

Picosecond kinetics of IR reflection and transmission in highly excited II-VI crystals

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The time evolution of the reflection and transmission of picosecond light pulses at a wavelength $\lambda = 2.8 \mu\text{m}$ in single crystals of CdSe and CdS_{1-x}Se_x excited by an intense pulse of a strongly absorbed light is studied. A competition among several mechanisms for the modulation of a complex refractive index of a substance is found to exist.

A very dense electron-hole plasma ($n \sim 10^{20} \text{ cm}^{-3}$) can be produced in semiconductors by exciting them with strong picosecond light pulses. Under these conditions it is generally assumed that the free nonequilibrium charge carriers are principally responsible for the IR-range modulation of the complex refraction index, and hence the reflection and absorption factors, of a substance.^{1,2} Our study of the dynamics of the optical properties in the IR range of direct-gap II-VI crystals showed that there is another competing mechanism with impurity centers.

We studied bulk single-crystal samples of CdSe and CdS_{1-x}Se_x, synthesized as parallel-plane plates of thickness 1–2 mm, with polished surfaces. As the master oscillator of picosecond light pulses we used a garnet laser ($h\nu = 1.17 \text{ eV}$) with an active-passive synchronization of modes. The isolated single pulses with a pulse repetition rate of 10 Hz were amplified by a four-channel amplifier. The crystals were pumped by a second-harmonic light of the fundamental frequency of the laser ($h\nu = 2.33 \text{ eV}$) with a maximum pulse energy of 1 mJ. Sensing was performed by an IR beam ($\lambda = 2.8 \mu\text{m}$) produced in a stimulated-Raman cell filled with methane, into which a fraction of the fundamental-frequency light from a picosecond laser was introduced. The pumping and sensing beams were aimed in the direction perpendicular to the surface of the samples. To analyze the most homogeneous region, we chose the beam diameters to be 1 mm and 0.3 mm, respectively. Calibrated photodiodes, whose signals were statistically analyzed by a microcomputer, were used to measure the strength of the reflected pulses and the pulses transmitted through the crystal. This microcomputer was also used to control the line of the optical delay between the pumping and sensing pulses.

Figures 1 and 2 show the experimental kinetics of reflection (upper curve, crosses) and transmission (lower curve, crosses), respectively, in CdSe and CdS_{0.6}Se_{0.4} crystals. On these curves we can single out a fast component and a slower component which is characteristic of the kinetics of the transmission in CdSe and in CdS_{1-x}Se_x. If, on the other hand, only a fast decay and recovery of the reflection is seen in the CdSe crystals, the behavior of a solid solution of CdS_{0.6}Se_{0.4} is such that the reflection changes sign and relaxes sufficiently slowly (on a time scale of $\sim 1 \text{ ns}$) to the original value upon completion of the exciting pulse (Fig. 2). It should be noted that this

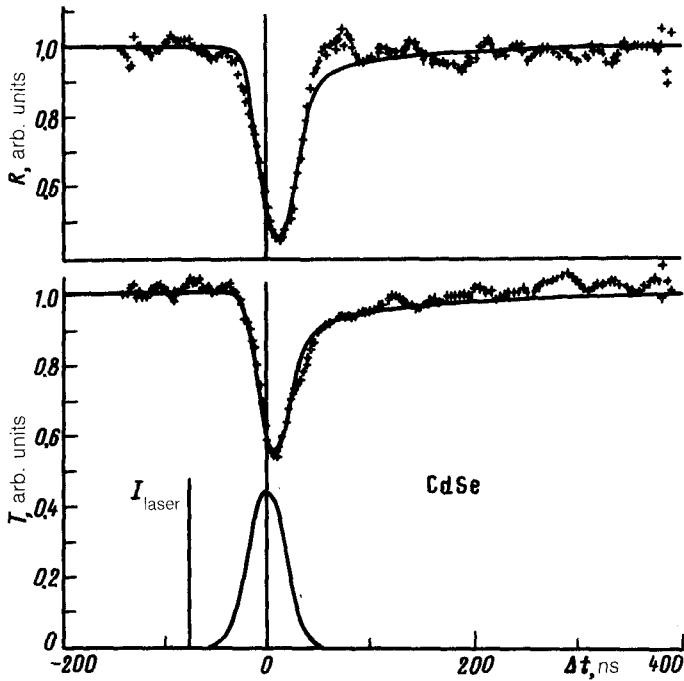


FIG. 1. The kinetics of reflection (upper plot) and transmission (lower plot) of the sensing light in CdSe single crystals at a pulse excitation energy of $\sim 300 \mu\text{J}$. Crosses—Experimental data; solid curves—calculation (see the text proper) carried out for the following parameter values: $I_0/h\nu d = 10^{31} \text{ cm}^{-3} \text{ s}^{-1}$, $\gamma_1 = 4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, $\gamma_2 = 8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, $\gamma_0 = 3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, $\tau_R = 5 \text{ ns}$, $N = 1.5 \times 10^{17} \text{ cm}^{-3}$, $\sigma^a I/h\nu = 3 \times 10^{11} \text{ s}^{-1}$, $\sigma^n I/h\nu = 2 \times 10^{12} \text{ s}^{-1}$, $\sigma_0 = 1.4 \times 10^{-14} \text{ cm}^2$.

behavior cannot be explained in terms of the plasma resonance,² since the reflection reaches the minimum value the second time in this case upon completion of the exciting pulse and only then relaxes to the original value. A doubt regarding the exclusive participation in this process of free nonequilibrium charge carriers results in a rather slow restoration of the reflection and transmission, since the lifetime of the nonequilibrium charge carriers in the direct-gap crystals should be much shorter, at these excitation levels, during the time interval under consideration because of the induced radiative transition and bimolecular recombination.³ A high level of imperfection of the solid solutions compared with the original II-VI compounds⁴ and a correlation between the slow parts of the kinetics of reflection and transmission (Fig. 2) suggest that impurity levels participate in the process. Analysis of various optical-transition models showed that all of the observable structural features can be explained in terms of only one recombination center which clearly is the ionized donor (see the inset in Fig. 2). In this case the kinetic equations for the concentration of nonequilibrium charge carriers, n , and neutral impurity centers, N^0 (those capable of absorbing the sensing beam) which constitute the total concentration N , after discarding the diffusion terms in them because of the short time interval, become

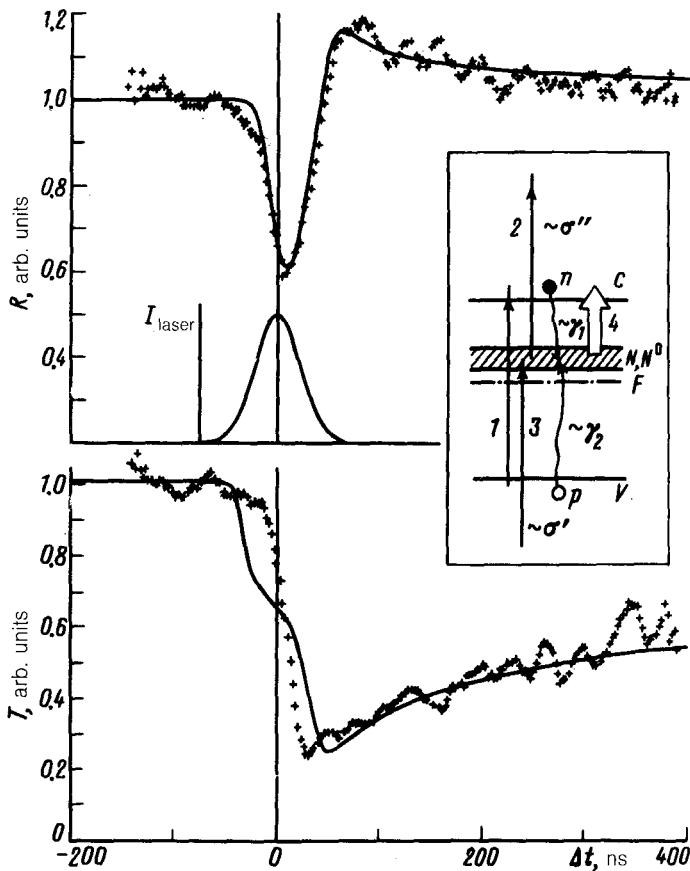


FIG. 2. Time evolution of the reflection (upper plot) and the transmission (lower plot) in single crystals of $\text{CdS}_{1-x}\text{Se}_x$. The conditions are the same as those given in Fig. 1. The concentration of the impurity centers $N = 3 \times 10^{18} \text{ cm}^{-3}$ was used in the calculation of the theoretical solid curves. The diagram of the optical transitions is shown in the inset.

$$\frac{dn}{dt} = \frac{I}{h\nu d} - \gamma_b n^2 - \frac{n}{\tau_R}, \quad (1)$$

$$\frac{dN^0}{dt} = \sigma' \frac{I}{h\nu} (N - N^0) - \sigma'' \frac{I}{h\nu} N^0 + \gamma_1 n (N - N^0) - \gamma_2 n N^0. \quad (2)$$

Here $I = I_0 \exp(-t^2/\tau^2)$ is the excitation power density with a characteristic Gaussian parameter $\tau \approx 20$ ps, γ_b is the bimolecular recombination coefficient of the non-equilibrium charge carriers, γ_1 and γ_2 are respectively the coefficients of the trapping of an electron and a hole, and σ' and σ'' are the cross sections for the capture of a photon of the exciting light by an impurity level in transition 3 and transition 2, respectively (see the inset in Fig. 2). In the model it is assumed that $n = p \gg N$ in the

time interval under consideration and that the excited region of thickness d is homogeneous. The time dependences n and N^0 determine the complex refractive index $\tilde{n} = n_R + ik$, which in turn is responsible for the reflection R and transmission T . In the case of a perpendicular incidence of the sensing beam we have

$$R = \frac{(n_R - 1)^2 + k^2}{(n_R + 1)^2 + k^2}, \quad (3)$$

$$T = (1 - R) \exp(-\alpha d). \quad (4)$$

Here $\alpha = \alpha_0 + \sigma N^0$ is the resultant absorption coefficient, where α_0 is attributable to the free nonequilibrium charge carriers, and σ is the cross section for the capture of a sensing-beam photon by an impurity center (transition 4 in the inset in Fig. 2). Using the familiar relations for the complex optical constants,⁵ the formulas for the Drude model,^{1,2} and Eqs. (1)–(4), we can calculate the kinetics of R and T . The results of such calculations are illustrated in Figs. 1 and 2 by the solid lines and the parameters used in the calculation are given in the figure captions. As we can see, the agreement is quite satisfactory if several arbitrary assumptions of the model are taken into account. Foremost among them is the assumption of the homogeneity of the excited region which actually contains a concentration gradient of nonequilibrium charge carriers and a filling gradient of the impurity levels. This assumption can apparently explain the more clearly defined differences between the experimental data and the theoretical curves for the kinetics of transmission in $\text{CdS}_{0.6}\text{Se}_{0.4}$ crystals with a larger concentration of impurity centers (the lower curves in Fig. 2).

We note in conclusion that the analysis carried out by us, in which we simultaneously compared the data on the kinetics of IR reflection and transmission of pulse-excited crystals, allows us to obtain information on the parameters of the recombination centers. In the case of solid solutions of $\text{CdS}_{0.6}\text{Se}_{0.4}$, for example, the optical transitions of an electron from the impurity level to the conduction band are more efficient than those from the valence band to the impurity level (arrows 2 and 3, respectively, in the inset in Fig. 2). The stored energy of this center is 0.1–0.44 eV, measured from the bottom of the conduction band, and the concentration is $3 \times 10^{18} \text{ cm}^{-3}$. Interestingly, the calculated concentration of such centers in CdSe is smaller by more than an order of magnitude.

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