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PHOTONEUTRALIZATION OF THE Fe^{3+} CENTERS IN THE ZnSe CRYSTALS HEAVILY DOPED WITH IRON

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Photoconductivity and optical quenching of the photoconductivity were measured. The photoneutralization of the Fe^{3+} centres has been found to occur for photon energies down to 0.8 eV (i.e. the threshold can not be at 1.1 eV, as often quoted). The conclusion from our previous paper that the lattice relaxation energy is small, has been confirmed. It has to be smaller than 0.1 eV.

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In ZnSe:Fe iron atoms substitute zinc and (speaking in the ionic language) in the Fe^{2+} charge state they are neutral with respect to the lattice. The presence of the Fe^{3+} (ionized) centres results from the compensation by shallow acceptors.

In our previous paper on the iron centres in ZnSe [1] we have described the first observation of the photoionization of the Fe^{2+} centres:

$$Fe^{2+} + h\nu \rightarrow Fe^{3+} + e_{CB} \tag{1}$$

and we have determined the optical ionization energy of the Fe^{2+} centres at 77 K— 2.1 eV $\pm$ 0.1 eV. As the thermal activation energy of the valence band — iron level transitions was found in the Hall effect measurements [2] to be 0.62 eV, and the energy gap at 77 K is 2.81 eV, we concluded that the lattice relaxation energy is small and the $Fe^{2+/3+}$ donor level in ZnSe is at 77 K both optically and thermally about 2.1 eV below the conduction band.

The aim of the present work was to reinforce those conclusions by the investigations of the photoneutralization transitions:

$$Fe^{3+} + h\nu \rightarrow Fe^{2+} + h_{VB}. \tag{2}$$

The transitions (2) were observed by Haanstra [2] in absorption. He found the threshold at 1.1 eV and ascribed the energy difference 0.48 eV = 1.1 eV − 0.62 eV to the large lattice relaxation. We disagree with this conclusion. In [1] we suggested that the threshold of the transitions (2) is actually at the lower photon energy, and the apparent threshold at 1.1 eV marks only the onset of the stronger transitions to the excited $^5T_2$ state of the iron centre (0.36 eV [3] above the ^5E ground state). Now we are going to show that the photoneutralization threshold is really below 1.1 eV.

The photoconductivity and optical quenching of the photoconductivity were measured in a single crystal of ZnSe:Fe ($2.2 \times 10^{19}\,cm^{-3}$). The electrodes were prepared by chemical deposition of a palladium–gold alloy. The photosensitivity spectrum measured between 0.8 eV and 1.7 eV at room temperature is presented in Fig. 1. It represents the spectrum of the photoneutralization cross section at

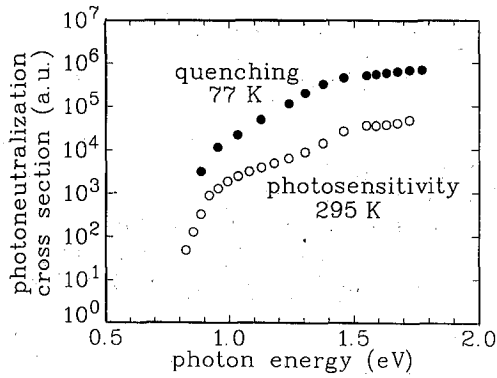

Fig. 1. The spectra of the photoneutralization transitions to the Fe^{3+} centres in ZnSe:Fe ($2.2 \times 10^{19}cm^{-3}$) derived from two different experiments: photosensitivity at 295 K – the D.C. photoconductivity and the relative value of the photon flux were measured at each point; quenching at 77 K – the photoionization current was generated by a steady flux of photons ($h\nu \approx 2.35$ eV). This photocurrent was quenched by the photons with varied $h\nu$ in the energy range 0.8÷1.8 eV.

room temperature on condition that the generation of holes from the Fe^{3+} centres dominates the photoconductivity in this region and the changes in the occupation of the iron level caused by the illumination can be neglected. At 77 K the photoconductivity below $h\nu \approx 2$ eV was too small to be measured. Nevertheless we observed the photoneutralization transitions by their quenching effect on the photoionization current. The photoconductivity spectrum at 77 K, related to the photoionization is presented in Fig. 2 and agrees well with the value of the optical

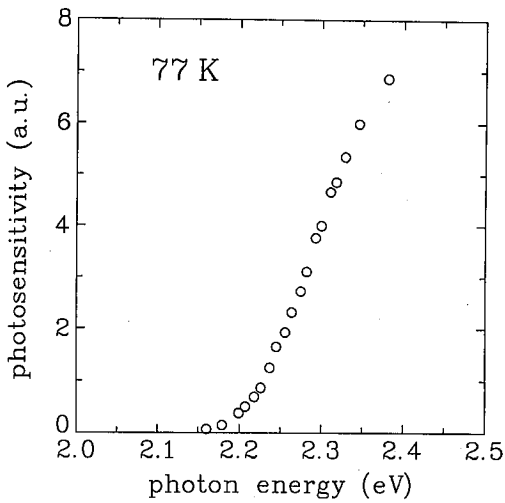

Fig. 2. The photoconductivity spectrum related to the photoionization of the Fe^{2+} centres in a ZnSe:Fe ($2.2 \times 10^{19}cm^{-3}$) crystal at 77 K.

ionization energy, determined in [1] from the absorption spectrum. It turned out that the photoionization current (carried by electrons) can be quenched by photons in the $0.8 \div 2$ eV energy range. It is practically an evidence that in this whole photon energy range the generation of holes by the photoneutralization transitions (2) occurs.

To obtain the spectrum of photoneutralization — the photocurrent I_1 was generated by a steady flux of photons with 2.3 eV $\leq h\nu \leq$ 2.4 eV. A second illumination with varied $h\nu$ and known relative photon flux $\Phi_2(h\nu)$ quenched the photocurrent from the value I_1 to the value $I_{12}(h\nu)$. We assume the following:

(a) the changes in the occupation of the iron level caused by the illuminations, the dark concentrations of electrons and holes, the thermal emission rates and the photocurrent carried by holes can be neglected;

(b) the recombination between the bands is proportional to the product np;

(c) the capture of a hole by the Fe^{2+} centre is much more likely than the recombination with a band electron. Then, we have a simple relation for the photoneutralization cross section:

$$\Sigma_p(h\nu) \propto \frac{I_1 - I_{12}(h\nu)}{I_{12}(h\nu)\Phi_2(h\nu)}. \tag{3}$$

The photoneutralization spectra derived from quenching at 77 K and from photoconductivity at room temperature are presented together in Fig. 1. The two

spectra are very similar (which means that at low photon energies the photoneutralization of iron really dominates the photoconductivity). The threshold cannot be determined, but certainly it is not at 1.1 eV and has to be below 0.8 eV. This information together with the previously determined photoionization threshold 2.1 ± 0.1 eV set the limits for the distance between the $Fe^{2+/3+}$ donor level and the valence band. It should be below 0.8 eV and above 0.6 eV ($E_g - 2.2 = 0.6$ eV). The lattice relaxation energy has to be smaller than 0.1 eV.

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