Saturation photoconductivity in $CdIn_2S_4$

S. Charbonneau and E. Fortin
Department of Physics, University of Ottawa, Ottawa, Canada K1N 6N5

A. Anedda
Dipartimento di Scienze Fisiche, Università degli Studi di Cagliari, I-09109 Cagliari, Italy
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At excitation energies corresponding to definite extrinsic transitions in $CdIn_2S_4$, the photoconductivity is investigated as a function of light intensity over a maximum of 12 orders of magnitude (10^{16} to 10^{28} photons/m^2 sec). For certain wavelength ranges a photoconductivity plateau is observed at high excitation intensities. This saturation effect is attributed to a saturation of high density levels within the gap at high light intensities.

I. INTRODUCTION

The ternary semiconducting compound $CdIn_2S_4$ has been well studied in the last ten years because of its interesting optical and photoelectrical properties. It has an indirect-band-gap energy $E_g^i = 2.28$ eV at room temperature[1] (RT) and 2.45 eV at liquid-nitrogen temperature (LNT). The direct transition occurs at 2.62 eV at RT.[1] At temperatures up to 403 K the crystal has a partially inverted spinel structure; that is, in the compound, Cd and In atoms are capable of occupying both tetrahedral and octahedral sites. Above this temperature, an order-disorder transition occurs in the cation sublattice of the crystals.[2,3] $CdIn_2S_4$ is a member of the family of ternary compounds $A^{II}B_2^{III}X_4^{VI}$ and shares, with other members of the family, the following properties: A large amount of intrinsic disorder; the absence of any excitonic structure in the low-temperature optical spectra; the existence of radiative recombinations between localized levels;[4,5] and, the presence of a continuous distribution of electron trapping levels.[6–10] These localized levels within the gap are related to structural defects which are in turn related to the conditions under which the samples were prepared. The study of photoluminescence[5,11–14] and photoconductivity[8,15–19] (PC), coupled with systematic changes in crystal preparation, has been used in the detection and characterization of localized levels.

The present work consists of two parts: the determination of PC spectra and the measurement of the photocurrent response as a function of light intensity. The PC spectra, at RT and at 100 K [in the (1.7–3.0)-eV excitation range], were recorded in order to determine the energies of the transitions involving the impurity levels in our samples. The photocurrent, which is proportional to the number of free carriers produced by the exciting light, was then measured for a specific extrinsic transition as a function of light intensity over 12 orders of magnitude. The aim of the work was to detect saturation effects—difficult to observe by absorption in thin samples in the extrinsic range—photoconductivity. Photoluminescence experiments[5] indicate that such saturation effects could be related to the emptying of deep acceptor levels, leading to possible population inversion between gap states.

II. EXPERIMENTAL TECHNIQUE

The $CdIn_2S_4$ single crystals of up to a few tens of cubic millimeters in volume were grown by the iodine transport technique.[8] All samples were n type with a conductivity at 300 K of about $10^{-5}\ \Omega^{-1}\,cm^{-1}$. PC spectra were obtained on smooth, natural surfaces of crystal a fraction of a millimeter thick. Silver paint contacts were ohmic in the temperature range studied (100 to 300 K). The low-intensity PC measurements were performed using standard synchronous detection techniques and a Bausch and Lomb monochromator as a source to provide intensities of up to 2.5 W/m^2. The PC response was corrected for equal incident intensity. A pulse dye laser (pulse width $\Delta t = 10^{-6}$ sec) was used as a source of excitation for higher intensities of up to 10^{11} W/m^2, and a waveform analyzer was used to record the PC signal. The photocurrent pulses were detected by measuring the voltage drop across a resistor R_s in series with the sample ($R_s \ll R_{\text{sample}}$). Great care was taken to eliminate circuit loading effects and to ensure that it was actually the photocurrent which was recorded. The intensity of the beam was varied by inserting calibrated neutral-density filters in front of the sample. Figure 1 shows the experimental apparatus for the high-intensity measurements.

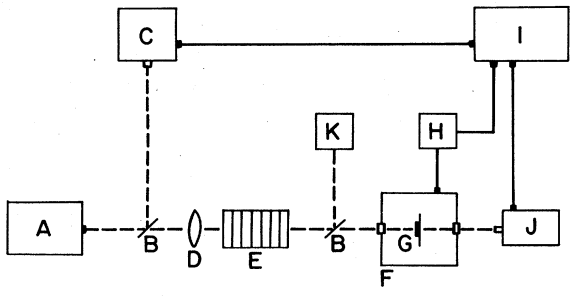

FIG. 1. Experimental apparatus for high-intensity measurements. *A*, pulse dye laser; *B*, beam splitter; *C*, optical trigger; *D*, lens; *E*, calibrated neutral density filters; *F*, optical cryostat; *G*, sample; *H*, measuring circuit; *I*, waveform analyzer (Lecroy 3500 SA or boxcar averager); *J*, photomultiplier; *K*, power meter.

III. RESULTS AND DISCUSSION

A. Photoconductivity spectra

In Figs. 2(a) and 2(b) the PC spectra of $CdIn_2S_4$ at RT and 100 K are reported for two different samples. The PC spectrum does not necessarily follow the optical-absorption spectrum, since PC depends on both the optical absorption and the lifetime of the photogenerated carriers in the crystal. For both samples, the RT spectra show two peaks: *A*, at approximately 500 nm (2.48 eV), and *B* at around 600 nm (2.10 eV), which at 100 K are shifted to 425 and 585 nm, respectively. There is good agreement between these results and those obtained by Anedda *et al.*[8] and Radautsan *et al.*[20] The exact shape of the spectra, and relative intensities of the peaks, depend upon preparation conditions and therefore vary from sample to sample.

The model of the band diagram for the excitation and recombination processes adopted in the present paper is the one proposed by Grilli *et al.*[5] (Fig. 3). This model incorporates the results of Anedda *et al.*,[8] which demonstrated the presence of a high density of electron trapping levels with an exponential distribution in energy and the presence of an acceptor level 0.25 eV from the top of the valence band in $CdIn_2S_4$ crystals. The origin of these levels has been attributed to antistructural defects due to In-Cd exchange, probably induced by the phase transition from the partial inverse spinel structure to the disordered spinel structure.[2] In this model, *E* will represent the compensated acceptors and *T* the trap distribution. It is important to remember that all the traps *T* and acceptors *E* are ionized due to the fact that the Fermi level lies about 2.2 eV from the top of the valence band.[21] The *V* center, placed at approximately 0.6 eV from the conduction band, is attributed to sulfur vacancies and is not believed to play any role here.

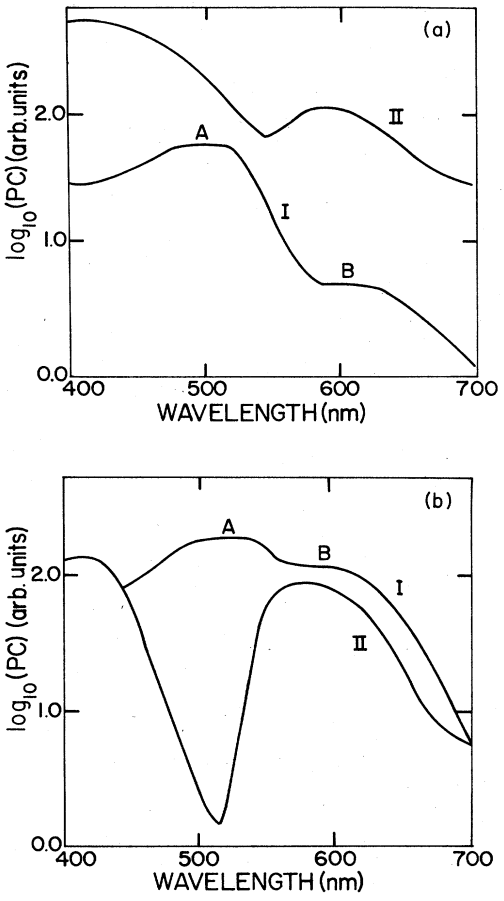

FIG. 2. Photoconductivity spectra at RT (I) and 100 K (II) for (a) sample 1 and (b) sample 2.

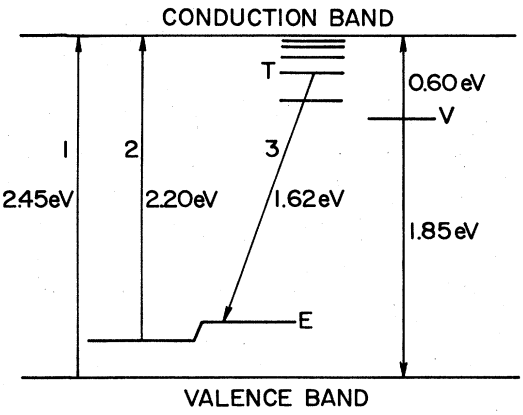

FIG. 3. Energy-level scheme and model of the recombination processes of photoexcited carriers in $CdIn_2S_4$ at LNT.

Peak *A* can be attributed to band-to-band transitions (1 in Fig. 3). Peak *B*, observed in the same position in luminescence excitation spectra,[5] has been assigned to electron transitions from the acceptor level *E* to the conduction band (2 in Fig. 3). Emission spectra reported by Grilli *et al.*[5] indicate that electron relaxation occurs via trap states *T* and transition 3.

B. Photoconductivity versus intensity

PC versus intensity measurements were performed for both samples in the region of peak *B* (transition 2) in an attempt to observe saturation effects. In that low-absorption region ($\alpha d \ll 1$), carriers are generated over the entire thickness *d* of the sample and the generation rate is proportional to the absorption coefficient α. Figure 4 shows the photocurrent as a function of light intensity for sample 1 at RT and 100 K at $\lambda = 600$ nm. The damage threshold was determined to be 10^{11} W/m^2. At both temperatures, a nearly linear dependence of the PC response at low values of light intensity was observed; however, as the light intensity was increased, a marked deviation from linearity is apparent, eventually attaining a plateau. This saturation effect is more easily seen in Fig. 5—an enlargement of Fig. 4 showing the PC values at the highest light intensities. The saturation effect, believed to be caused by an emptying of the acceptor levels *E* at high light intensities, are seen at both temperatures, however, it is more prominent at 300 K. Two phenomena might

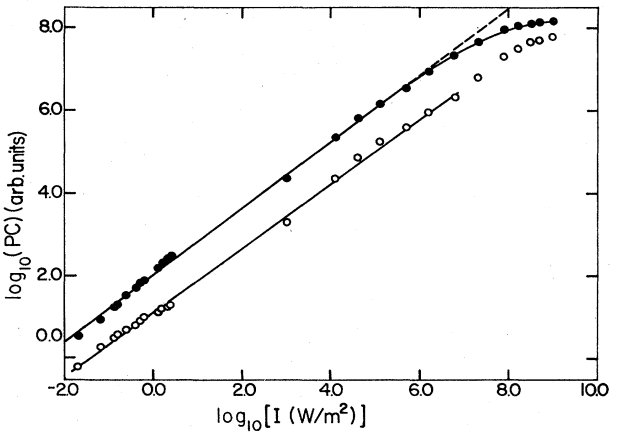

FIG. 4. Photocurrent versus intensity at $\lambda=600$ nm at RT (●) and 100 K (○).

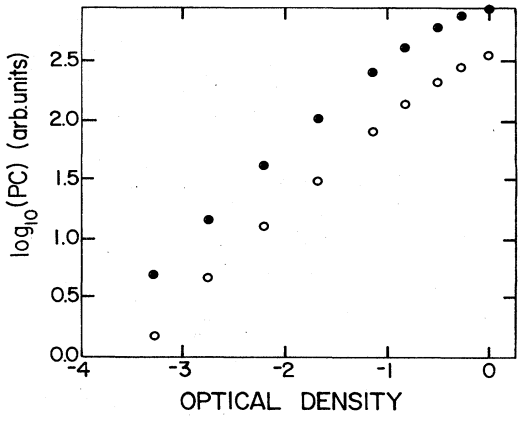

FIG. 6. Photocurrent versus intensity at $\lambda=600$ nm for sample 2 at RT (●) and 100 K (○).

cause this: (i) the relaxation rate, which governs the regeneration of the acceptor levels, is not necessarily the same at both temperatures, and (ii) the absorption coefficient decreases from $\alpha=3$ cm^{-1} at RT to $\alpha=1$ cm^{-1} at LNT.[1] A saturation of impurity PC at high intensity has also been reported for GaSe by Abdullaev and coworkers,[22] but for a discrete level only. The same result was obtained by Celler *et al.*[23] in *n*-type GaAs. In the case of our $CdIn_2S_4$ samples, the nonlinear effects were observed over a broad spectral range (585 to 670 nm) corresponding to peaks *B* of Fig. 2.

The above data were obtained on sample 1. In comparison, the saturation effects were less apparent for sample 2 (see Fig. 6). This difference can best be explained by inspection of the low-intensity PC spectra of Fig. 2(b). In sample 2, the fact that peak *B* is relatively more intense at both RT and 100 K indicates a greater density of acceptor levels *E*, making saturation more difficult to achieve. From Fig. 4, it is possible to estimate the density of acceptor levels *E*: Assuming negligible recombination during the exciting pulse at all intensities—and observation of the PC transients indicate an approximately constant lifetime $\tau \gtrsim \Delta t$—one only needs to calculate the number of photons absorbed per unit volume at the saturation point. If RI is the intensity of the reflected radiation, and TI the intensity of the transmitted radiation, it may readily be shown that

$$R = R_0\left[1+\frac{(1-R_0)^2 e^{-2\alpha d}}{1-R_0^2 e^{-2\alpha d}}\right] \tag{1}$$

and

$$T = \frac{(1-R_0)^2 e^{-\alpha d}}{1-R_0^2 e^{-2\alpha d}}\ , \tag{2}$$

where R_0 is the reflection coefficient at the surface of the sample. The total amount of radiation absorbed by the sample per unit time is equal to $I(1-T-R)$, and for low absorption the average rate of absorption per unit volume is equal to $I(1-T-R)/d$. Provided Eqs. (1) and (2) are valid, $(1-T-R)\rightarrow\alpha d$ when $\alpha d \ll 1$, and the radiation is uniformly absorbed throughout the sample at a rate αI per unit volume.

The saturation occurs at an intensity of $I_0 \simeq 1\times10^9$ W/m^2 at 600 nm. The number of acceptors can be calculated to first order as follows:

$$\begin{aligned} N_A &= I_0(1-T-R)\Delta t/h\nu d \\ &= \alpha I_0\,\Delta t/h\nu\ , \end{aligned} \tag{3}$$

where $\alpha=3$ cm^{-1} and $R_0=0.2$ (Ref. 24) at $\lambda=600$ nm and $h\nu$ is the energy of a photon in units of joules.

The calculated density of acceptors was found to be $N_A \simeq 1\times10^{18}$ cm^{-3}. Since the acceptor *E* and trap *T* originate from Cd-In lattice exchange, the calculated density of the acceptors should be of the same order as (or if complete compensation is not achieved, less than) that of the traps. The latter value was determined by Endo *et al.*[25] and Anedda *et al.*[8] and their values are in qualitative agreement with the value of N_A obtained here. Optical

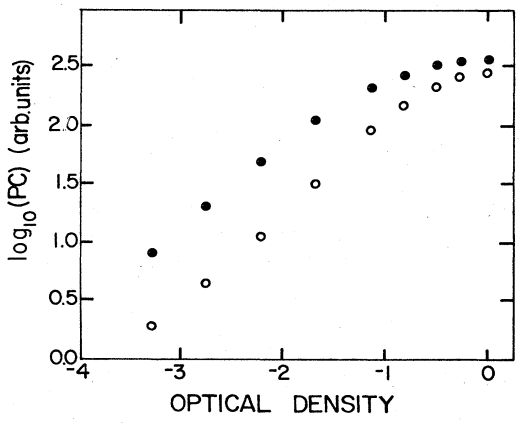

FIG. 5. Photocurrent versus intensity at $\lambda=600$ nm for sample 1 at RT (●) and 100 K (○).

absorption versus intensity measurements in the extrinsic range have been attempted, but because of the low contrast involved in this $\alpha d \ll 1$ range, few significant results have yet been observed. Photoluminescence experiments are now in progress using high excitation intensities in the saturation range observed here, and could display interesting effects because of population inversion between levels T and E.

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