PHOTOSENSITIVE SPIN RESONANCE IN CdS*

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The phenomena of trapping of free carriers has long played an important role in the interpretation of various luminescent and photoconductive properties of solids. However, it has not always been possible to obtain definitive information about the nature of the trapping center. The purpose of this paper is to report the direct observation of a trapping center and its identification using the techniques of paramagnetic resonance. The experiments described here were carried out on CdS crystals containing traces of iron impurities.

The sample was placed in a cavity[1] of an X-band EPR (electron paramagnetic resonance) spectrometer such that the sample could be illuminated at 4.2°K through a hole in the cavity while EPR measurements were being made. When the sample was first placed in the cavity at 4.2°K, little or no signal was observed. After illumination with visible light, a large spin-resonance signal was observed as shown in Fig. 1. By irradiating with infrared light the signal could be removed. It was found that light in the region around 5500 A was most effective in producing the spin resonance, while 2-micron radiation was most effective in removing the signal. In all cases the light level was kept quite low to avoid any heating effects. At 77°K and 300°K no spin-resonance effects were observed.

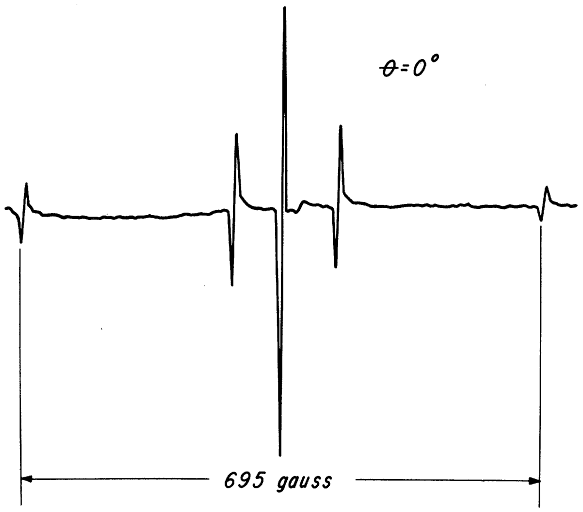

FIG. 1. Spectra obtained at 4.2°K after crystal was irradiated with visible light. The center line is at a position equivalent to $g=2.01$.

The structure and the angular dependence of the observed spin-resonance signal[2] indicate that the spin of the photosensitive center is $\frac{5}{2}$. When the c axis is parallel to the magnetic field, a simple 5-line spectrum with the weak satellites lying outside the strong ones is obtained. At 90°, the weak satellites lie inside the strong ones. Such a spectrum can be explained by a combination of a cubic and axial crystalline electric fields. The analysis of the spectra for 0° and 90° indicate that $D/a_0 \sim -0.5$, with $|D| = 30\times10^{-4}$ cm^{-1}, $g=2.01$. Here $3a_0$ is the ground-state splitting in zero field, with the doublet lying lowest. For intermediate angles, the satellites split into doublets, which is expected for a paramagnetic center of spin $\frac{5}{2}$ occupying inequivalent sites. It is interesting to note that the central $-\frac{1}{2}\leftrightarrow\frac{1}{2}$ line is also split into a doublet; calculations indicate that this is due to a second-order effect. Spectroscopic analysis indicated that iron concentration might be as high as 0.01%. Thus the photosensitive center is assigned tentatively to Fe^{3+}.

We interpret these effects as follows: Fe^{2+} is present in the CdS as an impurity. Its spin resonance is not observed, possibly being too broad. When free electrons and holes are produced by irradiation, the Fe^{2+} traps a hole and becomes Fe^{3+} which is readily observed since it is an S-state ion. The electrons must be trapped elsewhere. The action of the 2-micron infrared radiation is then to restore the electron back to the Fe^{3+} converting it to Fe^{2+}. The 2-micron light may release an electron from some other trap or may move it from the valence band into the Fe^{3+}. This point is not yet settled. In the latter case one could obtain directly the energy separation between the Fe^{3+} level and the valence band.

These measurements thus demonstrate directly the phenomena of trapping in photoconductors as well as the untrapping by infrared radiation. This technique should thus be extremely useful in testing various models of phosphors and photoconductors.

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ELECTRONIC SPECTRA OF EXCHANGE-COUPLED ION PAIRS IN CRYSTALS

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Trivalent chromium ions (Cr^{3+}) in many insulating crystal lattices fluoresce with the emission of sharp lines near 7000 angstroms. The strongest emission lines in this region are well understood from crystal field theory as transitions from a ^2E excited state to the $^4A_2$ ground state.[1] In MgO there is one ^2E line since in a strictly cubic field the degeneracy of the upper level is not split. In ruby (Al_2O_3), however, there are two ^2E lines due to the lifting of the upper level degeneracy by the trigonal component of the crystal field. The ground state is also split in ruby, but by a much smaller amount which is not usually resolved in the optical spectrum.

It has been known for many years that within a few hundred cm^{-1} of the ^2E lines there are other sharp lines and bands which are not accounted for by the crystal field theory.[2,3] It has been suggested[2,4] that these "satellites" are caused by transitions to excited lattice vibrational states, followed by the emission of a phonon, and this is probably correct for the broader band satellites. This suggestion does not fit the observations for the sharp lines, since at 4.2°K the satellite lines have different spacing in emission from those in absorption and the crossover point between absorption and emission does not coincide with the ^2E lines. One would expect the same satellite spacings in both emission and absorption, since the vibrational frequencies are a property of the host lattice, which is not changed by the electronic transition within the impurity atom. Vibrations of the O-Cr-O complex, which would change with excitation of the chromium ion, would not have frequencies less than 80 cm^{-1} from the crossover point.

We wish to propose that the satellite lines are not due to individual chromium ions, but to chromium ions paired with a neighboring chromium ion or with some other crystal defect. If the concentration of chromium is, say, 1 atomic percent, there is a probability varying from 3% to 12% depending on the local symmetry that a given ion will find another Cr^{3+} ion among its nearest neighbors. If there is any clustering of chromium ions, this probability will be still greater. Between such neighboring ions there will be strong exchange forces. Indeed, the exchange forces lead to antiferromagnetism in Cr_2O_3.

If the satellite lines are due to randomly distributed nearest neighbor pairs, at low concentrations of Cr^{3+} their intensity relative to the main lines should be proportional to the concentration. As shown in Fig. 1, this behavior has been observed in the fluorescence spectrum of ruby. At very low concentrations the satellites are vanish-

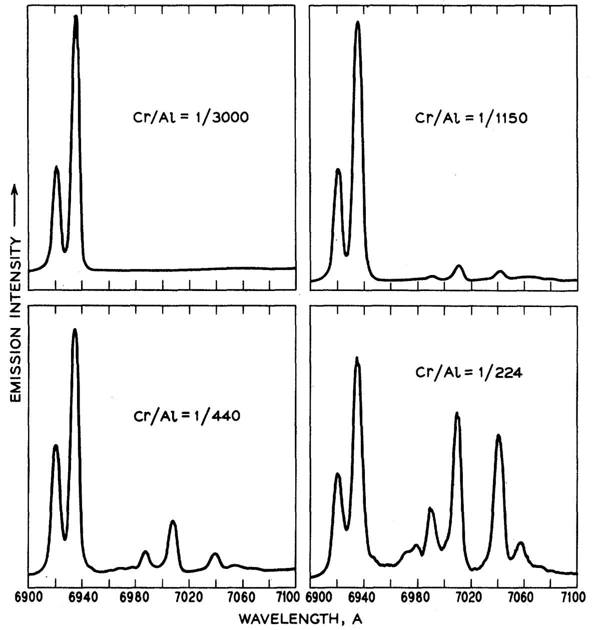

FIG. 1. Fluorescence spectrum of ruby at 77°K with different chromium concentrations (photoelectric recording at low resolution).