

HIGHLY DOPED CdS: OPTICAL PROPERTIES AND HIGH EXCITATION PHENOMENA

G. O. Müller, M. Rösler and R. Zimmermann

Akademie der Wissenschaften der DDR,
 Zentralinstitut für Elektronenphysik
 DDR 1080 Berlin

Highly Ga doped CdS monocrystals show an absorption edge rather independent of doping concentration and excitation intensity up to some MWcm^{-2} . No EHL indications were obtained. RPA theory including impurity induced self energies gives an upper limit in doping for phase separation but does not fit quantitatively to experiment.

Highly doped semiconductors have been the subject of widespread theoretical and experimental efforts during the last decades [1]. Assuming a Mott transition to take place at a certain doping level, which should not be the subject of this paper one might raise the question what the optical properties of the material are including its behaviour at such excitations, at which a first order phase transition into spatially separated phases - exciton gas and electron-hole-liquid (EHL) - occurs [2,3].

In an effort to answer this we investigated CdS doped up to about $n_d = 10^{19} \text{ cm}^{-3}$ by Ga determined by Hall measurements. One can be pretty sure that substitutional Ga forms a donor about 33 meV below the bottom of the conduction band. From plausibility a Moss-Burstein shift of the absorption edge due to the filling of the conduction band with donor electrons up to a Fermi level is expected. A self-energy shrinkage of the gap ($G = G_0 + \Delta_e + \Delta_h$) as in the case of (only) highly excited semiconductors might reduce the energy of the absorption edge

$$A = G_0 + \Delta_e + \Delta_h + E_e(k) + E_k(k) \quad , \quad k = k_{F,e} \quad (1)$$

to a value below the "zero" gap G_0 of the undoped material.

Exciting n non-equilibrium e-h pairs (charge neutrality reading as $n_e = n + n_d$, $n_h = n_d$) the chemical potential and gap shift can be naively computed as for highly excited undoped material [3] yielding μ^{pe} and $\tilde{G}^{pe}$ resp. Our calculations suggest phase separation (minimum of $\mu^{pe}(n; n_d)$ at fixed n_d) up to $n_d = 2 \cdot 10^{19} \text{ cm}^{-3}$.

But as a first experimental [4] indication against such an approach even at $n_d = 2 \cdot 10^{19} \text{ cm}^{-3}$ there is not the usual constancy of μ in dependence on excitation intensity encountered in undoped samples but the illustrated (Fig. 1 a,b) (small) shift of chemical potential.

Our theoretical approach to doped and highly excited semiconductors assumes the impurity ions to be positive point charges distributed randomly over the lattice sites of density N . The well-founded theory of interacting electrons in a disorder potential [5] tells us that the total screened potential is given by

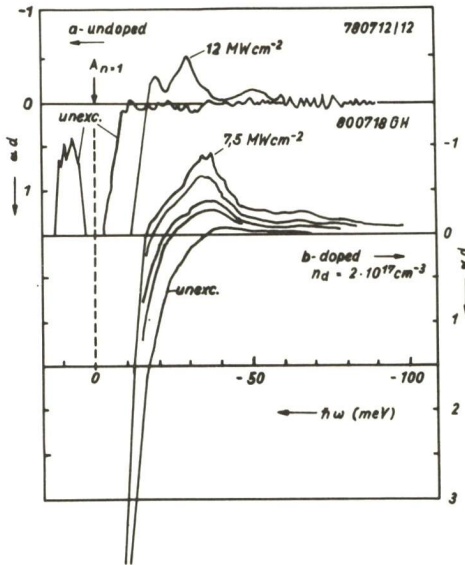


Fig. 1 Optical density α versus quantum energy $\hbar\omega$ relative to the exciton level ($A_{n=1}$) for a - undoped CdS, unexcited and excited by 12 MWcm^{-2} (337 nm radiation) resp. and b - $2 \cdot 10^{17} \text{ cm}^{-3}$ Ga-doped CdS, unexcited and excited by $I/I_0 = 1, 0.5, 0.12, 0.06$, resp. ($I_0 = 7.5 \text{ MWcm}^{-2}$)

$$w(q, \omega) = v_s(q, \omega) + \delta(\hbar\omega) v_s^2(q, 0) n_d (1 - n_d/N), \quad (2)$$

with the screened Coulomb potential $v_s = v/\epsilon$, the RPA dielectric function ϵ containing contributions from electrons, holes, and LO phonons as it is essentially for the polar material CdS. Analogous to undoped excited semiconductors [6] the first diagram 1) for the self energy, $\Sigma = w \cdot G$, is taken to calculate a (complex) quasi-particle energy shift Δ , which according to eq. (2) can be decomposed into $\Delta = \Delta^{\text{pl}} + \Delta^{\text{d}}$. The first term is specific for the e-h-plasma mentioned above and enters the chemical potential μ^{pl} together with the kinetic energy. Δ^{d} is given explicitly by

$$\Delta_v^{\text{d}}(k) = -n_d \left(1 - \frac{n_d}{N}\right) \sum_q v_s^2(q, 0) \left[\frac{\hbar^2}{2m_v} (q^2 + 2k \cdot q) + i\epsilon \right]^{-1}, \quad (3)$$

($v = e, h$)

and produces an extra distortion of the one-particle bandstructure due to the impurities. The corresponding contribution to the chemical potential is (at zero temperature)

$$\mu^{\text{d}}(n; n_d) = \text{Re}(\Delta_e^{\text{d}}(k_{F,e}) + \Delta_h^{\text{d}}(k_{F,h})). \quad (4)$$

The total chemical potential $\mu = \mu^{\text{pl}} + \mu^{\text{d}}$ is shown in Fig. (2). At intermediate doping levels, the usual EHL phase separation occurs between a low-density and a high-density liquid (horizontal line in Fig. 2). Obviously μ^{d} plays an essential role only at lower excitation, since with increasing n the impurity potentials are screened more effectively. μ^{d} acts to reduce drastically the maximum doping concentration for phase separation ($n_{d,c} = 5 \cdot 10^{17} \text{ cm}^{-3}$). The liquid binding energy φ (exciton energy minus EHL chemical potential) exhibits a remarkably small variation with n_d (Fig. 3).

1)

This is not able to produce a real impurity band or the donor bound state in the limit $n \rightarrow 0$, $n_d \rightarrow 0$, restricting the range of applicability to concentrations above the Mott one.

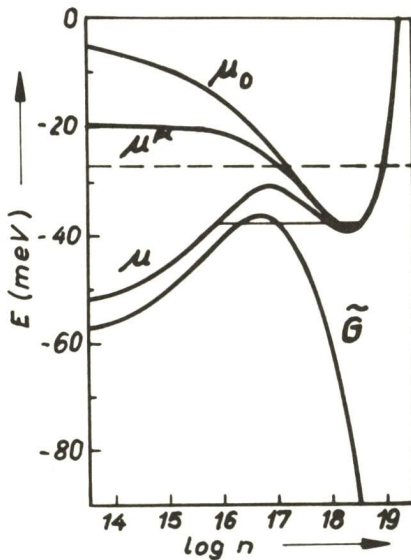


Fig. 2 Chemical potential (μ^* , μ) and shifted energy gap ($\tilde{G}$) of CdS doped with $n_d = 10^{17} \text{ cm}^{-3}$ in dependence on excited pair concentration n : The chemical potential for undoped CdS is shown for comparison (μ_0). Zero of energy is the polaron gap, the dashed line marks the exciton level (parameter values from [6])

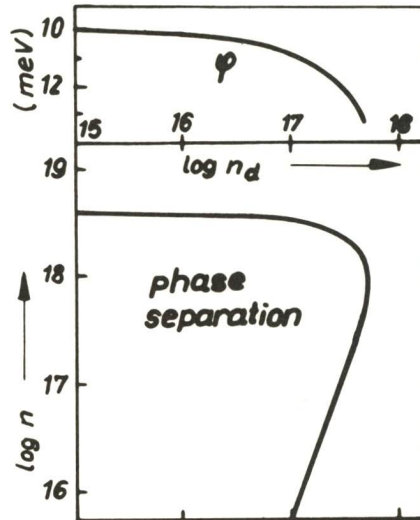


Fig. 3 Phase separation in dependence on doping level (CdS, $T = 0$): Upper part - binding energy φ , lower part - equilibrium densities

To compare our approach with that of Bergersen et al. [7] in the case of Si:P we note that by integrating $\mu^d(n, n_d)$ over n at fixed n_d the following contribution to the ground state energy comes out

$$E_0^d = \frac{n_d}{2} \left(1 - \frac{n_d}{N} \right) \sum_q [v_s(q, 0) - v(q)], \quad (5)$$

which is identical with formulas given in [7]. Also for the thermodynamics our procedure is completely analogous to [7] in contrast to Mahler's approach [8]. We would like to stress that our way using a self energy approach gives better insight into the impurity influence and consistently yields dispersions of the complex impurity induced shift as shown in Fig. (4) for two excitation levels corresponding to the phase separation in Fig. (2) (electron and hole contributions are proportional to each other, they have been added in Fig. (4) as it will be relevant for direct optical transitions). At low excitation, the band shift is strongly dispersive and damped, giving rise to somewhat like an impurity tail in the density of states. At higher excitations, absolute values diminish rapidly, and the band shift Δ^d is almost independent of k as wellknown from the exchange/correlation shift Δ^{pe} (the latter is not shown in Fig. (4)).

Nevertheless by simple comparison of Fig. (1) with Fig. (2) it is obvious that there is a striking quantitative disagreement. Even

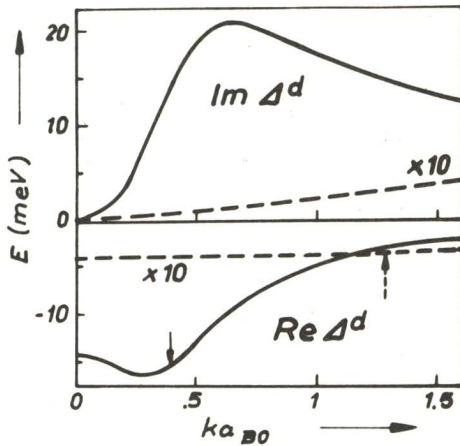


Fig. 4 Impurity induced quasiparticle shift $\Delta^d(k)$: CdS doped to $n_d = 10^{17} \text{ cm}^{-3}$ and excited to $n = 10^{16} \text{ cm}^{-3}$ (full) and $3.6 \cdot 10^{18} \text{ cm}^{-3}$ (dashed). Arrows at $k_{F,e}$

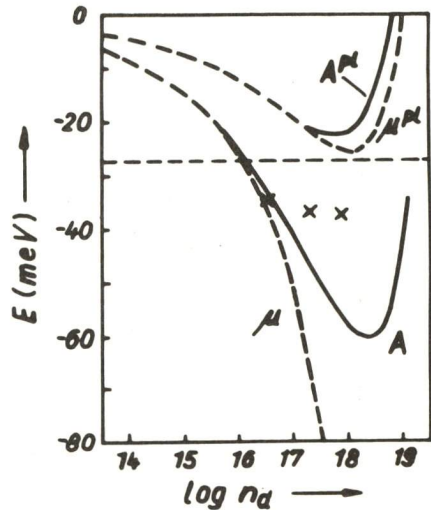


Fig. 5 μ^{re} , μ and absorption edge A^{re} , A for non-excited doped CdS calculated without and with impurity induced self-energies resp. compared to experimental values for A (crosses) deduced from $\alpha d = 4.2$

in the case of unexcited (low intensity probe light only) doped samples the absorption edges (crosses) show no resemblance to A^{re} nor to the total A (Fig. 5), the difference between A and μ being mostly due to the dispersion in $\Delta^d(k)$.

Unfortunately by reasons not understood at present $\tilde{G}$ could not be obtained from a line focus modulation technique [9]. Of course Fig. (1) tells that the inversion region $\mu - \tilde{G}$ is much wider in the doped samples, but a quantitative estimate of $\tilde{G}$ can hardly be got and even expected from experiments on such small amplifying path lengths.

In conclusion a refined theory appears necessary to account for the surprisingly small variation of μ with doping and excitation. One must concede a possibly large deviation of the experimental situation from thermodynamical equilibrium and a rapid expansion of highly excited surface plasma into the bulk of the crystal which might adjust the concentrations to only small excitation dependence even if one avoids too large lateral dimensions [10].

- 1) N.F. Mott: Metal-Insulator Transitions, Taylor & Francis 1974.
- 2) J.C. Hensel et al.: Solid State Phys. **32** (1977) 87.
- 3) G.O. Müller et al.: Proc. 14. ICPS Edinburgh 1978, p. 165.
- 4) G.O. Müller et al.: phys. stat. sol. (b) **91** (1979) 531.
- 5) H.J. Fischbeck: phys. stat. sol. (b) **69** (1975) 113.
- 6) M. Rösler et al.: phys. stat. sol. (b) **83** (1977) 85.
- 7) B. Bergersen et al.: Phys. Rev. **B14** (1976) 1633, **B15** (1977) 2432.
- 8) G. Mahler and J.L. Birman: Phys. Rev. **B12** (1975) 3221.
- 9) J.M. Hvam: J. Appl. Phys. **49** (1978) 3124.
- 10) W.D. Egorow: phys. stat. sol. (b), to be published.