2 (the latter from the line width) we could determine $\vec{\mu}$, the magnetic dipole moment matrix element for the transition, if we knew $\vec{H}_{rf}$ as a function of the microwave power level incident on the cavity. As it is difficult to know the exact field configu-

ration in the ruby, we made a rough estimate of $\vec{\mu}$ by comparing the ratio of powers needed to saturate the excited state compared to the ground state, using the values of T_1 and T_2 for the ground state from other work. We find the ratio of the transition probabilities to be approximately 0.005. Even this small transition probability is relatively large compared to that originally predicted theoretically.

We have also detected the ground-state resonances, by monitoring the change in fluorescent light when these resonances are swept through, again due to selective reabsorption. However, these are of secondary interest in this case.

We wish to thank A. M. Clogston for stimulating

our interest in the problem of studying excited states in solids by paramagnetic resonance. We are grateful to D. Linn for his extensive experimental assistance and to Professor J. Brossel, A. Javan, W. B. Mims, H. E. D. Scovil, and Professor S. Sugano for helpful discussions.

[1]Varsanyi, Wood, and Schawlow, preceding Letter [Phys. Rev. Letters 3, 544 (1959)].

[2]S. Sugano and Y. Tanabe, J. Phys. Soc. (Japan)

13, 880 (1958).

[3]The principle of this method was also suggested independently by Professor J. Brossel.

[4]F. Bitter and J. Brossel, Phys. Rev. 86, 308 (1952).

[5]S. F. Jacobs, thesis, 1957, John Hopkins University (unpublished), earlier established the approximate $\cos\theta$ variation of the $\bar{E}(^2E)$ Zeeman pattern from the optical Zeeman spectrum. Our work confirms this with an order of magnitude greater accuracy characteristic of microwaves. We are grateful to Professor G. H. Dieke for making this work available to us.

[6]A. M. Clogston (private communication).

OPTICAL DETECTION OF PARAMAGNETIC RESONANCE IN CRYSTALS AT LOW TEMPERATURES

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Paramagnetic resonance absorption has been extensively used to determine the structure of the ground state of paramagnetic ions in different crystal fields. As is well known, many absorption and fluorescence spectra of ions in a crystal lattice show very sharp optical lines besides the usual broad bands. The Zeeman effect of these lines has been observed in some cases, and the components are often strongly polarized.

A method of detection of magnetic resonance in the fluorescent state which utilizes the selective reabsorption of the components of the fluorescent radiation at low temperatures has been described in the preceding Letter.[1] We wish to discuss extensions of this method to other cases which may arise, as well as to indicate where the more conventional double resonance[2] techniques may be applied to the study of paramagnetic ions in crystal lattices. In addition, we want to point out that optical detection of magnetic resonances in the ground state may have some merits of its own.

The first step in doing resonance in an excited state is to obtain a population difference between the Zeeman substates. We will use the case of ruby to illustrate the different possibilities. Referring to Fig. 1 of Varsanyi, Wood, and Schawlow,[3] two cases may arise:

(A) Thermalization is fast. — This we feel will be the most common case. It is what happens in ruby, i.e., the Boltzmann distribution is reached between (a) and (b) before the atoms radiate. The fluorescent state can be reached in any con-venient way and one can rely on thermal relaxation to achieve the population difference. Absorption of light in any of the broad bands is particularly convenient because it can be filtered out at detection and need not come from a preferred direction.

(B) Thermalization is slow. — In this case, a population difference between the Zeeman levels of the excited state can be achieved, just as is done in gaseous double resonance experiments, by pumping with polarized resonance light. However, in a solid at low temperatures and high enough fields, one can even use unpolarized resonance radiation, because the lowest Zeeman level of the ground state is far more populated than the others, so that absorption will populate level (a) more than level (b).

Having obtained a population difference between the Zeeman levels of the excited state, the next step is to detect the change in this population on passing through magnetic resonance by observing the fluorescent light. At low temperatures selective reabsorption may be utilized as shown in the preceding Letter.

At temperatures very much above 4°K, however, selective reabsorption will not occur. In addition, selective reabsorption will be absent from a fluorescent line whose width is greater than the total Zeeman splitting of the ground state. In these cases, it follows from the transition probabilities shown in Fig. 1 of reference 3, and as explained in the preceding Letter, that the total light output is independent of the popula-
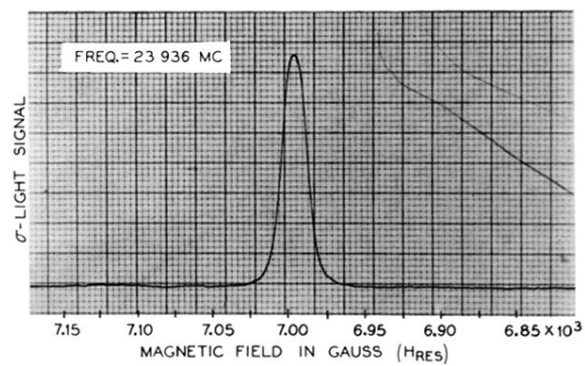
FIG. 1. Recorder trace of increase in σ component of fluorescent light as magnetic field is swept through resonance of excited $\bar{E}(^2E)$ state. This signal corresponds to approximately 10^{10} Cr^{3+} ions in the excited state. H is parallel to the c axis.
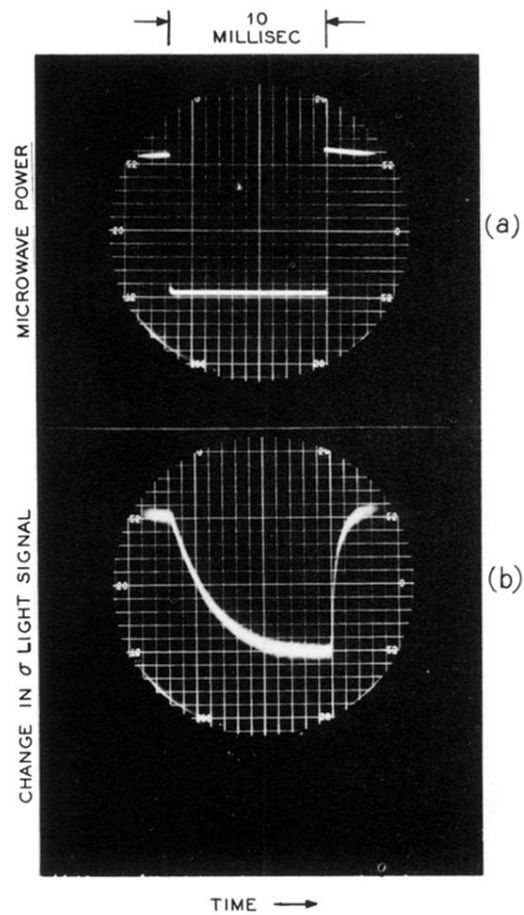
FIG. 3. (a) Oscillogram of microwave power square-wave modulated at 30 cps. The lower portion of the square-wave corresponds to the microwave-power-off part of the cycle. (b) Corresponding change in the σ component of the fluorescent light signal. From the decay of the increased fluorescent light signal when the microwave power is turned off, T_1 for the excited state ions is found to be 2.3 milliseconds.