PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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Nonlinear and optically bistable effects in cadmium sulphide

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Among the numerous optical nonlinearities known for CdS, we select here those connected with the transition from a low-density gas of excitons to an electron–hole plasma. The properties of the plasma are reviewed and it is demonstrated that the variations of the indices of absorption and refraction, which occur in this phase transition, allow for the realization of optical bistability.

1. Introduction

The invention of lasers gave a strong impetus to the investigation of nonlinear optical phenomena in semiconductors and insulators. The results of the first years have, for example, been reviewed by Bloembergen (1965). The common availability of spectrally narrow tunable dye lasers allowed in the last decade for detailed investigations in the spectral region of electronic resonances close to the absorption edge. In this region, the optical properties of semiconductors are dominated by exciton states. Excitons are bound electron–hole pair states analogous to the positronium or hydrogen atoms. For more details see, for example, Klingshirn & Haug (1981) and the references therein.

The reasons for the optical nonlinearities are manifold, but they can roughly be classified in three categories (for CdS see, for example, Kempf *et al.* (1981) and Kreissl *et al.* (1982)):

(i) excitation-induced modifications of resonances that exist already at low intensities, like a broadening of exciton resonances;

(ii) the appearance of new resonances with increasing excitation like those connected with two-photon transitions to the excitonic molecule;

(iii) the phase transition of a low-density gas of excitons to an electron–hole plasma.

In this paper we shall concentrate on the last point. We have selected CdS as a typical example for a direct-gap semiconductor. In §2 we summarize the properties of the electron–hole plasma, in §3 we present the variations of the optical properties connected with its formation and their application in the formation of laser-induced gratings, in §4 we present optical bistability and in §5 we give an outlook to further research activities and possible technical applications.

2. Properties of the electron–hole plasma

If electron–hole pairs are excited in a semiconductor at low density and temperature, they will form excitons. If the generation rate is increased, the density of excitons may become so high that their mean separation is comparable to their Bohr radius. Then excitons are no longer individual quasi-particles, but form a new collective phase, the electron–hole plasma. This transition from the insulating exciton gas to the metallic plasma-phase is also referred to as Mott transition.

This phase transition has consequences for the band structure. It has been found (see, for example, the literature cited by Klingshirn & Haug (1981)) that the width of the forbidden gap E_g is a monotonical decreasing function of the electron–hole pair density in the plasma n_p. The chemical potential of the plasma μ (the energetic distance between the quasi-Fermi levels of electrons and holes) depends strongly on n_p and the plasma temperature T_p. An analysis of the functions $E_g(n_p)$ and $\mu(n_p, T_p)$ shows that under thermodynamic quasi-equilibrium conditions there is a first-order phase transition below a critical temperature T_c from a low density exciton gas to an electron–hole plasma liquid. This phase transition is similar to the gas–liquid transition of real gases and has been analysed in great detail for the indirect-gap semiconductors Ge and Si. See, for example, the reviews written by Rice (1977) and by Hensel *et al.* (1977). In these materials the evolution of the liquid-like phase in the form of plasma droplets is favoured by the long lifetime of electrons and holes.

In direct-gap materials, and especially in CdS, it has been found that a plasma is formed, which, however, does not reach its liquid-like state because at the short lifetime of carriers of only about 100 ps (see Bohnert *et al.* (1981) and Kempf & Klingshirn (1984); Kempf (1984)). These authors find, in contrast to what is expected for a liquid-like plasma state, that n_p increases at constant T_p with increasing excitation intensity I_{exc} and at constant I_{exc} with increasing T_p. Because of the high optical gain $g(g \gtrsim 10^4\ \mathrm{cm}^{-1})$ connected with a degenerate electron–hole plasma in direct-gap semiconductors, only small volumes of some hundreds of cubic micrometres can be filled with plasma. Some authors speculated about a fast expansion of the plasma at the border of the excited volume over distances d of 100 μm and with expansion velocities v_d beyond 10^7 cm s^{-1}. For CdS it has been shown by Kempf & Klingshirn (1984) that the values of v_d and d are considerably smaller. A consistent set of plasma parameters for lattice temperatures around 5 K, which also fulfils the necessary condition

$$n_p = I_{exc}\tau_p/d\hbar\omega_{exc},$$

where τ_p is the lifetime of the carrier pairs in the plasma, and $\hbar\omega_{exc}$ is the photon energy of the exiting laser with intensity $I_{exc}(\hbar\omega_{exc} > \mu)$, is the following:

$$0.5\ \mathrm{MW\ cm^{-2}} \lesssim I_{exc} \lesssim 5\ \mathrm{MW\ cm^{-2}};$$
$$10^{18}\ \mathrm{cm^{-3}} \lesssim n_p \lesssim 3\times 10^{18}\ \mathrm{cm^{-3}};$$
$$10\ \mathrm{K} \lesssim T_p \lesssim 35\ \mathrm{K};$$
$$\tau_p = (150\pm 50)\ \mathrm{ps};$$
$$v_D \approx 2\times 10^6\ \mathrm{cm\ s^{-1}} \quad \text{and} \quad d = (3\pm 2)\ \mu\mathrm{m}.$$

This set of data has been deduced by Kempf & Klingshirn (1984) from spatially resolved transmission and reflection experiments. Deviations from this set of parameters will lead to internal contradictions. It should be noted that the observed values of n_p in CdS are slightly smaller than the calculated equilibrium density of the plasma, n_0, of 5×10^{18} cm^{-3} (Rösler & Zimmermann 1977). In CdSe, the value of n_0 is about one order of magnitude smaller. Here it is possible to reach values $n_p > n_0$ before crystal damage occurs. Preliminary results of spatially resolved gain spectroscopy indicate values of d of several micrometres (Majumder *et al.* 1984). Experiments with a spatially confined plasma help to avoid problems connected with plasma expansion, as has been demonstrated for $Ga_{1-x}Al_xAs$ by Capizzi *et al.* (1983).

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

3. Variations of the optical properties in the plasma

The variations of the absorption and refraction spectra around the absorption edge owing to the transition from a low-density exciton gas to an electron–hole plasma have been investigated in detail for CdS by Kreissl *et al.* (1982) for fixed $\hbar\omega_{\mathrm{exc}}$.

For purposes of optical bistability, it is necessary to know the variations at the photon energy of the exciting laser itself. The corresponding experiments and their results are presented in this section. The measurement of the absorption coefficient at the spectral position of the incident laser is rather trivial. The variation of the refractive index is determined by a weak probe beam, which is sent on the sample in the centre of the excitation spot. In contrast to the experiments of Kreissl, samples with a thickness between 0.5 and 2.5 μm are used, which are homogeneously excited within this range . The transmitted probe beam is nicely modulated by the Fabry–Perot interference structure produced by the platelet type samples. From the position of the interference maxima and minima and their shift with increasing excitation it is possible to deduce $n(\omega)$ and $\Delta n(\omega_{\mathrm{exc}}, I_{\mathrm{exc}})$. Obviously this technique works only in the spectral region where the sample is transparent. Figure 1*a* shows the variations of the absorption coefficient $\Delta\alpha(\hbar\omega_{\mathrm{exc}})$ for $I_{\mathrm{exc}} = 2$ MW cm^{-2}. Since the unexcited sample is transparent below 2.55 eV, $\Delta\alpha(\hbar\omega_{\mathrm{exc}}) = \alpha(\hbar\omega_{\mathrm{exc}})$. Figure 1*b* gives the refractive index $n(\omega)$ of the unexcited sample, while figure 1*c* shows its variation $\Delta n(\omega_{\mathrm{exc}})$ for $I_{\mathrm{exc}} = 2$ MW cm^{-2}. One finds that Δn is negative due to the disappearance of the exciton resonance; however, with the onset of a resonance-like structure if $\hbar\omega_{\mathrm{exc}}$ approaches the onset of absorption.

If two coherent monochromatic laser beams of equal frequency and intensity are falling on the sample under a small angle (see insert of figure 2), they produce an interference pattern. In the regions of constructive interference, the intensity is very high, producing the variation $\Delta\alpha$ or Δn shown in figure 2, while the intensity is small in between. Thus a laser-induced grating is formed. Figure 2 gives the efficiency of this grating for the first order as a function of $\hbar\omega_{\mathrm{exc}}$. By comparing figure 1*a* and *c* and figure 2 it is obvious that an absorptive grating is induced for $\hbar\omega_{\mathrm{exc}}$ between 2.545 eV and 2.540 eV, while a phase grating is formed below; however, with lower efficiency. More details about this experiment and about the influence of the other nonlinearities, mentioned in § 1, on laser induced gratings will be published by Kalt *et al.* (1984).

4. Optical bistability

The excitation-induced renormalizations of the refraction and absorption coefficients shown in figure 1 give rise to two different types of optical bistability. Bohnert *et al.* (1983) found first experimental indications of a dispersive optical bistability in Fabry–Perot-type CdS platelets at photon energies slightly below 2.54 eV and a new type of intrinsic absorptive bistability above. Dispersive optical bistabilities in semiconductors have been predicted by a number of authors (for example, Koch *et al.* 1981; Hanamura 1981) and are treated in several contributions to this meeting. We therefore concentrate here on the absorptive bistability. First hints have been found by Rossmann *et al.* (1983) in terms of an optical memory effect, but without a clear interpretation. Detailed experimental investigations, with rather poor temporal resolution, led Bohnert *et al.* (1983) to the correct qualitative interpretation, which will be given here together with new experiments. First quantitative calculations have been made by H. Haug and coworkers (see, for example, Schmidt *et al.* (1984) and Haug, this symposium). Later, Henneberger & Rossmann (1984) also adapted this interpretation.

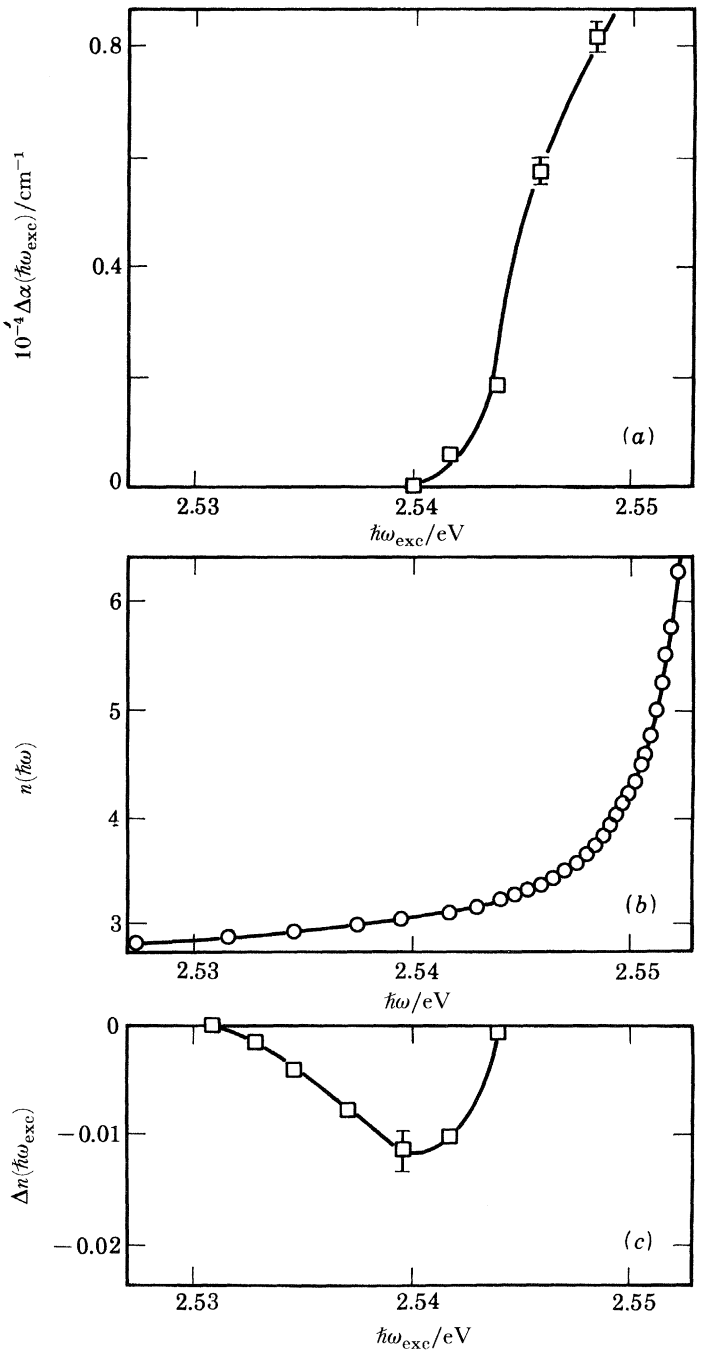

FIGURE 1. The variation of the absorption coefficient $\Delta\alpha$ of CdS as a function of photoenergy of the exciting laser $\hbar\omega_{exc}$ for constant excitation intensity $I_{exc} = 2$ MW cm^{-2} (*a*); the refractive index $n(\hbar\omega)$ of an unexcited sample (*b*); its variation $\Delta n(\hbar\omega_{exc})$ for $I_{exc} = 2$ MW cm^{-2} (*c*). ($\boldsymbol{E}\perp\boldsymbol{c}, \boldsymbol{k}\perp\boldsymbol{c}$, $T_L \approx 5$ K.)

The basic physical mechanism is now described. An incident laser pulse $I_0(t)$ incident on the sample is situated in the spectral region where the crystal is transparent for low excitation but becomes absorbing at high excitation. According to figure 1 this is, for example, the region between 2.55 eV and 2.54 eV. When the pulse rises, the sample is transparent. Owing to weak absorption in the tail of the absorption edge or owing to two-photon absorption, carriers are

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

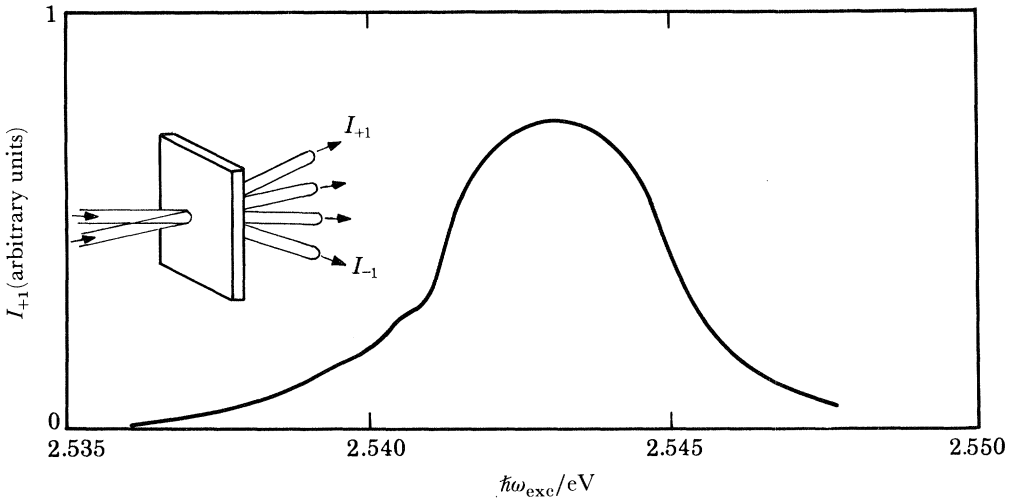

FIGURE 2. The spectral dependence of the efficiency of a laser-induced grating in CdS ($T = 5$ K, $\boldsymbol{E}\perp\boldsymbol{c}$, $\boldsymbol{k}\perp\boldsymbol{c}$, $I_{exc} = 1$ MW cm^{-2}).

created, but with low efficiency. If their density becomes sufficiently high, an electron–hole plasma is formed and strong one-photon absorption sets in because of the reduction of the band gap. The sample now becomes opaque and the transmissivity is switched down to low values. Since the one-photon absorption allows pumping of the plasma to be much more effective than the two-photon absorption, the sample remains in the state of low transmission down to excitation intensities, which are considerably below those necessary to produce the transition from high to low transmissivity. Thus the sample has two stable states, one of high and one of low transmissivity, i.e. optical bistability is achieved. This absorptive type of bistability needs no external feedback, for example in the form of a cavity. The 'feedback' occurs intrinsically in the electronic system.

Figure 3 shows the temporal shape of an incident and a transmitted pulse, $I_0(t)$ and $I_t(t)$, respectively, of an excimer-laser pumped dye-laser. The pulses are registrated by an Imacon

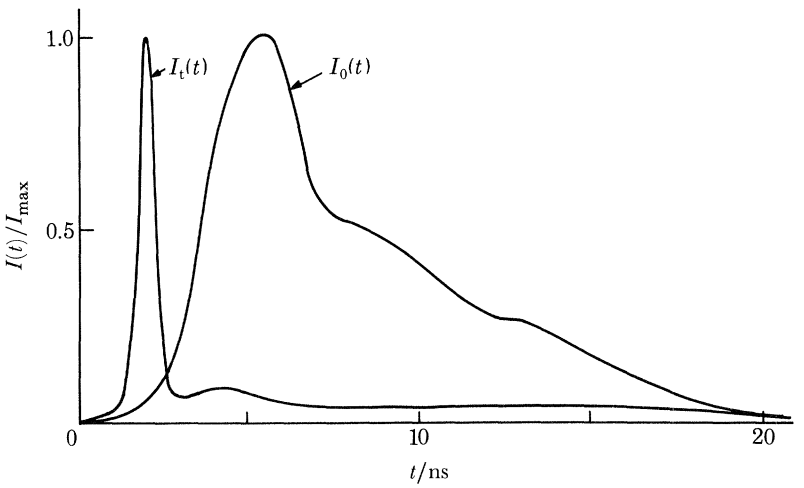

FIGURE 3. The temporal shape of incident and transmitted pulses $I_0(t)$ and $I_t(t)$. Thickness of the CdS sample is 2 μm; pulse-height normalized; $T = 5$ K, $\hbar\omega_{exc} = 2.548$ eV, $\boldsymbol{E}\perp\boldsymbol{c}$, $\boldsymbol{k}\perp\boldsymbol{c}$, $I_{0max} = 5$ MW cm^{-2}.

500 streak camera. The apparent switch-off time of about 200 ps is limited by the detection system. The real switching time is expected to be considerably lower.

From $I_0(t)$ and $I_t(t)$ a time-free plot $I_t = f(I_0)$ can be deduced, showing the hysteresis loop. Figure 4 gives two examples. In figure 4*a*, the peak intensity of the pulse is only slightly above

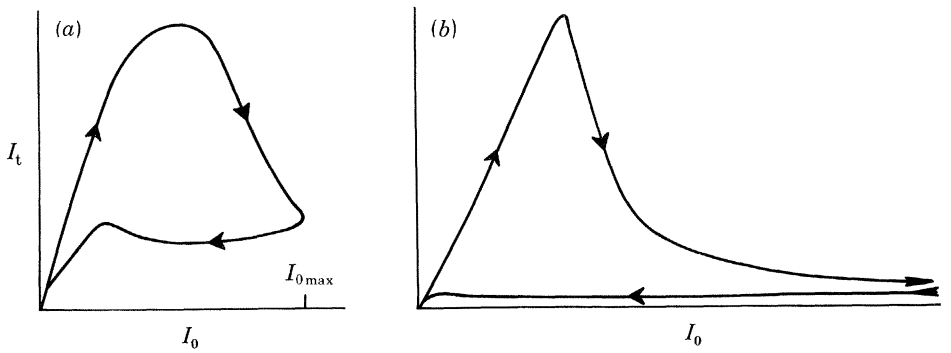

FIGURE 4. Hysteresis loops due to intrinsic optical bistability for (*a*) $I_{\max} = 0.25$ MW cm^{-2} and (*b*) 10 MW cm^{-2}. Intensities are given on all axes in arbitrary linear units (CdS, $T = 5$ K, $\hbar\omega_{\text{exc}} = 2.548$ eV, $\boldsymbol{E}\perp\boldsymbol{c}$, $\boldsymbol{k}\perp\boldsymbol{c}$).

the value for switching 'off'. In figure 4*b* the peak intensity of the pulse is more than an order of magnitude larger. It should be noted that the hysteresis loop is revolved clockwise in both cases, this means in the opposite direction to that for dispersive bistability or for an absorptive bistability, which is due to bleaching of an absorption band. Both cases need the feedback of a cavity.

5. OUTLOOK

Although the principal physical mechanism of this type of intrinsic absorptive optical bistability is rather clear now, a lot of details have to be investigated in the future, among others the actual switching times, the conditions for down switching, the holding power for the state of low transmission, the upper temperature limit at which the device works or the influence of the sample thickness compared to the diffusion length of the carriers in the plasma.

It should be pointed out that this optical device is presumably of great technical interest. The bistable operation can be used for fast optical storage. If the width of the hysteresis loop is made small, it can be used for the realization of the logic connection NOT, while the dispersive bistability realizes AND and OR. As has been mentioned already, there are indications for the latter phenomenon at longer wavelength. So one device could be used for different logic connections depending on the wavelength. If only one wavelength is available, the use of mixed crystals or graded-gap materials of the type $CdS_{1-x}Se_x$ or $Zn_{1-x}Cd_xS$ will allow for various functions depending on x.

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PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES