On the nonlinear absorption of light in ZnO single crystals

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A study is made of the intrinsic two-photon absorption processes in semiconducting ZnO crystals. It is shown that the nonlinear absorption spectra of these crystals are shaped not only by two-photon absorption but also by two-step impurity absorption. The earlier suggestion of several authors that the two-photon absorption processes are affected by deep-lying valence states is not borne out.

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One of the remarkable properties of two-photon spectroscopy is the possibility of studying optical transitions which are one-photon forbidden, since the symmetry selection rules for these processes are substantially different. This property of two-photon absorption was used by Pensl[1] to explain the experimental results in ZnO, where the two-photon absorption coefficient has been observed to grow sharply in the short-wavelength part of the spectrum. This increase in the nonlinear absorption has been interpreted on the basis of theoretical band-structure calculations[2] for hexagonal ZnO as a manifestation of two-photon transitions from the Γ_6^v band, which is located below the top of the valence band, into the conduction band with symmetry Γ_1^c. One-photon transitions between these states are forbidden by symmetry. An analogous explanation has been given for the increase of the two-photon-excited photoconductivity of ZnO in the same spectral region.[3] The existence of such two-photon transitions has also been conjectured[4,5] for the crystals CdS and ZnS, but this has not been supported by subsequent studies.[6,7]

In the present paper we report the results of a study of the spectral dependence of the two-photon absorption in hexagonal ZnO crystals undertaken to ascertain whether the deep-lying valence states influence the two-photon absorption in this semiconductor. A two-beam technique was used to measure the two-photon absorption spectra. As modulating sources we used a neodymium-glass laser ($\hbar\omega_L = 1.17$ eV) and also the first Stokes component of its stimulated Raman scattering in compressed hydrogen ($\hbar\omega_S = 0.655$ eV). The experiments were carried out on an automatic two-photon spectrometer.[8] The measurements with the stimulated-Raman laser were made on a new apparatus providing pulse-by-pulse detection of the signals and also their storage and averaging. The single-crystal samples, which had their natural hexagonal-prism shape, were grown by a gas-transport method and were not deliberately doped.

The nonlinear absorption spectra obtained at 300 K are shown in Fig. 1. Solid curves 3 and 4 show the theoretical spectral dependence of the two-photon absorption for allowed-forbidden transitions in the two-band model of Bredikhin and Genkin[9] with the electron-hole Coulomb interaction taken into account. These curves agree satisfactorily with the experimental spectra in the region $\hbar\omega < 2.9$ eV. It should be noted that the given two-photon absorption mechanism is also dominant in other wide-gap II-VI compounds (CdS, ZnSe, ZnS).

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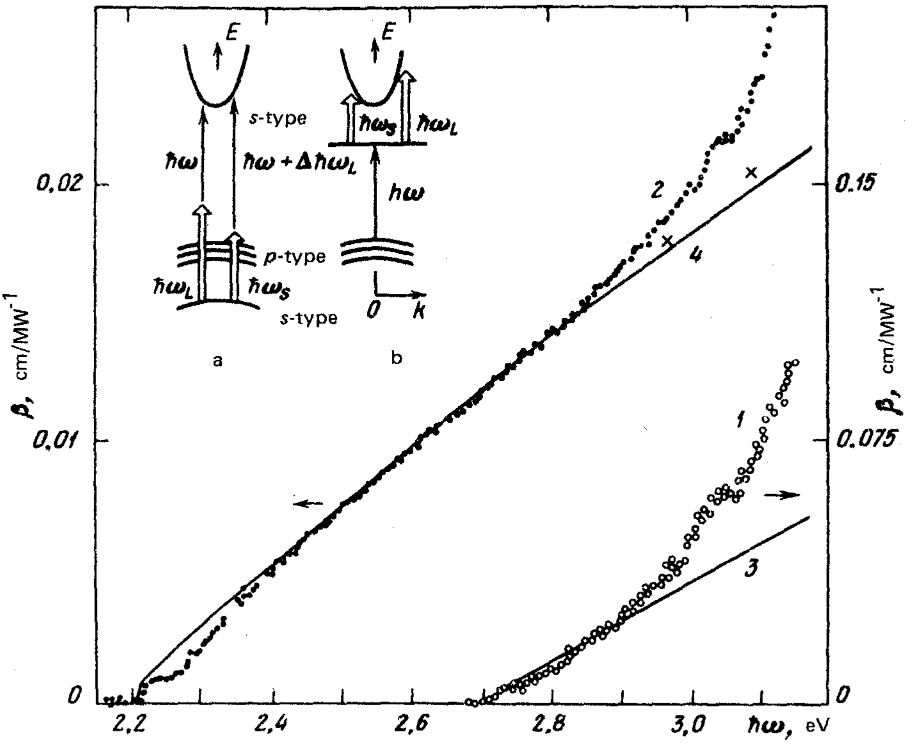

FIG. 1. Spectral dependence of the coefficient of nonlinear absorption of light in ZnO for cases with different modulating laser sources. 1) The spectrum obtained at $\hbar\omega_S = 0.655$ eV (40 MW/cm^2, at $\Delta t = 20$ nsec); 2) the spectrum for $\hbar\omega_L = 1.17$ eV (30 MW/cm^2); 3,4) the corresponding theoretical two-photon absorption spectra ($E_g = 3.38$ eV, $E_B = 42$ meV). The crosses indicate the values of the two-photon absorption constant extracted from the light-intensity measurements for spectrum 2. The inset shows two mechanisms for optical transitions, illustrating the difference in the reactions of these mechanisms to a change in the photon energy of the laser radiation: a) two-photon absorption from the deep-lying valence band Γ_6^v; b) two-step absorption through deep local states.

Our experimental two-photon absorption spectra (curves 1 and 2 in the figure) also display an increase in the nonlinear absorption in the short-wavelength part of the spectrum ($\hbar\omega > 2.9$ eV), corresponding to the same value of the photon energy of the probe light independent of the laser source used. Two-photon transitions, on the other hand, should begin at a definite combined energy of the absorbed photons equal to the energy gap between the Γ_6^v and Γ_1^c bands. The threshold values of the photon energy of the probe light for two-photon absorption should differ upon a change in $\hbar\omega_L$ by the difference between the photon energies of the lasers (see inset a in Fig. 1), which in this case is 1.17–0.655 = 0.505 eV. The experiment did not reveal a shift in the threshold of the additional absorption in ZnO on the scale of $\hbar\omega$ when a laser with a different photon energy was used; this suggests that the given absorption channel is due to an impurity mechanism. In fact, in the case of two-step absorption through deep local states in the band gap, the absorption edge is fixed by the equality of $\hbar\omega$ to the depth of the impurity level, independent of the photon energy of the modulating laser radiation. This situation is shown schematically in inset b in Fig. 1.

Characteristically, the impurity two-step absorption band has the same structure in spectra 1 and 2 (the dip at $\hbar\omega$ 3.05 eV), although its position with respect to the two-photon absorption edge is substantially different. The presence of structure in the two-step absorption band indicates that several types of deep centers participate in its formation. The presence of impurity nonlinear absorption effects in these experiments is also indicated by the light-intensity and polarization studies. From analysis of the light-intensity curves we separated out the contribution of the intrinsic two-photon absorption to the total absorption (indicated by crosses in Fig. 1), and the result agrees with the theoretical spectral dependence.

In conclusion we note that we did not observe in crystalline ZnO the previously conjectured substantial influence of deep-lying valence bands on the shape of the two-photon absorption spectra. The increase in the nonlinear absorption in the short-wavelength part of the spectrum observed by Pensl[1] and Koren[3] is evidently due to impurity two-step absorption processes.

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