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ELECTRON PARAMAGNETIC RESONANCE OF PHOTOEXCITED DONOR-ACCEPTOR PAIRS IN ZINC-SULFIDE CRYSTALS*

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(Received 25 June 1965)

We wish to report the observation of photoexcited electron paramagnetic resonance (EPR) for hexagonal ZnS:Cu, Ga single crystals which we attribute to paramagnetic states of donor-acceptor pairs. The photoexcited EPR signals are observed at 77 and 4.2°K with crystals and powders containing 10^{-3} to 10^{-5} Cu, Ga per ZnS (equivalent concentrations of Cu and Ga). At the same temperatures we also observed the orange-red luminescent emission attributed to electron-hole recombination on approximately the fifth nearest neighbor Cu-Ga pairs.[1]

A Varian V-4500 X-band EPR spectrometer with 100-kc/sec modulation and with a cavity operating in the TE_{012} mode was used. The cavity has a slotted window for optical irradiation. Without irradiation no signal was observed. With irradiation by blue light several EPR lines were observed, their number and intensities depending upon Cu, Ga concentration. For crystals containing 10^{-3} Cu, Ga four strong lines appear at $g = 1.056$, 1.142, 1.635, and 3.916. The two high-field lines are approximately one gauss in width; the two low-field lines are somewhat wider. All four are very nearly isotropic in spectral positions and intensities. With 10^{-5} Cu, Ga the intensities of the EPR signals are reduced by a factor of approximately 1000 and additional lines are resolved in the regions of the lowest field and two high-field lines. The g values in the neighborhood of high-field lines are 1.149, 1.145, 1.142, and 1.062, 1.059, 1.156. The relative intensities of the four lines are approximately the same in over 30 crystals measured. When the irradiation is extinguished the four EPR signals of the more heavily doped crystals all decay with the same rate, and the initial decay constant is of the order of 0.5 sec and is followed by a slower decay with a time constant of several seconds.

The intensity of the EPR signal as a function of wavelength of optical excitation, which we denote EPR excitation spectrum, is shown in Fig. 1 for the more heavily doped crystals. The maxima in the EPR excitation spectra are at the same wavelength for all four g values. For crystals with 10^{-5} Cu, Ga the maximum shifts to 5000 Å, compared to maximum EPR signal at 4500 Å for crystals with 10^{-3} Cu, Ga. There is some evidence for differences in the EPR excitation spectra of the different resolved lines of the more lightly doped crystals. The photoconductivity spectrum was measured, and no photoconductivity was found in the wavelenght range 4500 to 5000 Å, the threshold being at 4200 Å.

The EPR excitation spectrum, the absence of photoconductivity, the occurrence of pair

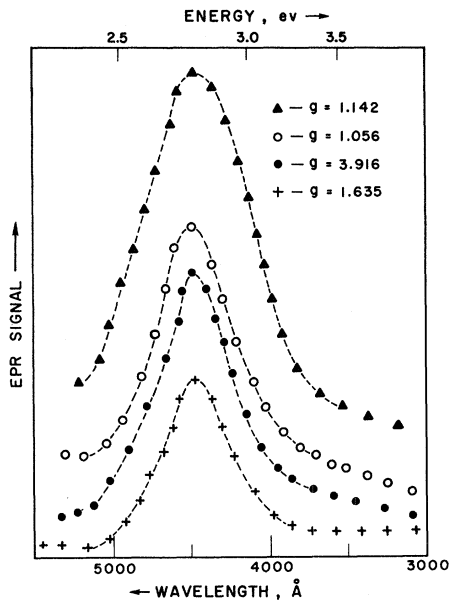

FIG. 1. Intensity of EPR signal versus wavelength of optical excitation.

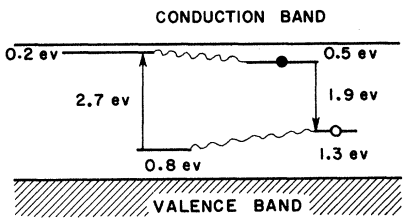

FIG. 2. Band-theory model for states and transitions involved in photoexcitation of paramagnetic donor-acceptor pairs.

luminescence in crystals which show these EPR signals, and the dependence of intensities of the signals on Cu, Ga concentration are all in accordance with the EPR signals originating from paramagnetic states of Cu-Ga pairs. The band model for the states and optical transitions is shown in Fig. 2. Following optical creation of an electron and positive hole on the donor-acceptor pair, lattice polarization occurs so that the electron and hole states shift away from their band edges. In addition, the wave functions for electron and hole become more localized, therefore reducing the overlap integral of these wave functions. The transition matrices for optical excitation and de-excitation of pairs with donor and acceptor at equivalent sites are linearly dependent on overlap of electron and hole wave function in the effective mass approximation,[2] and this is valid approximately for pairs with deep donor and acceptor states. The change in transition matrix with state of occupancy allows direct optical excitation to the paramagnetic state of the pair with appreciable oscillator strength and also appreciable lifetime of the paramagnetic state. For example, for fifth nearest neighbor pairs with interimpurity distance of 8.8 Å and for the states shown on Fig. 2 we estimate the overlap integral as 3.6×10^{-2} for excitation and 0.5×10^{-2} for emission. In other words, the lifetime of the paramagnetic state increases by a factor of 50 because of lattice polarization following excitation. More distant pairs will have greater changes in transition matrices and lifetimes. The absence of EPR signals with band-to-band excitation or with acceptor–conduction-band excitation indicates that capture of carriers by the paramagnetic states of the pairs is not very probable. The superlinear dependence of EPR signals on Cu, Ga concentration is consistent with pairs being involved, rather than isolated Cu or Ga, since the fraction of Cu, Ga in pairs increases with concentration. The pronounced dependence on excitation transition energy shown in Fig. 2 is in accordance with a fairly specific part of the pair spectrum being responsible for the EPR signals. The requirements for pair luminescence and for pair EPR signals are different so that somewhat more distant pairs and, of course, triplet rather than singlet states are probably responsible for the EPR signals. It is further suggested that the resolved lines observed with the more lightly doped samples are due to pairs characterized by specific interimpurity distances.

The g values of the photoexcited EPR signals do not seem understandable on the basis of spin-only atomic orbitals. We suggest that states with finite orbital angular momentum, as well as spin, are involved, and that the electron and positive hole on the pair respond to the magnetic field in part in accordance with their effective masses. Theoretical studies are in progress to clarify the magnetic states of the pairs.

We are pleased to acknowledge the preparation of crystals by Dr. I. Dev and R. Lauer and the photoconductivity measurements by Dr. L. Van Ruyven.

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*Work supported in part by the U. S. Army Research Office (Durham).

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