Photoconductivity Measurements in Ruby and Sapphire*†

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Photoconductivity in ruby was discovered during an unsuccessful attempt to explore the Zeeman splitting of the fluorescent optical levels in ruby with a microwave spectrometer. Investigations showed that sapphire, the Al_2O_3 host crystal of ruby, is responsible for this photoconductivity. At 350°K and a light intensity of about 5 W/cm² (high pressure H_g arc spectrum between 3500 to 7000 Å) the order of magnitude of these photoconductivities for sapphire is 4.10^{-8} $(\Omega m)^{-1}$ for 9390-Mc/sec microwave absorption with 100-cps modulated illumination; 10^{-11} $(\Omega m)^{-1}$ for photoconductivity with 100-cps modulated illumination; and 4.10^{-13} $(\Omega m)^{-1}$ for photoconductivity with steady illumination. Temperature and light frequency dependence of the conductivities were investigated and a Hall-type experiment pointed to electrons as charge carriers. For sapphire these results can be explained by assuming that electrons from an occupied impurity level are excited by light to the 7-eV conduction band. According to the measurements, this impurity level would have to be 0.85 to 1.1 eV below the 7-eV conduction band.

INTRODUCTION

THE optical spectrum of ruby has been studied extensively.[1-4] We were mainly interested in the two very broad absorption bands between 3500 and 6000 Å and the fact that most of the Cr ions excited to these bands decay in radiationless transitions to two fluorescent levels at 6943 and 6929 Å. Both of these levels can be split in a magnetic field into two Zeeman levels.

These characteristics permit the use of a strong broad-band light source such as a high pressure mercury-arc lamp to excite the fluorescent levels. Our original intention was to explore the microwave structure of these excited states.

With a microwave magnetic-resonance spectrometer we were able to see the depletion of the ground-state levels due to light absorption. The largest signals measured had a signal-to-noise ratio of 300 to 1. Calculations indicated that just about a sufficient number of Cr ions should have been raised to the fluorescent energy levels to give a signal detectable with a microwave spectrometer. This was under the assumption that the values of the matrix elements and relaxation times, measured[5] around 2°K, can be extrapolated to 300°K by using the temperature dependence for similar values of the ground-state levels. A search for microwave lines was unsuccessful, but did reveal photoconductivity in ruby and sapphire.

The photoconductivity was measured first at the microwave frequency of 9390 Mc/sec, modulating the light at 100 cps for purposes of detection. In order to explore possible frequency dependence of the photoconductivity, additional experiments were performed to measure the photoconductivity at essentially zero frequency using steady illuminations, and finally 100-cps-modulated illumination.

The sign and mobility of the charge carriers involved were found with a Hall experiment.

EXPERIMENTAL ARRANGEMENT

This is shown by the block diagram in Fig. 1. The incident light was modulated and lock-in detection was employed in the microwave-spectrometer output. The presence of a signal indicated that microwave absorption was being produced by the light. This proved to be independent of magnetic field over a range from 0 to 7000 G. Careful investigation showed that the signal was really due to microwave absorption in the sample. After a suggestion of Dr. Herzfeld, the ruby sample was replaced by sapphire and the signal was now about twice as strong.

These facts and the following experiments lead to the conclusion that this loss is due to photoconductivity in the Al_2O_3 crystal and is unrelated to the Cr impurity in ruby.
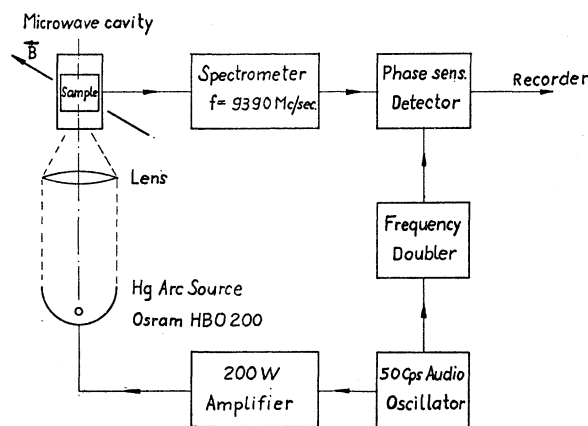

Fig. 1. Light source and microwave spectrometer with phase-sensitive detector.

[1] G. H. Dieke and L. A. Hall, J. Chem. Phys. **27**, 465 (1957); J. Opt. Soc. Am. **47**, 1092 (1957).

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

[3] S. Sugano and I. Tsujikawa, J. Phys. Soc. Japan **13**, 899 (1958).

[4] D. S. McClure, Solid State Phys. **9**, 488 (1959).

[5] S. Geschwind, R. J. Collins, and A. L. Schawlow, Phys. Rev. Letters **3**, 545 (1959).

PHOTOCONDUCTIVITY MEASUREMENTS

Microwave Measurements at 9390 Mc/sec with 100 cps Modulated Illumination

The photoconductivity in the microwave cavity results in a change of Q. We found that $\Delta Q_0/Q_0 \simeq 1.8 \times 10^{-5}$ for sapphire at 350°K and a light intensity of about 5 W/cm².

In terms of the conductivity σ, we may write (for a sample filling the whole cavity):

$$\frac{\Delta Q_0}{Q_0} = \frac{\Delta P}{P} = \frac{\frac{1}{2}\sigma \iiint_{\text{cavity}} E^2 d\tau}{\omega\epsilon/2Q_0 \iiint_{\text{cavity}} E^2 d\tau} = Q_0\sigma/\omega\epsilon.$$

By taking σ outside of the integral we assumed σ to be a scalar quantity independent of position in the cavity.

Experiments showed the losses to be proportional to the microwave power in the range

$$10 \leq P \leq 100 \text{ mW}.$$

Proportionality between photoconductivity and light intensity was observed in the range $0.2 \leq I \leq 5$ W/cm².

For sapphire the σ defined as above turns out to be $4.2 \times 10^{-8} (\Omega m)^{-1}$ at 350°K and a light intensity of about 5 W/cm².

The influence of the light frequency and temperature on the photoconductivity was also measured and is given by curves (Figs. 2 and 3).

Photoconductivity with Steady Illumination

The dc conductivity was measured by using the same ruby and sapphire samples connected to an electroscope in the form of an x-ray dosimeter, 0 to 0.2 R, charged to 130 V. A semitransparent silver film served as the light entrance surface.

Measuring the time constant of the discharging electroscope with and without light on the sample led to the following values of dc conductivities for sapphire at 350°K:

$$\sigma \simeq 8 \times 10^{-15} (\Omega m)^{-1} \text{ no light}$$

$$\sigma \simeq 4 \times 10^{-13} (\Omega m)^{-1} \text{ with light (5 W/cm}^2).$$

Photoconductivity with 100 cps Modulated Illumination

Figure 4 shows the experimental arrangement. The time constant and experimental accuracy are such that we can without much error neglect the time constant and replace the actual circuit by a simpler one given by Fig. 5. The peak-to-peak value of

$$e_{p-p} = E(r/R+r) \simeq E(r/R) \quad \text{for} \quad R \gg r,$$
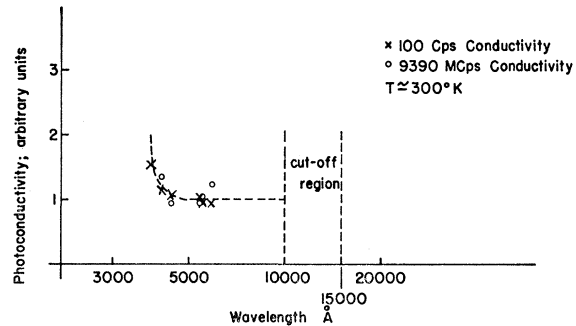
or

$$R \simeq (E/e)r.$$

FIG. 2. Photoconductivity spectrum of sapphire.

A σ was calculated by using the dimensions of the sample and gave for sapphire at 350°K and light intensity of about 5 W/cm² $\sigma \simeq 10^{-11} (\Omega m)^{-1}$.

Figure 3 shows that the temperature dependence of the photoconductivity is about the same one as seen for the microwave case.

Figure 6 shows the nonlinear relationship between light intensity and the photoconductivity measured with 100-cps modulated light. Since this saturation effect was not present in the microwave measurements, one has to suspect the carrier injection process between the contacts of fired-in silver paint and the sapphire.

HALL EFFECT

Finally a Hall experiment was performed to measure the sign and mobility of the charge carriers involved in the photoconductivity process.
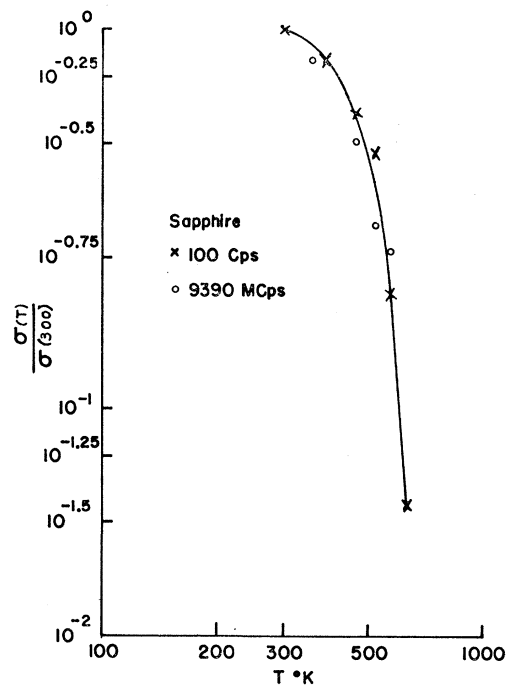

FIG. 3. Photoconductivity versus temperature.
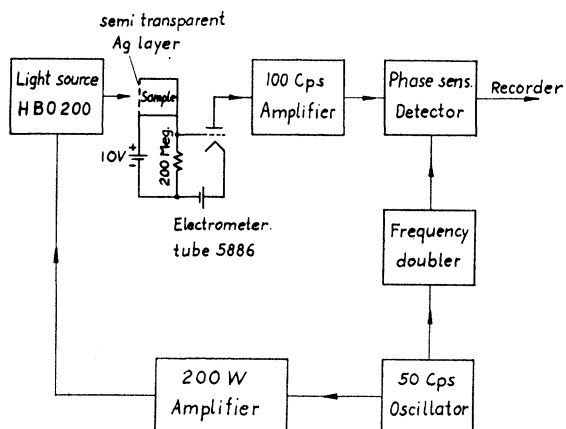Light intensity $\simeq 5$ W cm⁻².

FIG. 4. Detection scheme to measure photoconductivity changes due to modulated light.

The same sapphire sample was used in a differential amplifier circuit with two Victoreen 5800 electrometer tetrodes. Each tube was separately shielded with Mumetal and the whole circuit was enclosed in a steel container 70 cm away from the magnet. A brass pipe contained the connecting wires and light filters between sample and input grids. The short time stability was such that a change of 5 μV in the grid circuit taking place in a few seconds could be seen.

For a magnetic flux density $B \simeq 7000$ G we measured the voltage ratio

$$V_H/V = 4.8 \times 10^{-6},$$

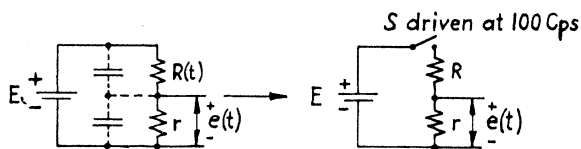assuming that a linear potential distribution leads to

FIG. 5. Simplified circuit used to estimate the 100-cps photoconductivity.

$E_H/E = 3.7 \times 10^{-6}$ with the correct sign for moving electrons.

The result was the same with the light on or off. Equilibrium of the forces on the moving electrons

$$e\mathbf{v} \times \mathbf{B} = -e\mathbf{E}_H$$

and $\sigma = ne\mu$ lead to an estimate of the mobility μ:

$$\mu \simeq (1/B)(E_H/E) \simeq 5.2 \times 10^{-6} \text{ m}^2/\text{V sec at } 300°\text{K}.$$

EXPERIMENTAL ERRORS

The experimental accuracy was such that most of the conductivity results should be accurate to within about a factor 2, except for the measurements of the quite low dc conductivities.

Unverified assumptions may be another source of errors. One such source is the potential distribution in the sample between two electrical contacts. The Hall experiment gave a check for the potential in the middle of the sample and this agreed with the assumption of a linear potential distribution but is no proof that the contacts were perfect. We can only say that contacts made with fired-in silver paint always gave reproducible results.

Photoconductivity measurements as a function of the light frequency had to be made with broad-band light filters and can therefore show no details.
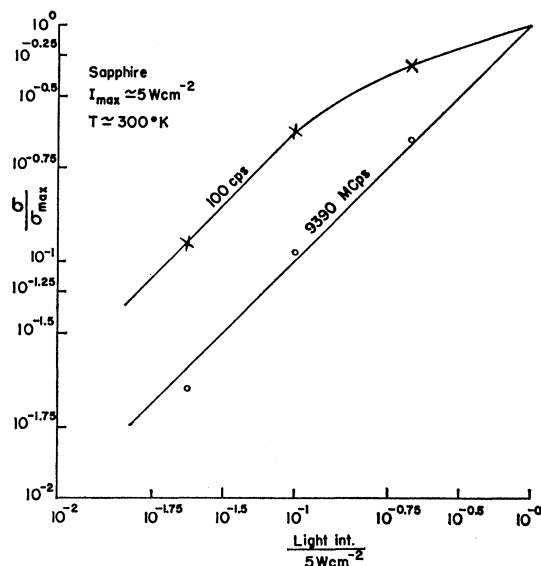

FIG. 6. Photoconductivity versus light intensity.

The pink ruby and sapphire samples used were cut from standard 60° boules made by the Linde Company. A 90° pink ruby from Trident Company gave similar 100 cps results as the ruby sample from Linde Company. Otherwise it was not verified if samples from other batches or sources would furnish equal results.

CONCLUSIONS

There is much work to be done to give a complete picture of the processes responsible for the measured effects. At this point one can only give the simplest
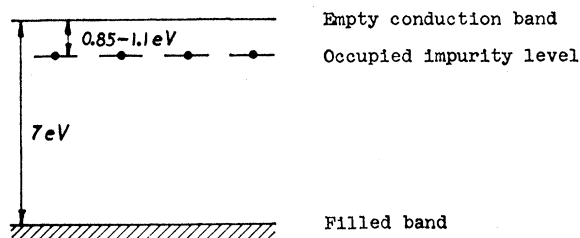

FIG. 7. Energy level diagram.

model that does not contradict the results. For sapphire this could be the 3-level system given in Fig. 7.

At room temperature, both the ordinary as well as the photoconductivity result from electrons lifted from the occupied impurity level to the empty conduction band. This would explain why the light had no influence on the mobility measured in the Hall experiment.

Low mobilities are expected in ionic crystals,[6] but the measured 0.05 cm^2 V sec is quite low.

The large gap distance in the model is given in the literature[7] and the 0.85 to 1.1 eV gap comes from photoconductivity measurements as a function of light frequency. To have enough intensity we had to use broad-band infrared filters resulting of course in loss of structure details if present.

To check these gap values we plotted $\ln\sigma$ versus T^{-1}. For this we used ordinary high-temperature conductivity values of sapphire published by the Linde Company completed with the room-temperature value of our sample. The high-temperature slope of the curve leads to a gap of 7 eV; the low-temperature slope to a gap of 0.6 to 1.2 eV in fairly good agreement with the value given before. The spread depends on the kind of model assumed.[8]

[6] R. H. Bube, *Photoconductivity of Solids* (John Wiley & Sons, Inc., New York, 1960), p. 256.

[7] N. B. Hannay, *Semiconductors* (Reinhold Publishing Corporation, New York, 1959), p. 54.

[8] A. J. Dekker, *Solid State Physics* (Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1959), p. 314.

Spin-Spin Relaxation and Spin Temperatures

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(Received 2 August 1963)

The equilibrium and nonequilibrium properties of an assembly of interacting spins are analyzed in the case of paramagnetism (nuclear). The evolution towards equilibrium is described by a generalized Pauli equation. This equation contains two relaxation times: a first one characterizing the evolution of the dipole-dipole system to equilibrium and a second one describing the energy exchange between the dipole-dipole and the Zeeman system. The real temperature of the system is the dipole-dipole one whereas the state of the Zeeman system is given by a "chemical potential" fixing the mean magnetic moment. It is shown that the Zeeman dipole-dipole relaxation may also be considered as a kind of Brownian motion problem of a collective Zeeman coordinate in the "dipole-dipole heat bath."

INTRODUCTION

IN contrast with the rich development of the theory of irreversible processes in many body systems[1-3] (gases, plasmas, solids) there is a relative paucity of fundamental work in the field of spin-spin relaxation of paramagnetic substances. The difficulties in this domain follow from the peculiar structure of the Hamiltonian. The results of the general theory cannot directly be applied to this particular problem because one does not know the properties of the unperturbed Hamiltonian. One has to go formally ahead, working in an unknown representation. If the final expression can be written as traces, they may then be evaluated following Van Vleck. Let us also note that in many situations, series expansions may be used in the powers of the ratios of local

magnetic field over external field H_l/H_0 and $\hbar\omega/kT$, a level splitting over the thermal energy. These expansions greatly simplify the problems. A general treatment has been given by Caspers,[4] starting from the expressions given by Kubo and Tomita to calculate the spin-spin relaxation time. An important progress in understanding the spin-spin relaxation mechanism has recently been made with the introduction of the notion of Zeeman and dipole-dipole temperatures by Anderson, Hartmann,[5] and Provotoroff.[6] As shown by Jeener[7] several problems are then easily handled using thermodynamical methods. However, a justification of these notions from first principle has not yet been given. In

[1] I. Prigogine, *Nonequilibrium Statistical Mechanics* (Interscience Publishers, Inc., New York, 1962).

[2] R. Kubo, J. Phys. Soc. Japan 12, 570 (1957).

[3] L. Van Hove, Physica 21, 512 (1955); 23, 441 (1957).

[4] W. J. Caspers, Physica 26, 778 (1960).

[5] A. G. Anderson and S. R. Hartmann, *Magnetic and Electric Resonance and Relaxation*, edited by J. Smidt (North-Holland Publishing Company, Amsterdam, 1963).

[6] B. N. Provotoroff, Zh. Eksperim. i Teor. Fiz. 42, 882 (1962) [translation: Soviet Phys.—JETP 15, 611 (1962)].

[7] J. Jeener, following paper, Phys. Rev. 133, A478 (1964).