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Co²⁺ CENTRES IN ZnTe CRYSTALS HEAVILY DOPED WITH COBALT*

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Co²⁺ centre in ZnTe has been proved to be an acceptor, contrary to the previous assignment, but in agreement with the general trend in the behaviour of the transition metal impurities in the II-VI compounds. The threshold of the $\text{Co}^{2+} + h\nu \rightarrow \text{Co}^{1+} + h$ transition has been found in the spectrum of photoconductivity at about 1.4 eV, close to the value already reported.

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There has been only one paper describing the photoionization of the Co centres in ZnTe. Gnatenko et al. [1] studied the optical absorption of ZnTe:Co at 4.5 K, and from the analysis of the spectrum they derived the value of the optical ionization energy of an alleged donor as 1.53 eV. They mentioned the onset of the photoconductivity at 1.38 eV.

The analysis of the optical spectra is very difficult, because for Co²⁺ in ZnTe the photoionization transitions occur in the same range of the photon energies as the strong intracentre transitions. A combination of the absorption measurements with other types of measurements has obvious advantages. While measuring the photoconductivity spectra we have confirmed the position of the photoionization threshold, but the transport experiments allowed us to show unambiguously that the Co²⁺ centre is an acceptor (not a donor).

We have studied the ZnTe crystals heavily doped with cobalt (up to 1 at.%) and the crystals co-doped with aluminium (about 10^{19} cm^{-3}). The crystals were grown in our laboratory by a modified Bridgman method. The absorption spectra were measured and the presence of very strong absorption bands characteristic of Co²⁺ confirmed the presence of huge amounts of the cobalt centres in the Co²⁺ charge state.

The photoconductivity spectra were measured for both types of crystals and are presented in Fig. 1 and Fig. 2. In both figures one can see the threshold at about 1.4 eV. This threshold corresponds to the threshold observed by Gnatenko et

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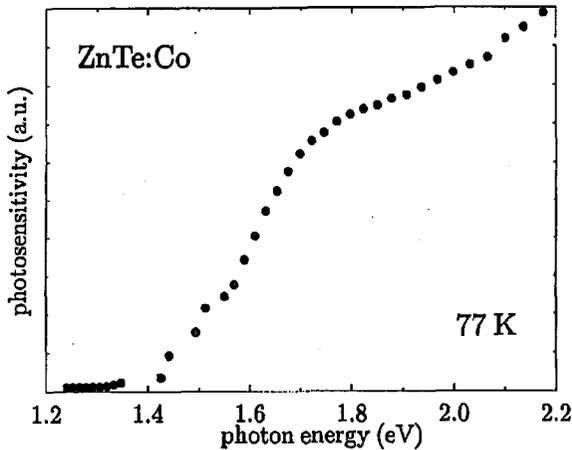


Fig. 1. The photoconductivity spectrum of a ZnTe:Co crystal at 77 K. The modulated illumination was used and the photosensitivity was defined as the AC signal divided by the photon flux. The dependence of the signal on the photon flux was checked to be nearly linear. The regions of the strong intracentre transitions (1.36–1.41 eV and 1.45–1.49 eV) were omitted in the measurement. The photoconductivity was relatively fast, and the spectrum of the steady-state photoconductivity was very similar to the presented one.

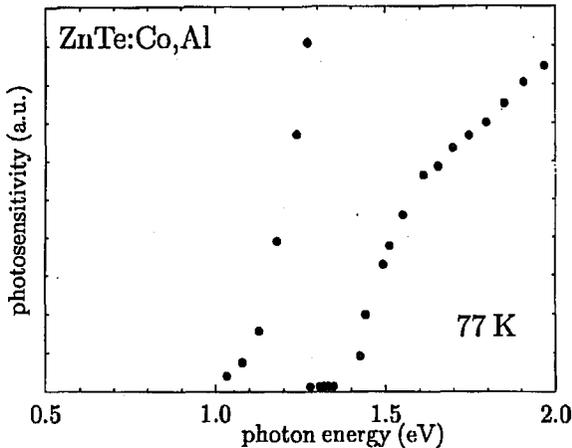


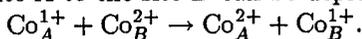
Fig. 2. The photoconductivity spectrum of a ZnTe:Co,Al crystal at 77 K. The photosensitivity was defined as the measured steady-state value of the photoconductivity divided by the photon flux. The photoconductivity below 1.3 eV (presented on an extended scale) was measured with an InP filter to avoid illumination by the light scattered in the monochromator.

al. [1], who interpreted it as the threshold of the photoionization of the Co^{2+/3+} donors. According to such an interpretation, the Co^{2+/3+} donor level would lie more than 1 eV over the valence band, and in our samples, because of the high concentration of the cobalt centres — the acceptor levels lying below the cobalt level as well as the valence band would be filled with electrons (stripped of holes). Our measurements of the transport properties of the ZnTe:Co crystals have shown something quite opposite.

The Hall effect and thermoelectric power were measured. Both measurements have indicated that the current carriers are holes. The measurement of the temperature dependence of conductivity gave the activation energy as 0.14 eV, which means that shallow acceptors control the transport in the valence band. These results exclude the possibility of a Co^{2+/3+} donor level lying above 1 eV over the valence band. Thus, we have proven the acceptor character of the Co²⁺ centres and we ascribe the observed photoionization to the transition: Co²⁺ + $h\nu$ → Co¹⁺ + hole. The Co^{2+/1+} acceptor level lies at 1.4 eV (minus part of the Franck–Condon shift) over the valence band.

The acceptor character of the Co²⁺ centre in ZnTe and the value of the ionization energy are in agreement with the general trend in the behaviour of the transition metal impurities in II–VI compounds [2, 3]. On the ground of this widely accepted trend, the description (Gnatenko et al. [1]) of the Co²⁺ centres in ZnTe as donors has been already criticised in Refs. [2, 4].

Having established the acceptor character of the Co²⁺ centres in the ZnTe, we will be able to understand the observed properties of the ZnTe:Co,Al crystals, in which the Co acceptors are partially compensated by shallow Al donors. Such compensated crystals significantly differed from the crystals doped solely with Co. The conductivity turned out to be very low, the measurement of the thermoelectric power indicated a negative sign of the current carriers and the Arrhenius plot of the temperature dependence of conductivity presented straight line between 77 K and 293 K, with the activation energy of 0.16 eV. Because the concentration of the Co acceptors is much higher than the concentration of all donors (in particular Al donors), the levels above the Co^{2+/1+} level are empty, and the activation energy of 0.16 eV cannot describe the transport in the conduction band controlled by a shallow level. We suggest that the conductivity of our ZnTe:Co,Al crystals is due to the thermally activated hopping of electrons between cobalt centres, similarly to the case of (Zn,Ni)Se crystals [5]. In such hopping a jump of an electron from the site *A* to the site *B* can be depicted as



We believe that the number of electrons from the Al donors was sufficient to fill all the levels (belonging to the residual impurities) below the cobalt acceptor level and to turn some of the cobalt centres from the Co²⁺ into the Co¹⁺ charge state, enabling the hopping.

The idea of a non-band transport in the ZnTe:Co,Al crystals has found an additional support in the Hall effect. The Hall voltage at room temperature was unmeasurably small, indicating mobilities below 0.4 cm²/(V s).

Beside the photoionization threshold at 1.4 eV discussed above, there is another threshold in the photoconductivity spectrum of the ZnTe:Co,Al crystals

at about 1.1 eV at 77 K. As we already explained, in those compensated crystals any levels below the cobalt level are filled with electrons. Therefore, the energy of 1.1 eV is too small for the transitions of holes from any impurities to the valence band, and the transitions in question have to be electron transitions to the conduction band either from unknown donor levels situated close to the cobalt levels or just from the Co^{1+} centres. We suspect the second case.

As the threshold energies for the optical transitions from the deep impurity to both bands lie between the corresponding thermal and optical ionization energies, the sum of the observed threshold energies compared with the energy gap determines a lower limit of the Franck-Condon shift as 0.06 eV.

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