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OPTICAL DETECTION OF PARAMAGNETIC RESONANCES IN EXCITED STATE $\bar{E}(^2E)$ AND GROUND STATE $^4A_2$ OF Cr^{3+} IN Al_2O_3

BY

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ABSTRACT

The optical detection of the electron paramagnetic resonances is reported on Cr^{3+} ions in the excited state $\bar{E}_+(^2E)$ and the ground state $^4A_2$ of ruby. The principle of the detection we used is the same as that by S. Geschwind et al.. The detailed description of our apparatus is given. The g values obtained for the excited state are in good agreement with those of S. Geschwind et al. Some detailed studies were also made on the change in the fluorescent light intensities corresponding to the paramagnetic resonance transitions between the ground state sublevels. In contrast to the signals in the excited state, the positive and negative signals could be observed for the ground state. The temperature and the concentration dependence of the signals were also studied.

§1. Introduction

We wish to report here the optical detection of the electron paramagnetic resonances in the optically excited state $\bar{E}\,(^2E)$ and in the ground state $^4A_2$ of Cr^{3+} in Al_2O_3.

Several papers[1-8] have so far been published on optical detections of electron paramagnetic resonances in optically excited states[1-6] and those in the ground states[7-8]. We restrict, however, our interest to the detection of the paramagnetic resonances of Cr^{3+} in ruby, and quote here several papers on it only.

I. Wieder tried an optical detection of paramagnetic resonances in the ground state. He detected one percent change in R_2 fluorescent light transmitted through a ruby from another ruby when the complete microwave saturation of the ground state Zeeman sublevels was achieved in the former. T. H. Maiman detected three percent population change of Cr^{3+} in the ground state due to the intense optical excitation by pulse light from $^4A_2$ to the broad absorption bands $^4T_1$ and $^4T_2$.

S. Geschwind et al. optically detected the paramagnetic resonances in the excited state $\bar{E}\,(^2E)$ of ruby. They used the selective reasorption[9] in the ground state Zeeman sublevels of the fluorescent light from the excited state at very low temperature. They reported the values of g and relaxation time of the excited state and said that they had also optically detected the resonances in the ground state but without any detailed descriptions.

The principle of the detection of the paramagnetic resonances we repoted

here is the same as theirs. Now we described briefly our method of the detection of the paramagnetic resonances in the excited state $\bar{E}$ (^2E) and in the ground state $^4A_2$ of Cr^{3+} in ruby using the selective reabsorption of the fluorescent light in the ground state Zeeman sublevels.

Cr^{3+} ions are optically excited to the broad bands $^4T_1$ and $^4T_2$ (Fig. 1) by a suitable light. The Cr^{3+} ions excited to the bands fall in a short time ($\sim 10^{-7}$ sec)[8] to the metastable states $\bar{E}$ (^2E) and $2\bar{A}$ (^2E) through a radiationless process. And further they fall to the ground state emitting fluorescent lights R_1 and R_2 respectively.

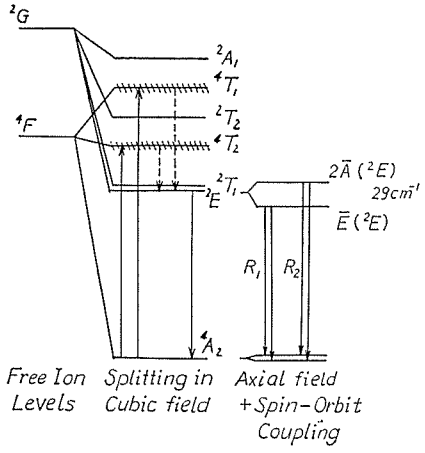

Fig. 1. Partial energy-level scheme for Cr^{3+} ions in Al_2O_3[3].

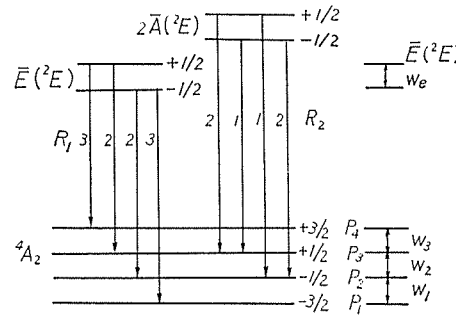

Fig. 2. Relative transition probabilities of the R lines in ruby[10]. $H//C$ axis (σ light only).

The Zeeman sublevels involved in our experiment are shown in Fig. 2, where w_1, w_2 and w_3 denote the transitions between the ground state Zeeman sublevels; $\left(S_z=-\frac{3}{2},\ -\frac{1}{2}\right)$, $\left(-\frac{1}{2},\ +\frac{1}{2}\right)$ and $\left(+\frac{1}{2},\ +\frac{3}{2}\right)$ respectively, and w_e the transition between the excited state Zeeman sublevels. Each Zeeman component of the fluorescent lights R_1 and R_2 emitted in the sample is selectively reabsorbed, and the amount of the reabsorption depends on the population in the level on which it terminates. If we introduce the microwave power corresponding to one of the Zeeman sublevels, for instance w_1, and change the populations p_1 and p_2, then the intensities of the fluorescent lights which terminate on the levels $S_z=-\frac{3}{2}$ and $-\frac{1}{2}$ are changed generally in different ways, and therefore the change of the monitored intensity of the total fluorescent light results.

The detailed description of the apparatus is given in Sec. II and the results of the experiment and the discussions in Sec. III.

§ 2. Description of Apparatus

The block diagram of the system is shown in Fig. 3. The sample in the microwave cavity immersed in the helium bath is continuously irradiated by a

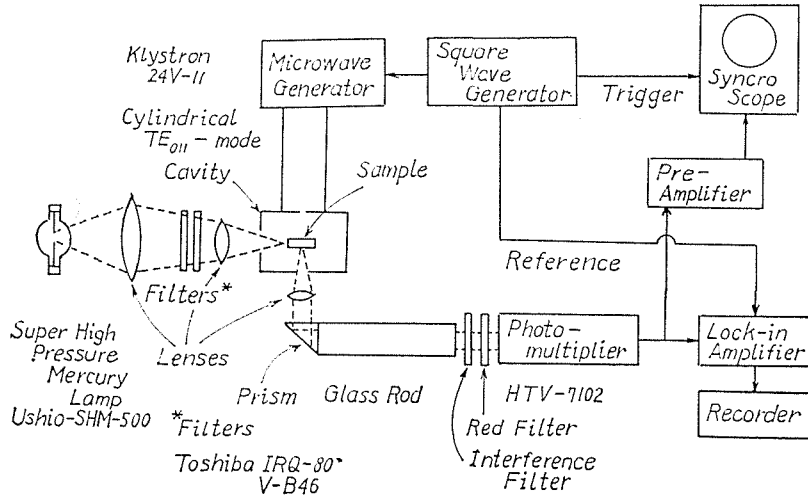

Fig. 3. Block diagram of the system used for optical detection of ESR of $\bar{E}\,(^2E)$ and $^4A_2$ in $Al_2O_3:Cr^{3+}$. (Magnet is not shown.)

pumping light. The change of the output fluorescent light is detected by a photomultiplier. In order to improve the S/N ratio the microwave power is chopped and the phase sensitive detection system is used. Magnetic field is swept slowly through resonance and the signal is displayed on a pen-recorder. A triggered oscilloscope is also used for the detection of the transient phenomena. Further details are as follows.

A) Sample

The samples we used were in the form of a cylinder. Their dimension was 2 mm in diameter and 4 mm in length, and the crystal c-axis was perpendicular to the axis of the cylinder. Concentrations of these samples were 0.1, 0.3, 0.5 and 0.7 percent Cr_2O_3 by weight. And they were supplied by Shinko-Sha.

B) Microwave Cavity and Power

The sample was mounted along the axis of a cylindrical $T\,E_{011}$ mode K-band microwave cavity (Fig. 4). As a microwave generator we used a klystron 24V-

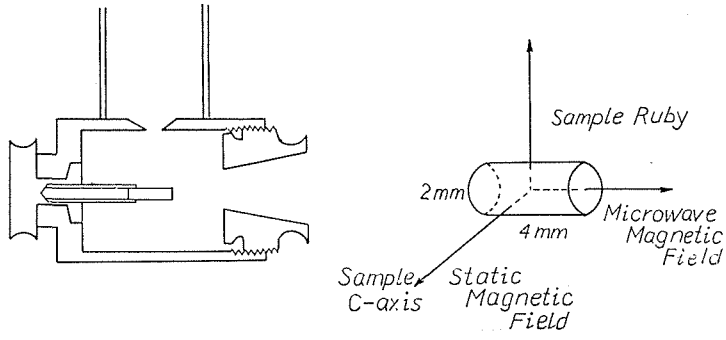

Fig. 4. Microwave cavity and sample.

11 whose maximum power was 500 mW which was sufficient to saturate the electron paramagnetic resonance of the excited state $\bar{E}$ (^2E) as well as those of the ground state $^4A_2$. The microwave power was amplitude modulated by a 80 cps square wave (100 V_{p-p}) fed on the reflector of the klystron. The klystron was immersed in an oil bath cooled by water.

C) Pumping Light

The sample was continuously irradiated by a super-high-pressure mercury lamp Ushio SHM-500 through a hole (4 mm in diameter) in the end wall of the microwave cavity. No special effort was made to stabilize the pumping light. A super-high-pressure mercury lamp is very suitable for our experiments because it has intense spectra at 1.83×10^4 and 2.47×10^4 cm^{-1} which just correspond to the absorption bands $^4T_1$ and $^4T_2$ (1.8×10^4 and 2.5×10^4 cm^{-1} above the $^4A_2$, respectively). Moreover it has no intense spectra in the red region which disturb the observation of the fluorescence.

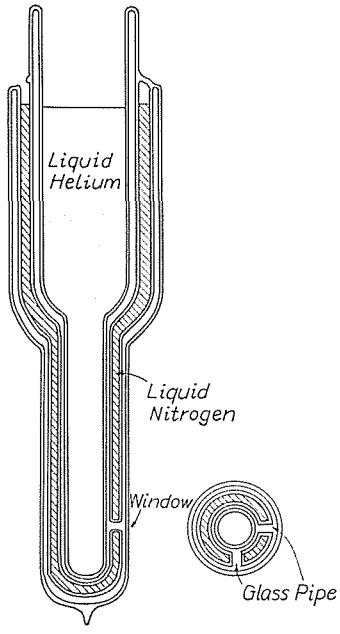

Fig. 5. Design of Special glass dewar.

To avoid undesirable heating of the sample and liquid helium and to remove the troublesome red light near the fluorescence, the pumping light was filtered by two pairs of glass filters Toshiba IRQ-80 and V-B 46, and concentrated aqueous solution of $CuSO_4$.

D) Helium Cryostat

To remove the bubbles of liquid nitrogen in an optical path, we modified an ordinary double glass dewar as follows. In the gap between the outer and the inner dewars we inserted the third vessel made of cupreous foil filled with liquid nitrogen whose bottom was just above the optical path.

Also we made a special dewar (Fig. 5). The outer and the inner dewars of the ordinary double glass dewar were connected in the vicinity of the bottom with glass pipes to pass the light keeping free from liquid nitrogen bubbles and at the upper part of the dewar they were connected to strengthen mechanically. This dewar was not so stout and not so handy but very useful for optical experiments.

E) Optical Detector

The fluorescent light is viewed along the static magnetic field through a vertical slot (2 mm×5 mm) in the side wall of the microwave cavity, gathered by a small lens (7 mm in diameter and 8 mm in focal distance) deflected through ninety degrees by a small prism outside of the cryostat, and guided by a glass rod (90 cm long and 10 mm in diameter) to the photomultiplier 7102 preceded by an interference filter of 150 Å half width centered at 6930 Å. Only 20 percent of the total incident fluorescent light is transmitted by the rod. The optimum length of the rod was determined by a compromise of the attenuation of the light and the decrease of the sensitivity of the photomultiplier caused by a stray magnetic field. The output signal was amplified by a con-

ventional narrow band amplifier and phase sensitively detected, and finally displayed on a penrecorder. When the signal was displayed directly on an oscilloscope to observe the transient phenomena, a preamplifier with L-C high pass and R-C low pass filters (Fig. 6) was used to eliminate the shot noise of the photomultiplier, which was beyond 10 percent of the photocurrent. We could not reduce the shot noise even though we cooled the photomultiplier to 77°K. Of course, we could greatly reduce the dark current by cooling.

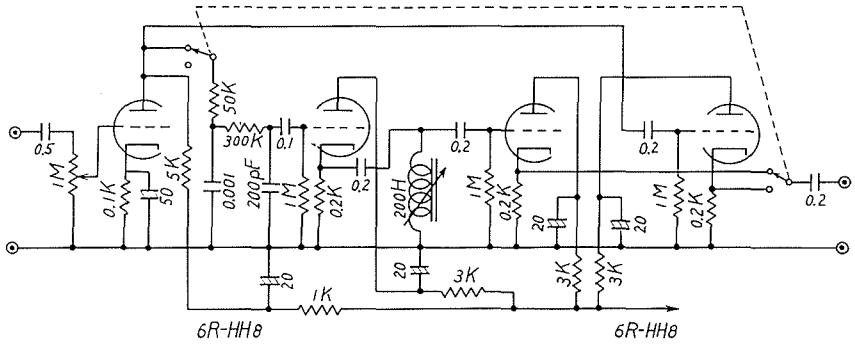

Fig. 6. Circuit diagrams of the preamplifier and filters.

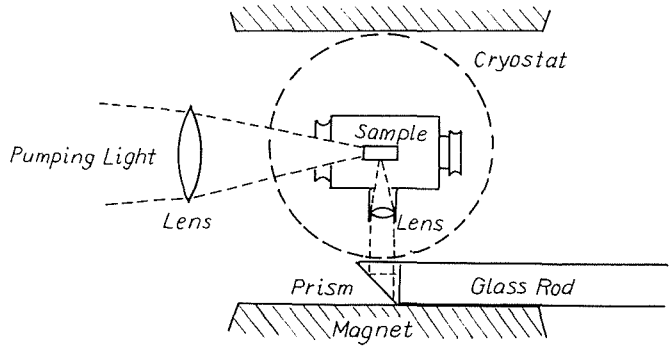

Fig. 7. Location of the helium cryostat and the glass rod in the magnet.

F) Magnet

The gap of the magnet we used is 65 mm. Into this space the helium cryostat (55 mm in diameter) and the prism (7 mm×7 mm×10 mm) were stuffed (Fig. 7). Wider gap is desirable for such an optical experiment observing light along the field direction.

§ 3. Experimental Results and Discussions

Fig. 8 shows a recorder trace of the optically detected paramagnetic resonance signal of the excited state $\bar{E}\,(^2E)$. Since in the present experiment the chopping of the microwave power is used instead of the usual magnetic field modulation, the height of the signal is proportional to the change in the light intensity (but not to the derivative). The change in the light intensity at the peak is roughly estimated to be three percent. The number of the Cr^{3+}

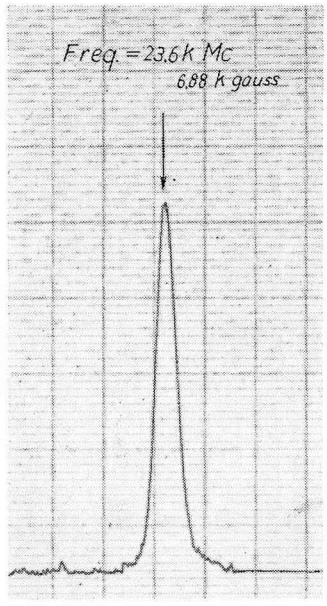

Fig. 8. Typical recorder trace of the signal corresponding to w_e at 1.8°K in 0.1 percent ruby.

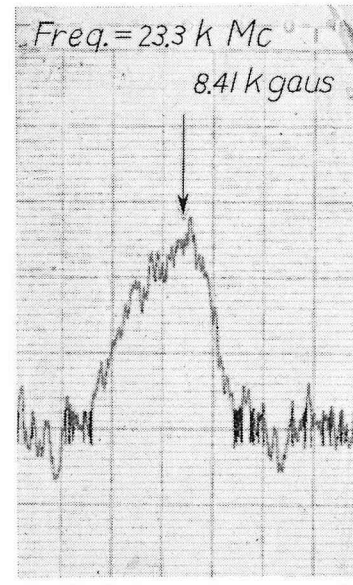

Fig. 9. Typical recorder trace of the signal corresponding to w_2 at 1.8°K in 0.1 percent ruby.

ions contributing to the signal is about 10^{11}.

Fig. 9 shows a signal corresponding to the resonance in the ground state $^4A_2$. The S/N ratio is generally poor for the ground state signals. The linewidths of the ground state signals are much broader (200~500 gauss) than those of the excited state ones. It is partly due to the fact that the saturation factor becomes very large even though the microwave power is the same as for the excited state signals. In fact, as we reduce the microwave power, the line becomes narrower but weaker, till it becomes too weak to detect when the microwave power is reduced to the unsaturated region.

The relative intensities of the optical signals corresponding to the transitions w_1, w_2, w_3 and w_e at 1.8°K and 4.2°K are tabulated in Table 1. The blanks in the table mean that we could not observe the corresponding signals.

Table 1. Relative signal intensities obtained in the experiment.

	Sample Concentration	w_1	w_2	w_3	w_e
1.8°K	0.1	+2	+1		+5
	0.3	−1	−2	−4	+5
	0.5	−1	−1	−1	
4.2°K	0.1				
	0.3	+1	+1	−1	
	0.5	−1	−1	−1	

The comparison of the intensities between different samples (different concentrations) was not made and the values in different rows in Table 1 are to be regarded as those for different normalizations.

The value of $g_{\parallel}$ of the excited state $\bar{E}$ (^2E) is observed to be 2.45 which is in good agreement with the value obtained by S. Geschwind et al. The linewidths of the excited state signals are 19 gauss (0.1 percent ruby) and 34 gauss (0.3 percent ruby). They are somewhat larger than those by S. Geschwind et al. perhaps because of the crystal strains.

The optical signals of the ground state change in sign as well as in magnitude, depending on the concentration and temperature. The plus and minus signs in Table 1 denote the increase and decrease of the fluorescent light intensity caused by the microwave saturation between Zeeman sublevels. This feature is not fully explained.

Though not shown in Table 1, the signal intensity due to the resonance w_e in 0.3 percent ruby is much weaker than that in 0.1 percent ruby. Moreover we could not detect such a signal for 0.5 percent ruby. These imply that the increase of the sample concentration reduces the signal intensity, and it

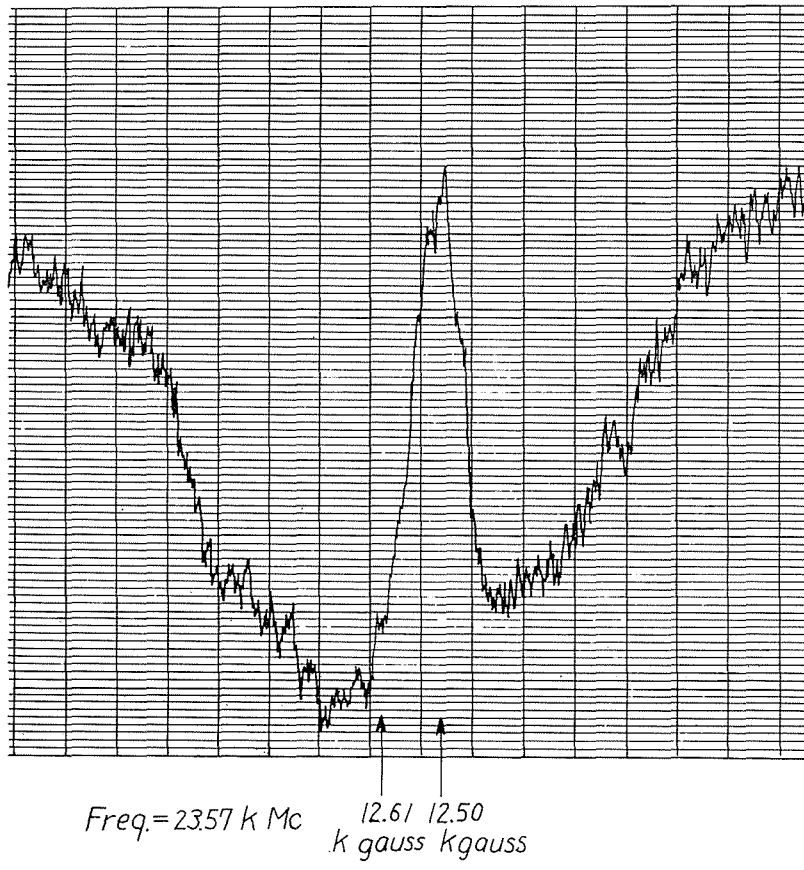

Fig. 10. Recorder trace of an extraordinary signal like 'hole burning' corresponding to w_3 at 1.8°K in 0.3 percent ruby.

may look opposed to what one might expect by intuition. But it is explainable as follows. For a fairly concentrated sample we must take into account the fact that Cr^{3+} ions in the center of the sample are irradiated less strongly than those near the surface by the pumping light. Then the effective strength of the pumping light is expected to fall exponentially with the increase of the sample concentration. Hence when the concentration becomes very large, the intensity of the fluorescent light will be too weak to detect the small change in it.

At 4.2°K we could not detect the resonances in the excited state. This is due to the fact that the microwave power is not sufficient to saturate the resonances, since at this temperature the relaxation time of the excited state is very short (0.1 m sec.)[6] and the value of $g_\perp$ is very small (<0.06)[1], and hence much more microwawe power is needed to saturate the resonances of the excited state than those of the ground state.

As the microwave power was increased, the ground state signals were broadened and somewhat distorted. We observed an extraordinary signal like 'hole burning' as shown in Fig. 10 which is for w_3 transition of 0.3 percent ruby. At present we do not observe such a line shape for other transitions or for other samples. This dip becomes deeper as the microwave power is increased. The position of the dip is not at the center of the line but is shifted to the lower field side (with a fixed microwave frequency) by about 100 gauss. We could not explain the feature based on the simple saturation theory. Further researches are now in progress.

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