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Direct Electron-Hole Recombination in Cadmium Sulfide

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(1. V. 68)

Abstract. By strong photoexcitation of single crystals of CdS, free carriers were generated, whose number appeared to be proportional to the cubic root of exciting light intensity. It is suggested that this behaviour is due to direct radiative recombination between free holes and electrons. The recombination coefficient, as obtained from a modified van Roosbroeck-Shockley calculation and experimental data, gives reasonable order of magnitude of hole lifetime and diffusion length, and further gives an order of magnitude of the hole diffusion coefficient that is consistent with previous determinations.

In the compound semiconductors of IIB-VIA type, like cadmium sulfide, the electrical conductivity is known always to be *n*-type [1-3]. It is believed that holes, injected or photoelectrically created, are trapped in deeplying centers after a short time. Only indirectly, from investigations including magnetic phenomena, one can estimate the magnitude of the mobility and lifetime of holes in CdS to about $(1/10) \mu_n \simeq 20 \text{ cm}^2/\text{volt sec}$ and 10^{-8} to 10^{-6} sec, respectively [3-6].

By illuminating single crystal plates of cadmium sulfide with intensive light of photon energy greater than the fundamental gap, photoconductivity, as well as free carrier optical absorption, was observed [7]. As is seen from Figure 1 the variation of the absorption coefficient and of the conductivity with the intensity of exciting light were identical, with possible exception of the inaccurately determined low-level values. The variation is strongly sublinear and follows well a cubic root law. The only simple recombination process that would give such a variation is the Auger process. The Auger recombination, however, is known to have a small probability, compared to other processes. The following discussion will bring arguments for the conception that at the actual high excitation level the different indirect recombination steps are overbridged, and the phenomenon is to be understood in terms of ambipolar diffusion and direct recombination of electrons and holes.

The penetration depth of the exciting light is less than one micron, and the ionization will thus be considered as occurring at the surface. We then presume a predominating bimolecular recombination between electrons and holes, both of concentration n , far in excess of the equilibrium density. The one-dimensional diffusion equation, ruling the diffusion of carrier pairs in the direction x , perpendicular to the illuminated surface, will then be:

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - \varrho n^2. \quad (1)$$

Here, D is the ambipolar diffusion coefficient, probably near equal to the diffusivity for holes, D_p , if $D_p \ll D_n$. The recombination coefficient $\varrho = \langle \sigma(v_r) v_r \rangle$, connected with the recombination cross section σ and the relative velocity v_r , will be discussed below. For the stationary state, $\partial/\partial t = 0$, the solution of Equation (1) is

$$n(x) = n(0) \left\{ 1 + \left(\frac{\varrho n(0)}{6D} \right)^{1/2} x \right\}^{-2} \quad (2)$$

provided $n(\infty) = 0$ (thick sample).

The boundary condition, giving $n(0)$, is:

$$-D \left(\frac{dn}{dx} \right)_{x=0} = \varphi_{eff} - S(n(0)), \quad (3)$$

where φ_{eff} is the effective photon flux per unit area and $S(n(0))$ is the surface recombination term. Supposing S be neglected, we get from Equations (2) and (3)

$$n(0) = \left(\frac{3 \varphi_{eff}^2}{2 \varrho D} \right)^{1/3}. \quad (4)$$

The quantity which is determined through the conductance as well as through the absorption coefficient, is the surface carrier concentration:

$$N = \int_0^{\infty} n(x) dx.$$

From Equations (2) and (4):

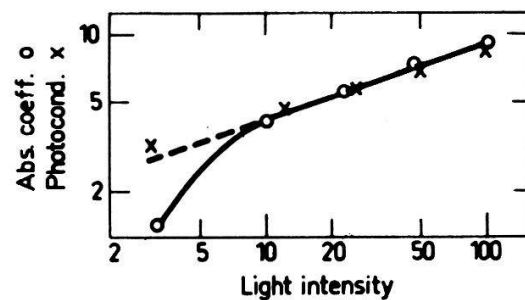
$$N = \left(18 \frac{D}{\varrho^2} \varphi_{eff} \right)^{1/3}. \quad (5)$$

This agrees with the experimental curve in the Figure.

The direct recombination is the reverse of the fundamental optical absorption and can be calculated according to the theory of VAN ROOSBROECK and SHOCKLEY [8], using the concept of detailed balancing. For an anisotropic crystal, like CdS, their formula has to be modified [9]. With optical data for cadmium sulfide, [10], from such a calculation we obtain

$$\rho = 1.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1},$$

which means $\langle \sigma \rangle \sim 10^{-17} \text{ cm}^2$. The order of magnitude of ρ or σ confirms the theoretical result [11] that CdS is a direct material.



Absorption coefficient (○) and electrical conductivity (×) of CdS as functions of intensity of exciting light. Arbitrary units. $T = 330^\circ \text{K}$.

In order to apply the model developed here on our experiments, the effective photon flux,

$$\varphi_{eff} = \int (1 - R(\nu)) \eta(\nu) I(\nu) d\nu \quad (6)$$

has to be determined. This is extremely difficult, since it does not only involve the spectral intensity I and the surface reflectance of the sample R , but also the quantum yield η , which is unknown and may be frequency-dependent. Supposing $\eta = 1$ in the whole actual interval, we obtain from the black temperature of the light source (xenon discharge lamp), $\varphi_{eff} \simeq 1.3 \times 10^{20} \text{ cm}^{-2} \text{ s}^{-1}$. The measured conductance and the known electron mobility ($\mu_n = 160 \text{ cm}^2/\text{volt sec}$) determines N . In a typical run, $N = 4 \times 10^{13} \text{ cm}^{-2}$. Then, solving Equation (5) for D

$$D \simeq 0.4 \text{ cm}^2/\text{s}$$

which is the order of magnitude previously obtained [5, 6].

From Equation (4) one obtains $n(0) \sim 10^{17} \text{ cm}^{-3}$ and thus $1/\rho n(0) \sim 10^{-7} \text{ sec}$. This value is of the same order of magnitude or less than the hole lifetime obtained for low excitation levels. A suitable definition of ambipolar diffusion length is, due to Equation (2)

$$x_d = \left(\frac{6D}{\rho n(0)} \right)^{1/2} \simeq 5 \times 10^{-4} \text{ cm} \left(n(x_d) = \frac{1}{4} n(0) \right),$$

which is an order of magnitude larger than the average penetration depth of the ionizing photons.

The conclusion is that under the actual conditions, direct radiative hole-electron recombination may successfully compete with the ordinary hole trapping process. More accurate tests of the validity of the suggested model should be possible from, for example, studies of photo-electromagnetic effect.

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On the Conductivity Character of Rare-Earth Compounds

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(1. V. 68)

Abstract. The conductivity type of the rare-earth compounds is correlated with the electronic configuration of the cations. Simple halides, chalcogenides, pnictides as well as dihydrides, dicarbides and hexaborides are briefly discussed.

My interest in rare-earth compounds derives from the search of ferromagnetic semiconductors which was proposed to me as early as 1955 by Prof. G. BUSCH. It is a great pleasure for me, therefore, to honour Prof. BUSCH on his 60th birthday by dedicating to him the present notes on rare-earth compounds, the physics of which has been elucidated considerably by his investigations.

With certain exceptions the rare-earth atoms Ln in chalcogenides, pnictides or even in intermetallic compounds behave like transition elements of the scandium group with additional f electrons in discrete levels. The exceptions reflect the small differences in the ionization energies of the f electrons of $4f^q$ cations. Because of the strong spin-orbit coupling and the small radius of the $4f$ electrons the crystal field is

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