

erhalten, wobei die In-Konzentration ca. 1000 ppm betrug. Die außerordentlich starke Konzentrationsabnahme wird auf die Bildung von Cu-In-Komplexen zurückgeführt. Offenbar handelt es sich dabei um die Bildung der aus Lumineszenzmessungen bekannten Donator-Akzeptor-Zentren. Diese Ergebnisse sind ganz ähnlich denen, die AVEN und HALSTED¹ für die Diffusion von Cu in ZnSe-Al gefunden haben.

Abb. 6. Konzentrationsverlauf für die Diffusion von Cu in ZnS (a) und ZnS: In (b).

Light Induced Modulation of Absorption (LIMA) of CdS Crystals*

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Dedicated to Professor H. GOBRECHT on the occasion of his 60th birthday

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With chopped high intensity optical excitation a modulation of the optical absorption in a wide wavelength-range in CdS was observed. This light induced modulation of absorption is attributed to a redistribution of carriers over levels in the band gap following the chopping frequency. With this method the energy spectrum of certain traps and recombination centers can be determined and their frequency factor and capture cross section obtained. This method permits also the analysis of fast recombination centers.

Intense optical excitation can change the optical transmission of crystals in certain wavelength ranges and can be used for defectcenter analysis. Optical bleaching at one wavelength and associated increase in absorption in a different wavelength range were tools employed early in the study of the defect structure and, e.g., gave most convincing indication about the connection between F and F' centers in alkali halides. However, this method is restricted to a few centers for which the reaction kinetics allows accumulation of redistributed charges to an extent that they can easily be observed.

The increase of excitation density by using lasers has extended the sensitivity range of investigation and thereby allowed observation of states with considerably shorter lifetime (e.g., F* in KI^{1,2}). With

this method an increase of absorption in CdS near 850 nm has been reported recently³. The use of modulated optical excitation and a phase sensitive amplification of the change in optical absorption has further increased the sensitivity⁴.

With this highly sensitive method the possibility exists, in principle, of investigating changes of the optical absorption, caused by redistribution of electrons over a wide energy range in the band gap due to optical excitation into valence- and conductionbands. The excitation can be accomplished with modulated high intensity extrinsic⁵ light close to the band edge (chopped laser beam) and the light induced modulation of absorption (LIMA) can be observed with a low intensity⁶ detection light beam.

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¹ K. PARK, Phys. Rev. **140**, A 1735 [1965].

² D. FRÖHLICH and H. MAHRA, Phys. Rev. **141**, 692 [1966].

³ K. MAEDE and A. KASAMI, Proc. Intern. Conf. on II-VI Semiconducting Compounds, Providence, R. I. 1967, p. 1323.

⁴ G. CHEAROTTE and V. GRASSANO, Nuovo Cim. **46**, 78 [1966].

⁵ In order to prevent excessive temperature modulation due to laser heating and to provide volume-homogeneous excitation.

⁶ To avoid two quantum absorption as e.g. described by J. J. HOPFIELD, J. M. WORLODE, and K. PARK, Phys. Rev. Letters **2**, 414 [1963].



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In this paper results obtained for CdS-single crystal platelets are reported and discussed. These results confirm and extend some preliminary data obtained earlier⁷.

1. Experimental Arrangement

The experimental set-up used is shown in Fig. 1. For excitation a Krypton-ion cw-laser (Carson Co.) was used at a wavelength $\lambda = 520.8$ nm and a power density of ~ 1 W/cm² at the position of the CdS crystal. This light was chopped with a selected chopping frequency between

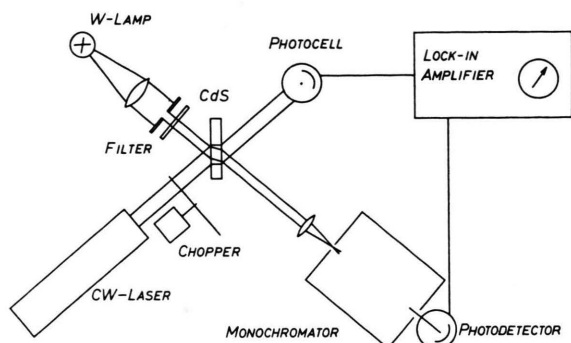


Fig. 1. Experimental Set-up.

15 and 200 Hz. For measurement of the change in absorption, a dc-operated Unitron source was used with a color-temperature of $\sim 2800^\circ\text{K}$ at about 1000 ft c (at the CdS crystal). For detection of the LIMA, a Bausch & Lomb grating monochromator in conjunction with a photomultiplier or a PbS photocell was used. The signal was amplified with a PAR-lock-in-amplifier, phase controlled by the output from a vacuum photocell in the path of the chopped laser light. The sensitivity of this set-up was of the order of 10^{-7} for changes in the absorption ratio in the extrinsic range $520 < \lambda < 750$ nm, and about one order of magnitude less in the infrared range.

The CdS single crystal platelet ($15 \times 12 \times 1$ mm³) was vapor grown, doped with approximately 50 ppm Ag and Al, and the larger two surfaces were highly polished. Other non-homologous elements were not detectable in the crystal by spectro-analysis (limit $\lesssim 1$ ppm). Several other CdS-crystals of less defined doping and less optical quality were used for some preliminary investigations.

2. Experimental Results

Several CdS crystals have been studied with this method, and all have shown LIMA in the entire extrinsic range from the fundamental edge (about 520 nm) up to $1.5 \mu\text{m}$, the limiting wavelength of

the optical equipment used. (In a previous short note⁷, using different equipment, LIMA was observed up to $2.0 \mu\text{m}$.) In general, close to the absorption edge a decrease in absorption (bleaching), and in the longer wavelength range an increase of absorption is observed.

Figure 2 gives the spectral distribution of the relative changes in the optical absorption for the CdS: Ag, Al — crystal. Below 700 nm bleaching is observed with two bleaching maxima at about 530 and 580 nm. Above 700 nm an increased absorption occurs with three maxima at about 730, 870 and 1430 nm. For these and the following measurements, if not otherwise stated, a chopper frequency of 17 Hz was used.

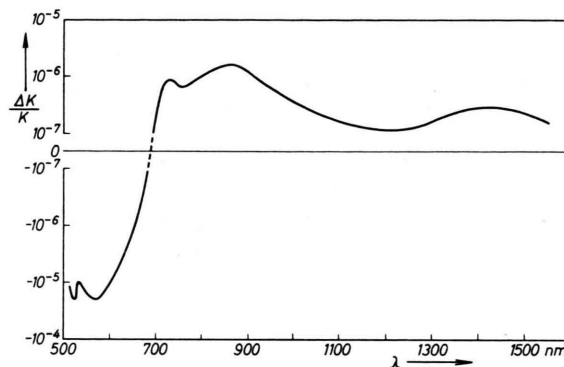


Fig. 2. LIMA as a function of the wavelength.

The bleaching increases linearly with excitation light (see Fig. 3, for 585 nm). The increased absorption (712 nm), however, changes as the square root of the excitation intensity.

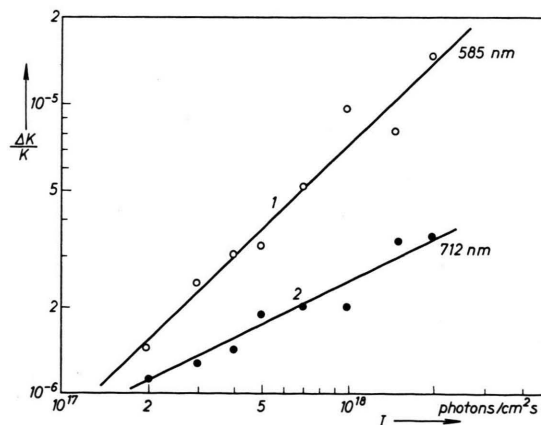


Fig. 3. LIMA as a function of the intensity of the exciting Laser beam, measured at 585 nm and 712 nm.

⁷ K. W. BÖER and EDMUND J. CONWAY, NASA Techn. Rep. No. TND-4466 [1968].

The cross-over wavelength between bleaching and increased absorption is nearly intensity-independent (705 nm) for lower optical excitation densities and decreases slightly with increase intensity (see Fig. 4).

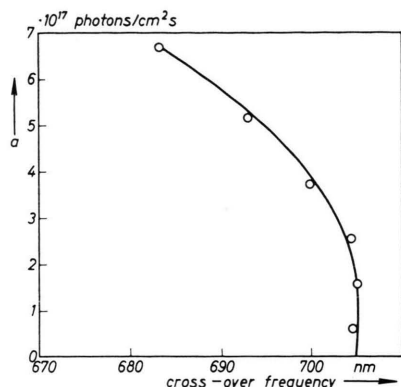


Fig. 4. Cross-over frequency between induced bleaching and enhanced absorption as a function of excitation intensity.

The relative change in absorption decreases with increasing chopping frequencies essentially as $1/\omega$ starting usually at a lower frequency for larger excitation wavelengths (in the bleaching range). Typical curves are given in Fig. 5.

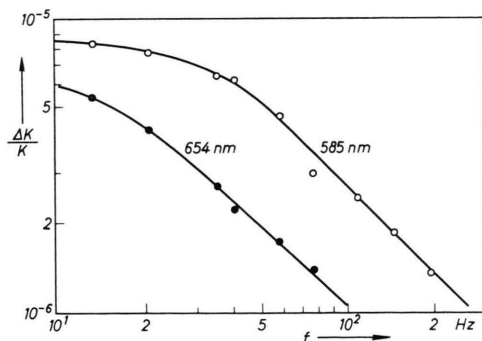


Fig. 5. LIMA as a function of the chopping frequency for 585 nm and 654 nm.

For comparative purpose the spectral distribution of this CdS-crystal was measured (Fig. 6) using an excitation density of about 2×10^{13} photons/cm²s. Evaporated Ti/Al layers⁸ were used as slit-electrodes (5 mm slit width, 12 mm slit length).

Figure 7 gives the increase in photocurrent with increasing intensity of the laser light, showing a power law with essentially the same power of 0.55 in the entire investigated range.

⁸ K. W. BÖER and R. HALL J. Appl. Phys. **37** 4739 [1966].

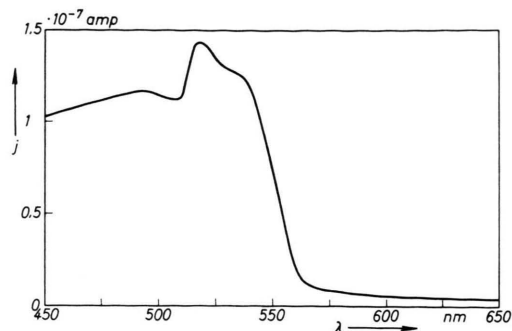


Fig. 6. Spectral distribution of the photocurrent of the investigated CdS-crystal.

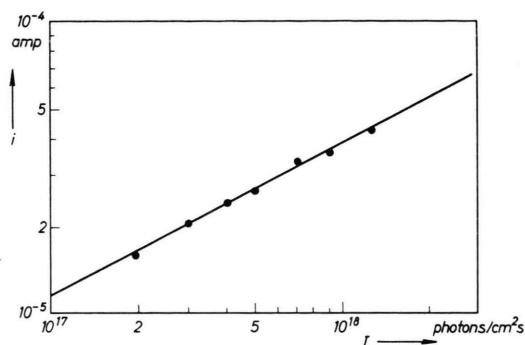


Fig. 7. Photocurrent as a function of the photon flux at intensities comparable to the laser excitation used for the LIMA-analysis.

3. Discussion

The observed properties of LIMA suggest that the laser excitation causes a redistribution of electrons over the defect levels in the band gap. Electrons are pumped from levels below the Fermi-level into levels closer to the bands involving transitions over the conduction and valence band. Thereby, short wavelength optical absorption (1 in Fig. 8) is reduced and long wavelength absorption (2–5) is increased, as observed (see Fig. 2).

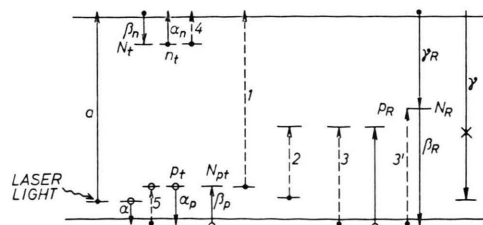


Fig. 8. Band model of a photoconductor with electron traps N_t , hole traps N_{pt} and recombination centers N_R and important carrier transitions.

Several features of the LIMA-curve in Fig. 2 can be recognized from the photoconducting behavior, as e.g. the 530 nm LIMA-bleaching maximum, which seems to be related to the 535 nm photoconductivity maximum; the 870 nm and the 1400 nm LIMA maxima for increased absorption seem to be related with the well known quenching maxima at approximately the same wavelengths. The two LIMA-features at 580 nm and at 730 nm do not have a marked counterpart in the photoconductive spectrum. These transitions obviously are less active for photoconductivity and we will return to their discussion later.

For the following analysis we will assume that the laser light excites electrons from holetraps into the conduction band and thereby produces holes in these traps which can thermally equalize with the valence band within times short compared to the chopping time of the laser light. With a thermal excitation probability (α , see Fig. 8) of

$$\alpha = \alpha^* \exp(-\Delta E_v/kT) \quad (1)$$

and an assumed frequency factor of 10^{12}s^{-1} one sees that such equalization can easily take place at room temperature for hole traps up to at least 0.5 eV above the valence band within 10^{-2}s (corresponding to a chopping frequency of 100 Hz).

The produced free holes will in turn recombine with slow and fast recombination centers and cause the optical absorption of these centers to change. Simultaneously electrons will fill up traps or recombine with recombination centers and also change their optical absorption.

The concentration of carriers in electron and hole traps is given by

$$dn_t/dt = \beta_n n (N_{nt} - n_t) - \alpha_n n_t \quad (2)$$

$$\text{or} \quad dp_t/dt = \beta_p p (N_{pt} - p_t) - \alpha_p p_t \quad (2a)$$

(for explanation of the symbols see Fig. 8). Up to a maximum distance from the respective bands, given by Eq. (1), quasi-stationarity can be achieved within every chopping cycle and is given by

$$n_t \cong (\beta_n/\alpha_n) N_{nt} n$$

$$\text{or} \quad p_t \cong (\beta_p/\alpha_p) N_{pt} p, \quad (3a)$$

i.e. the concentration of electrons and holes in these traps is modulated as the carrier density in the respective bands.

Since the density of hole traps usually is large compared to the density p of free holes, it follows that p is proportional to the laser excitation density (as long as N_{pt} does not act as recombination center), and therefore the modulation of holes in hole traps also is proportional to the laser light intensity. It is therefore expected that the modulation of the transition 1 (Fig. 8) increases linearly with the laser light. This is in good agreement with the experimental observation for LIMA-bleaching (curve 1 in Fig. 3), and indicates that levels up to $E_c - E_p \cong 1.8\text{ eV}$ act as hole traps.

The density of electrons in the conduction band, however, is not generally lower than the available trap density. Therefore one would expect a linear behavior, as mentioned above, only for lower laser intensities and a square root behavior (bimolecular electron-hole recombination) at higher intensities for a LIMA-transition of type 4 (Fig. 8). This LIMA-behavior is expected for wavelengths above $2\text{ }\mu\text{m}$ ($E_c - E_t < 0.6\text{ eV}$).

The density of holes in recombination centers (N_R in Fig. 8) is given by

$$dp_R/dt = \beta_R p (N_R - p_R) - \gamma_R n p_R, \quad (4)$$

and, although far from the respective bands, thus thermal excitation can be neglected, this density may follow the modulation of the carriers if the recombination coefficients are not too small and the chopping frequency is not too fast. Close to stationarity the hole density in these recombination centers is given by

$$p_R \cong (\beta_R/\gamma_R) N_R \cdot p/n. \quad (5)$$

For an optical excitation at which n and p both depend linearly on the excitation density it is expected that no LIMA is observable since according to Eq. (5) p_R is independent of the excitation density (a) and consequently cannot be modulated with a chopped laser. At high intensities, however, when n increases proportional \sqrt{a} the LIMA should also increase proportional to the square root of the optical excitation. The experimental LIMA observation shows such a law in the range of increased absorption ($\lambda > 700\text{ nm}$ in Fig. 2, and 3' in Fig. 8), and indicates bimolecular electron recombination. This is in good agreement with the observed increase of photoconductivity with laser-light intensity (Fig. 7).

This analysis holds for fast and slow recombination centers and therefore one would expect to see both

centers in LIMA, while only excitation from slow recombination centers will show up in the photoconduction spectrum (quenching). It is very probable that a fast recombination center is responsible for the 730 nm-LIMA maximum. Other fast recombination centers may be hidden in the farther infrared range. A differentiation between different centers may be possible by a LIMA-analysis at different chopping frequencies. Holes will be trapped faster at slow centers, electrons faster at fast recombination centers, where, in general, the electron capture seems to be the slower, i.e. modulation determining process. Therefore LIMA should decrease at smaller frequencies for slow than for fast centers.

The observed frequency dependence of LIMA for hole traps presents a possibility to determine directly the frequency factor. For instance, at 585 nm a marked decrease of LIMA is observed starting at about 40 Hz. With $\Delta E_v \cong 0.4$ eV and $\alpha = 40$ one obtains from Eq. (1), $\alpha^* \cong 10^8 \text{ s}^{-1}$. This value is rather low and seems to indicate that excitation from this level may occur to an excited state inside the conduction band, allowing for a larger ΔE_v . At 654 nm a similar decrease of LIMA starts slightly below 10 Hz, yielding, with $\Delta E_v \cong 0.6$ eV, a frequency factor of $\alpha^* \cong 10^{11} \text{ s}^{-1}$, which is a more reasonable value. Certainly more detailed investigation on the energy- and temperature dependence of these characteristic chopping frequencies are needed before conclusive results for the frequency factor of different hole traps can be obtained. However, it should be pointed out that a LIMA analysis with different chopping frequencies should, in principle, allow a differentiation between hole traps of different frequency factors (and therefore different capture cross sections). It is possible that the LIMA-transparency-maximum at 575 nm could be attributed to a hole trap with exceptionally large capture cross section. This center need not to contribute more strongly to the photoconductivity than other centers in the extrinsic range and therefore no photoconductive maximum is observed at 575 nm.

The cross-over frequency separates to some extent recombination centers from hole-traps and compares with an effective demarcation line.

The observed shifting of the cross-over towards shorter wavelength, i.e. shifting of this line with increased excitation density closer to the valence band favors this explanation. However, competing LIMA of different centers may screen somewhat a clean transition. For hole traps close to this cross-over energy a frequency factor of $\alpha^* \cong 10^{13} \text{ s}^{-1}$ is calculated and indicates that only such traps with small capture cross section for holes can be determined here. There is no reason why not other hole-traps even further away from the valence band, or such with larger capture cross section for holes exist near this energy. But these centers should only be observable with LIMA, if one could go to extremely small chopping frequencies.

4. Summary

With chopped laser light electrons and holes are excited and redistributed over levels in the band gap. Electron- and hole traps and recombination centers in a wide energy range can follow this modulation and cause a slightly modulated optical absorption, which can be detected with a second light beam and a phase-sensitive detection method.

Using such LIMA-analysis, hole traps and recombination centers can be distinguished by their different kinetic behavior and dependence on excitation intensity. Certain levels, as e.g. some fast recombination centers can also be detected, their energetic position and the smaller capture cross section for carriers can be determined. Using different chopping frequencies and different temperatures, a differentiation of levels in respect to their frequency factor or capture cross section can be expected.

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