

TWO PARALLEL MECHANISMS OF CARRIER CAPTURE ON ONE RECOMBINATION CENTER

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Fig. 1

Figure 1: Fig. 1

Abstract**Full Text**

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PHYSICS**M. K. SHEINKMAN, A. V. LYUBCHENKO****TWO PARALLEL MECHANISMS OF CARRIER CAPTURE ON ONE RECOMBINATION CENTER***(Presented by Academician A. V. Shubnikov on 21 VII 1965)*

The existence, repeatedly described, of several parallel recombination channels in semiconductors is associated with the presence in them of several kinds of corresponding centers (levels). We are not aware of cases in which carrier recombination proceeds along several channels through one type of recombination center. In the present communication it is shown that such a situation is observed in CdS, where the capture of a hole by the so-called sensitizing recombination r -center can proceed in parallel by two paths—through a certain excited state and bypassing it.

According to the generally accepted model ⁽¹⁾, infrared (i.r.) quenching of the photocurrent in CdS is caused by transfer of a hole from the r -center to the v -zone either directly by a quantum $h\nu_1 = 1.4$ eV, or first to an excitation level (by a quantum $h\nu_2 = 0.9$ eV) with subsequent thermal excitation—transitions 1 and 2 in Fig. 1a. Some of the liberated holes then rapidly recombine with free electrons through s -centers of fast recombination ^(1–3).

Fig. 1. *a*—optical and thermal transitions of a hole in an r -center upon absorption of i.r. quanta of 1.4 and 0.9 eV (transitions 1 and 2). *b*—two parallel processes (channels) of hole capture on an r -center (transitions 1 and 2)

We investigated the kinetics of i.r. quenching by the methods of ^(2,3) when CdS single crystals were illuminated with weakly absorbed bias light, on which was superposed a short $\Delta t_i \ll \tau$ (τ is the smallest of the photocurrent relaxation times) weak i.r. pulse from both quenching maxima (1.4 and 0.9 eV).

For the direct transition (1) the amplitude of the decrease in the concentration of free electrons in the quenching pulse is equal to ^(2,3)

$$v_1 = g_s \gamma_1 I_1 P_r,$$

where γ_1 is the capture cross section for an i.r. quantum of 1.4 eV; I_1 is the total number of quanta in the pulse incident on 1 cm²; P_r is the concentration of holes on r -centers, and g_s is the fraction of the total number of liberated holes ($\gamma_1 I_1 P_r$) that were captured on s -centers. The amplitude for the combined transition 2 is

$$v_2 = g_s \gamma_2 I_2 P_r B \exp(-E_B \beta) [A + B \exp(-E_B \beta)]^{-1},$$

where γ_2 and I_2 are the capture cross section and the number of 0.9 eV quanta; A is the probability of return of an excited hole to the ground state; $B \exp(-E_B \beta)$ is the probability of thermal transition of a hole from the level E_B to the v -zone; $\beta = 1/kT$;

T is the absolute temperature. The frequency factor B is related to the capture cross section of a hole to the excited level of the r -center S_B : $B = S_B v Q_v$; v is the thermal velocity of a hole; Q_v is the statistical factor of the v -band. Obviously, the dependence

$$\frac{A}{B} \exp(E_B \beta) = \left[\frac{v_1}{v_2} \left(\frac{v_2}{v_1} \right)_{\infty} \left(1 + \frac{A}{B} \right) - 1 \right] \equiv \psi(T),$$

where v_2 and v_1 are measured experimentally, and $(v_2/v_1)_{\infty}$ is the limiting value of v_2/v_1 at high T , makes it possible to find E_B and A/B (here it is essential that $A/B \ll 1$; see below).

For a typical CdS specimen No. 17, $\psi(T)$ is shown in Fig. 2a, curve 1. For the 7 specimens investigated, E_B lay within the limits $E_B = (0.39 \pm 0.02)$ eV and $A/B = 10^{-7} \div 3 \cdot 10^{-9}$. We note that this value of E_B is twice as large as the estimate of E_B given in ^(1,4), where, however, no direct measurements of this quantity were made. In a recent work ⁽¹⁰⁾ the authors find an activation energy of 0.41 eV in CdS, but give it another explanation.

Measuring v_1 and v_2 by the methods of ^(2,3), we also determined the cross sections γ_1 and γ_2 . They turned out to differ little: $\gamma_1 \simeq (1 \div 5) \cdot 10^{-16}$ cm² and $\gamma_2 \simeq 0.3 \cdot 10^{-16}$ cm². Knowing γ_2 and the half-width of the quenching band (0.2 eV), one can find the oscillator strength for the transition of a hole to the excitation level, and from this, considering the reverse transition radiative ⁽⁵⁾, estimate A . This estimate gives $A \sim 10^7$ s⁻¹. Consequently, $B \sim 10^{15}$ s⁻¹ and $S_B \sim 10^{-11}$ cm² (for $v = 10^7$ cm/s and $Q_v = 3 \cdot 10^{19}$ cm⁻³). The large value of B obtained appears, however, quite possible if it is compared with theoretical results for the F -center ⁽⁵⁾.

From the described model of the r -center* (Fig. 1a) there follows an important consequence for the process of hole capture by an r -center. Indeed, if in the

capture process to the ground state the hole necessarily passes through the excited state E_B (transition 2, Fig. 1b), then the presence of thermal emission from there into the v -band (the so-called thermal barrier; see ⁽⁶⁻⁸⁾) will lead to an obvious temperature dependence of the cross section for hole capture by the center

$$S_1 = S_B \left[1 + \frac{B}{A} \exp(-E_B \beta) \right]^{-1}.$$

Consequently, at high T , when the long-wavelength IR quenching (v_2) ceases to depend on T ($B \exp(-E_B \beta) \gg A$), the cross section S_1 , on the contrary, should fall exponentially with increasing T , with activation energy E_B . The fall of S_1 will lead to a sharp decrease in the probability of hole capture by r -centers g_r , which is proportional to S_1 ⁽²⁾, and this, in turn, will cause temperature quenching of the stationary photocurrent I_ϕ with activation energy E_B , since recombination will now proceed through s -centers of fast recombination. In experiment, however, we never observed such a phenomenon. Strong temperature quenching, as usual, occurred at considerably higher temperatures ($T > 400^\circ\text{K}$) and its activation energy was 1.0-1.2 eV.

Kinetic methods ⁽²⁾ allowed us to measure $g_r(T)$ directly for all 7 crystals. For specimen No. 17, $g_r(T)$ and $I_\phi(T)$ are given in Fig. 2b. As is seen, in the actual temperature range ($-80 \div +20^\circ\text{C}$) the decrease of g_r and I_ϕ with increasing T does not exceed 40%, and subsequently g_r and I_ϕ do not fall.

We found a way out of the described situation by assuming that, simultaneously with the capture process through the excited state E_B (transition 2, Fig. 1b), the hole can enter the ground state by another path as well, bypassing this excited state—transition 1, Fig. 1b, with capture cross section S_p . Such a transition in principle may be either direct, i.e., radiative, or be effected through another (other) excited state (not

* It is analogous to the model of a V' -center in alkali-halide crystals.

E_B); the essential point is only that in this process the thermal barrier does not appear in the temperature range under consideration.

If it is assumed that both capture mechanisms 1 and 2 compete and, moreover, that holes are captured at s -centers, the following dependence can be obtained for $g_r(T)$:

$$\frac{A}{B} \exp(E_B \beta) = \left[\frac{\alpha g_{r\infty} (1 - g_r)}{g_r - g_{r\infty} + g_r (1 - g_{r\infty}) \alpha (1 + B/A)^{-1}} - 1 \right]^{-1} \equiv \varphi(T),$$

where $g_r(T)$ is measured experimentally (see Fig. 2), $g_{r\infty}$ is the limiting value of $g_r(T)$ at high T ; $\alpha = S_B/S_p$ is the ratio of the cross sections for the two

Figure 2

Figure 2: Figure 2

capture processes. The dependence of $\log \varphi$ on $1/T$ —curve 2 in Fig. 2a—taking into account, as

Fig. 2. **a**—temperature dependences of the expressions ψ (1) and φ (2), obtained respectively from the process of infrared quenching of the photocurrent and from the recombination process g_r . —temperature dependences of the steady-state photocurrent I_ϕ and of the probability of hole capture at r -centers g_r ; — temperature dependence of the cross section for hole capture at the r -center S in the presence of two parallel capture processes; $\alpha = 10$, $B/A = 10^8$, $E_B = 0.38$ eV

before, $A/B \ll 1$ makes it possible to find the quantities E_B and A/B . The values of α are found from the expression

$$\alpha = \left(1 + \frac{A}{B}\right) \frac{g_{r0} - g_{r\infty}}{g_{r\infty}(1 - g_{r0}) - (g_{r0} - g_{r\infty})A/B},$$

where g_{r0} is the limiting value of $g_r(T)$ at low temperatures.

The values of E_B and A/B obtained in this way for all samples lay within the ranges $E_B = (0.34 \div 0.37)$ eV, $A/B = 10^{-7} \div 5 \cdot 10^{-9}$, which agrees well with the values of E_B and A/B obtained above from the infrared-quenching process. One may suppose that the level E_B corresponds to the lowest excited state of the hole in the r -center, into which it enters as a result of a multistep process⁽⁹⁾; the subsequent transition A is radiative.

The values of α (taking into account the accuracy of measuring g_r) lay within $\alpha = 5 \div 20$ for all samples. From the known values of α , E_B , and B/A , the temperature dependence of the cross section for hole capture at the r -center was constructed,

$$S = S_p \left\{ 1 + \alpha \left[1 + \frac{B}{A} \exp(-E_B \beta) \right]^{-1} \right\},$$

which is shown in Fig. 2.

The possibility, demonstrated in the present work, of the simultaneous existence of two different mechanisms (channels) for carrier capture at a center should be taken into account both in interpreting recombination and luminescence processes at impurity centers in semiconductors and in studying the properties of various F - and V -centers in alkali-halide crystals.

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