PARAMAGNETIC RESONANCE DETECTION OF TRAPPING IN A PHOTOCONDUCTOR

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The trapping of free carriers is necessary to explain many luminescent and photoconductive properties of ZnS-type phosphors. Information concerning the nature of the traps may be inferred from glow curve measurements, from the buildup and decay of photocurrents, from the voltage-current characteristic of the photoconductivity, and from the long-wavelength cutoff of absorptions in the material.

Where the trap is paramagnetic either before and/or after the trapping process, direct observation of the trapping may be made using paramagnetic resonance techniques.[1,2] Such a process has been observed at room temperature in a ZnS sample to which 0.02 molar percent Gd had been added during preparation. The apparatus used has been previously described[2] except that an improved cavity design suggested by Smith was used. The rectangular cavity operating in a TE_{102} mode had at one end a series of copper fins parallel to the narrow face of the waveguide. This enabled light to enter the cavity and irradiate the sample but constituted a set of waveguides beyond cutoff for the microwaves. Its Q was approximately twice that of a cavity using a screen at one end.

It was observed that in the dark there was a small Gd^{3+} electron paramagnetic resonance (EPR) signal. On irradiating the sample with light near 385 mμ, the Gd^{3+} signal increased twelve times in magnitude. Figure 1 gives the wavelength dependence of the Gd^{3+} resonance. If the irradiating light is removed, the Gd^{3+} resonance decreases slowly in magnitude to half value in approximately an hour and to tenth value in a few days. The decrease can be speeded up, that is, the Gd^{3+} resonance quenched by shining on the sample light of various wavelengths. The quenching of the Gd^{3+} resonance as a function of irradiating wavelength is plotted in Fig. 2. There is a broad peak centered around 650 mμ and with a long wavelength cutoff near 900 mμ. Quenching of the resonance was also observed for wavelengths between 280 mμ and 335 mμ.

The luminescent properties of the sample were found to have a correlation with the observed paramagnetic properties. Irradiation with 385 mμ caused it to fluoresce in the green. Removal of the 385 mμ resulted in a green phosphorescence. This phosphorescence could be quenched by irradiating with light between 475 and 900 mμ. This luminescent behavior is similar to that observed by Meijer[3] in ZnS:Cu and the model he proposed for that case can conveniently be applied to ZnS:Gd.

It is proposed that gadolinium is normally present in the lattice as Gd^{2+}. This is reasonable considering the divalent nature of the cation. Irradiation with 385-mμ light causes an electron to be released from the Gd^{2+} site to the conduction band. The electron is eventually trapped at some unknown sites near the conduction band.

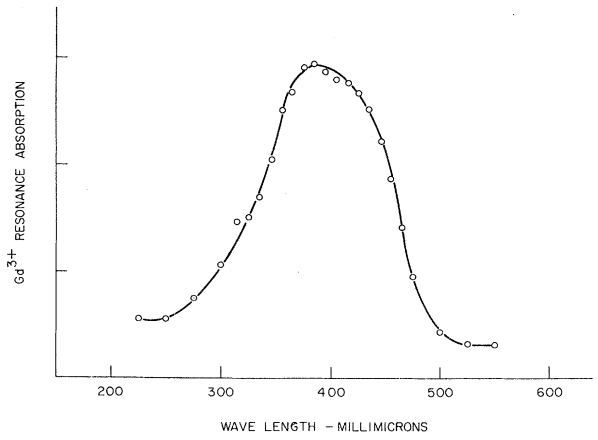

FIG. 1. Dependence of the magnitude of the Gd^{3+} resonance on irradiating wavelength.

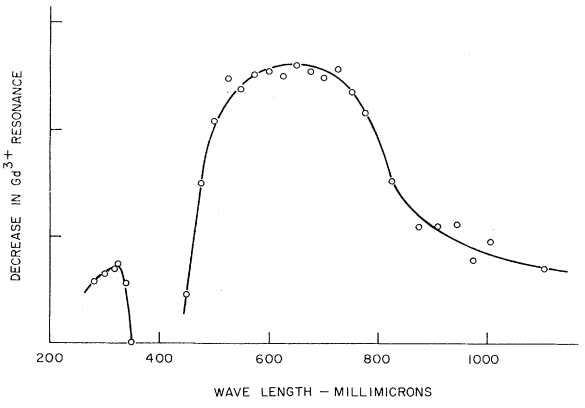

FIG. 2. The quenching of the Gd^{3+} resonance as a function of irradiating wavelength.

This process has the effect of converting Gd^{2+} to Gd^{3+}. The latter has an $^8S_{7/2}$ ground state and its EPR spectrum is easily observed at room temperature. The sites at which the electrons are trapped are sufficiently deep that thermal release of electrons is slow. It is these thermally released electrons recombining at Gd^{3+} sites which results in the green phosphorescence and accounts for the slow decrease in the magnitude of the Gd^{3+} EPR spectrum. The quenching of the Gd^{3+} resonance by radiation between 475 mμ and 900 mμ is caused by excitation of an electron from the valence band to the Gd^{3+} site, reconverting it to Gd^{2+}. This leaves a hole in the valence band which eventually recombines nonradiatively with the electrons in the traps. The quenching of the Gd^{3+} resonance by wavelengths between 280 mμ and 335 mμ is also easily understood. The band gap of ZnS at room temperature is 335 mμ.[4] Shining on light between 280 mμ and 335 mμ causes the formation of electron-hole pairs. Some of the electrons are captured at Gd^{3+} sites, accounting for the quenching of the Gd^{3+} resonance at these wavelengths. The holes recombine with the trapped electrons. Some of the quenching of the Gd^{3+} resonance, particularly at higher wavelengths, may be due to the excitation of electrons from the traps to the conduction band from where they recombine with Gd^{3+} ions. This is, however, believed to be small as no enhancement of the green emission is observed during quenching.

As indicated in the above explanation, associated with the ionization of Gd^{2+} by 385-mμ light, there should be a photocurrent due to the presence of electrons in the conduction band. Photoconductivity manifests itself as a loss in the electric susceptibility. The same apparatus used to measure the EPR spectrum was used to measure the photoconductivity. The sample was moved from maximum magnetic field at the center of the TE_{102} cavity to the position of maximum electric field (either the one-quarter or three-quarter position). The presence of photoconductivity disturbed the balance of the microwave bridge in which the cavity sat. The light producing the photoconductivity was chopped so that ac detection methods could be used. This measurement does not, of course, require the use of a magnetic field. The steady state photoconductivity as a function of wavelength of irradiating light is given in Fig. 3. It is noticed that there is a peak corresponding to the excitation peak of the Gd^{3+} resonance in Fig. 1. In addition, a conductivity due to the presence of holes in the valence band should manifest itself during the quenching of the Gd^{3+} resonance. To observe this, Gd^{3+} sites were created by irradiating the sample with 385-mμ light. Subsequent irradiation with the quenching radiation resulted in a photoconductivity which decreased as the number of Gd^{3+} sites decreased, in agreement with the proposed model.

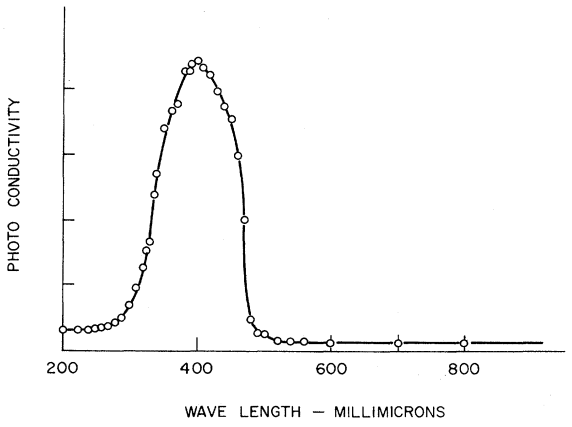

FIG. 3. Photoconductivity of ZnS:Gd as a function of irradiating wavelength.

These measurements represent the first direct observation of trapping in a photoconductor at room temperature. In addition, the technique of observing the trapping by paramagnetic resonance and using the same apparatus to measure the photoconductivity should prove generally useful. The technique has the added merit that the complications of electroding the sample are avoided.

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[4]R. H. Bube, Proc. Inst. Radio Engrs. 43, 1836 (1955).