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Compensation of hole conductivity in CdTe crystals doped with Cr

E.S. Nikonyuk¹, Z.I. Zakharuk², M.I. Kuchma¹, M.O. Kovalets¹,
A.I. Rarenko², I.M. Yuriychuk²

¹National University of Water Management and Conservation

11, Soborna str., 35011 Rivne, Ukraine; phone: (0362)230420, e-mail: semirivne@mail.ru

²Chernivtsi National University

2, Kotsyubynsky str., 58012 Chernivtsi, Ukraine

Phone: (0372)584875; e-mail: microel@chnu.cv.ua

Abstract. We present the results of optical and electrophysical investigations of CdTe:Cr crystals. A model explaining a considerable shift of the fundamental absorption edge in the crystals into the long-wave region is proposed. It is found that the doping of cadmium telluride crystals with Cr impurity leads to the introduction of deep donors with $E_v + 0.19 \dots 0.32$ eV.

Keywords: CdTe, chromium, doping, mobility, Hall effect, electrical conductivity, optical transmission.

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1. Introduction

Cadmium telluride crystals doped with Cr impurity have recently attracted considerable interest as a promising material for high-performance lasers in the middle infrared range [1] and as a semimagnetic semiconductor in spintronics [2]. At the same time, there are few works devoted to the study of optical and electrophysical properties of CdTe:Cr [3-7], and the problem of the mechanism of the introduction of Cr impurity into the CdTe lattice remains to be solved. On the base of earlier studies [4], it was considered that the doping of CdTe with Cr does not involve the introduction of electrically active centers. This conclusion is refuted by the results in [5], since the reliably observed semiinsulating state of CdTe-Cr crystals cannot be attributable only to the presence of uncontrolled impurities. In addition, it should be taken into account that Cr ions can be in different charge states [5, 6], as well as that this impurity can form clusters in CdTe crystals [5].

An isolated chromium atom in the cadmium telluride lattice should have the electronic configuration $3d^4s^2$ (state Cr^{2+}), which means the absence of impurity electrical activity [4]. At the same time, the magnetic studies of CdTe:Cr crystals [5] suppose the existence of the Cr^+ state in the case where the impurity is a part of a cluster. This provides the possibility to realize a quasicomplex reaction of the donor type:

$Cr^+ \rightarrow Cr^{2+} + e^-$. Since there is no reason to expect that these donors are shallow, the donor nature of an impurity can be established only by studying a series of doped and undoped crystals under similar technological conditions.

CdTe and CdTe:Cr single crystals were grown from a charge, prepared from stoichiometric weights of Cd and Te additionally purified by the zone melting. Chromium at the concentration $C_0 = 10^{18} \dots 10^{19} \text{ cm}^{-3}$ was loaded into a quartz ampoule together with Cd and Te. Following a long synthesis of the charge, single crystals were grown by the Bridgman method (the temperature gradient at the crystallization front was $10 \dots 15 \text{ K/cm}$, and the growth rate was 2 mm/h).

The temperature behaviors of the electrical conductivity (σ) and the Hall constant (R_H) were studied by standard methods on the rectangle-shaped samples in the temperature range $77 \dots 400 \text{ K}$. Samples for measurements were cut of different parts of doped ingots. The position of a specimen in the ingot was characterized by a reduced coordinate $g = x/L$, where L is the ingot length, and x is the distance from the beginning of the ingot. Two pairs of probe contacts manufactured of the following alloys were used: Cu+In – for high-resistance specimens of the p -type; Au+Cu+In, with a preliminary spark treatment of contact pads – for high-resistance specimens of the p -type; Cu+(In+Sn) – for low-resistance specimens of the n -

type. The mobility of carriers was calculated by the formula $\mu = R_H \sigma$, i.e. the Hall factor was assumed equal to unity. The ionization energies of acceptors or donors were found from the temperature dependences of R_H in the framework of the model of compensated centers.

For optical measurements, the 1-mm-thick polished wafers were made. The measurements were performed at room temperature on the universal spectral computer system including an MDR-12 monochromator.

The study of the optical transmission at $T = 300$ K showed that the doping with chromium causes a noticeable displacement of the fundamental absorption edge into a long-wave region as compared with pure CdTe depending on the impurity concentration [$\Delta = (0.15 \dots 0.25)$ eV in different samples, Fig. 1]. A similar displacement was observed in [3] at $T = 4$ K.

The temperature dependences of the Hall coefficient of seven samples with different impurity concentrations C_0 in a melt are represented in Fig. 2. Only one sample (7) has electron conductivity, the rest – hole conductivity. In the samples with hole conductivity, the carrier concentration p lies at 300 K in the interval $(2 \cdot 10^{11} \dots 10^{14}) \text{ cm}^{-3}$ which is several orders less than that in the undoped crystals, where $p = (10^{15} \dots 10^{16}) \text{ cm}^{-3}$. The energy of ionization centers (ε_A), which determine p -conductivity (let's formally call them acceptors), is equal to $(0.19 \dots 0.32)$ eV and monotonously increases with decrease in the carrier concentration. The Fermi level lies well above all the energy levels of acceptors (for example, for sample 6 with $\varepsilon_A = 0.32$ eV, the Fermi level lies at 300 K at $E_v + 0.6$ eV), which testifies to a very high degree of compensation of acceptors: $k = [A^-]/[A] = (0.99 \dots 0.999)$. It is worth noting the increase of k with the ionization energy of acceptors, which is not typical of undoped p -CdTe crystals with casual deep acceptors.

The above regularities can be understood on the assumption that the experimentally observed levels at $E_v = (0.19 \dots 0.32)$ eV are caused not by heavily compensated acceptors, but by weakly compensated very deep donors (DD) related to the chromium impurity as a part of a cluster. The donor action of Cr ions is provided by the quasichemical reaction $\text{Cr}^+ \rightarrow \text{Cr}^{2+} + e^-$ with the subsequent capture of an electron by acceptors A_1 ($E_v + 0.05$ eV) and A_2 ($E_v + 0.13$ eV). As long as the binding energy of an electron must depend on the cluster structure (the number of impurity ions and intrinsic defects, mutual arrangement, etc), one should expect a wide energy spectrum of deep levels (Fig. 3). In a specific doped specimen, the "acceptor" thermal transition (T) of an electron from the v -band to the lowest compensated level takes place. The character of compensation is determined by the ratio arising under these conditions between the chromium impurity concentration in clusters of different configurations, acceptors A_1 and A_2 , and shallow donors D_1 ($E_c - 0.01$ eV) always present in CdTe crystals.

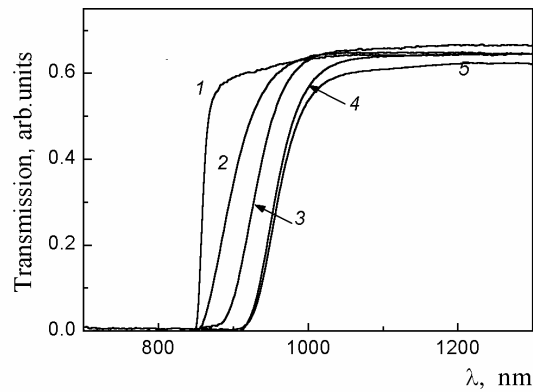


Fig. 1. Optical transmission spectra of CdTe:Cr crystals: 1 – CdTe; 2 – $C_0 = 10^{18} \text{ cm}^{-3}$ ($g = 0.25$); 3 – $C_0 = 6 \cdot 10^{18} \text{ cm}^{-3}$ ($g = 0.3$); 4 – $C_0 = 10^{19} \text{ cm}^{-3}$ ($g = 0.3$); 5 – $C_0 = 10^{19} \text{ cm}^{-3}$ ($g = 0.8$).

Let us give the qualitative estimates which will confirm the possibility to realize the above-described situation. The total concentrations of acceptors A_1 and A_2 can be estimated at the level of $\sim 10^{17} \text{ cm}^{-3}$. As long as none of the samples exhibits the signs of at least the beginning of the area of full ionization of the centers at high temperatures, one can expect (for examples, for samples 1 and 2) that this area is realized at $p_{\text{sat}} \geq 10^{16} \dots 10^{17} \text{ cm}^{-3}$. This gives, with regard for the degree of compensation of cluster centers, the value within $10^{17} \dots 10^{18} \text{ cm}^{-3}$. The concentration of the dissolved chromium impurity can be of the same or somewhat larger value, taking into account its high solubility [5] and the fact that the coefficient of segregation of this impurity in cadmium telluride is a little less than unity [7].

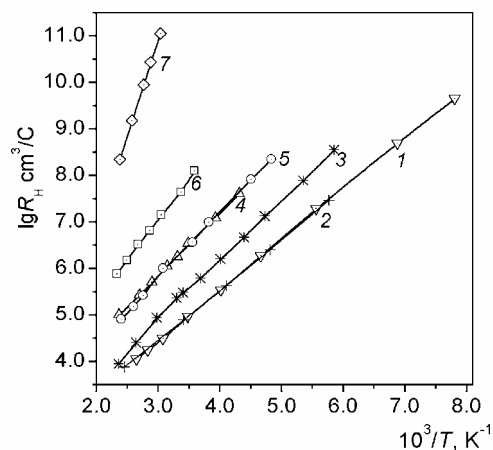


Fig. 2. Temperature dependences of the Hall coefficient in CdTe-Cr crystals prepared from different parts of doped samples: 1, 2 – $C_0 = 10^{18} \text{ cm}^{-3}$ ($g = 0.3, 0.76$); 3 – $C_0 = 6 \cdot 10^{18} \text{ cm}^{-3}$ ($g = 0.8$); 4, 5 – $C_0 = 8 \cdot 10^{18} \text{ cm}^{-3}$ ($g = 0.06, 0.74$); 6, 7 – $C_0 = 10^{19} \text{ cm}^{-3}$ ($g = 0.29, 0.81$).

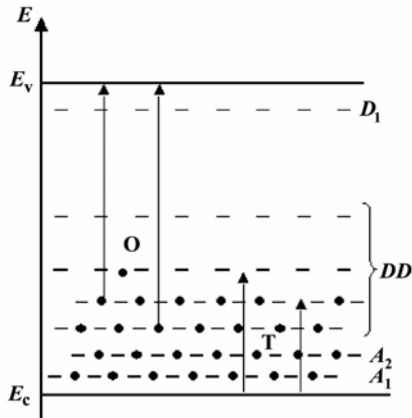


Fig. 3. Energy diagram of CdTe-Cr crystals.

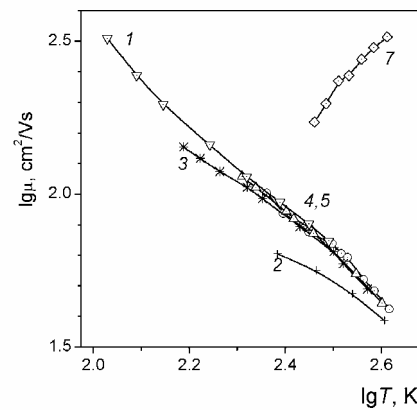


Fig. 4. Temperature dependences of the mobility of carriers in CdTe-Cr crystals (the numbering of samples as in Fig. 1).

The mobility of carriers in p -type samples (Fig. 4) monotonously increases with decrease in the temperature. On the one hand, this testifies to the absence of drift barriers for carriers, that is the absence of a potential relief caused by the inhomogeneous spatial distribution of electrically active centers. On the other hand, the concentration of these centers (N_i) (calculated from the $\mu = f(T)$ dependence) does not exceed $5 \cdot 10^{17} \text{ cm}^{-3}$, which is in agreement with $(N_i) = 2([A_1] + [A_2]) \approx 2 \cdot 10^{17} \text{ cm}^{-3}$ (perhaps, except sample 2). At the same time, the mobility of carriers in the only one sample of the n -type quickly drops with decrease in the temperature, which attests to the existence of drift barriers ($\epsilon_{\text{bar}} \approx 0.06 \text{ eV}$) caused by the presence of overlapped space charge areas [8]. In this case, the impurity clusters in the context of carrier scattering processes cannot be considered, obviously, as point formations any longer. In this case, the binding energy of an electron must be essentially different from that in the p -type samples. If the above suggestion is correct, one can state that the binding energy should be reduced with a complication of the cluster structure, *i.e.* the donor level approaches the c -band.

The proposed model allows us to explain the presence of a powerful optical absorption band ($\alpha \geq 10^2 \text{ cm}^{-1}$) with a long-wave edge at $h\nu = (1.35-1.45) \text{ eV}$ which is observed at 4 K in the samples with $C_0 = (10^{18}-10^{19}) \text{ cm}^{-3}$ [3]. This band is due to the optical (O) transitions of electrons from the uncompensated (filled with electrons) deep levels to the c -band. Assuming the equality of thermal and optical ionization energies, the sum of the energies of optical and thermal transitions should be somewhat greater than the band gap. Really, we have $(1.35 \dots 1.45) \text{ eV} + (0.32 \dots 0.19) \text{ eV} > E_g = 1.60 \text{ eV}$. In addition, the shifts of the absorption band edge $\Delta = (0.15 \dots 0.25) \text{ eV}$ at 300 K (Fig. 1) are in agreement with the activation energies of thermal “acceptor” transitions $\epsilon_{A} = (0.19-0.32) \text{ eV}$ (taking into account the thermal reduction of the band gap $E_g^{300} = 1.49 \text{ eV}$).

The doping of cadmium telluride crystals with the Cr impurity is accompanied by the introduction of deep donors, whose levels lie in the lower half of the forbidden band gap ($E_v + 0.19 \dots 0.32 \text{ eV}$). We suppose that the donor action reveals Cr impurity ions as a part of impurity clusters according to the quasichemical reaction $\text{Cr}^+ \Leftrightarrow \text{Cr}^{2+} + e^-$ in the forward direction. The opposite direction of the reaction is realized as the thermal “acceptor” transitions that determine the temperature dependence of the concentration of holes.

References

1. A.G. Bluiett, U. Hommerich, R.T. Shah, S.B. Trivedi, S.W. Kutcher, C.C. Wang, Observation of lasing from $\text{Cr}^{2+}:\text{CdTe}$ and compositional effects in Cr^{2+} -doped II-VI semiconductors // *J. Electronic Mater.* **31**(7), p. 806-810 (2002).
2. K.Y. Ko, M.G. Blamire, Temperature dependent magnetization in Cr-doped CdTe crystals // *Appl. Phys. Lett.* **88**, p. 172101-172101 (2006).
3. P.I. Babiy, N.P. Gavaleshko, Yu.P. Gnatenko, P.A. Skubenko, V.I. Oleinik, Optical properties of CdTe crystals doped with V and Cr // *Fiz. Tekhn. Poluprov.* **12** (11), p. 2202-2206 (1978) (in Russian).
4. V.M. Sal'man, V.A. Chapnin, The influence of Fe, Mn, Cr on the properties of cadmium telluride // *Kratkiye Soobshcheniya Fiz.* **2**, p.17-21 (1979) (in Russian).
5. P.I. Babiy, N.P. Gavaleshko, Yu.P. Gnatenko, et al., // *State of 3d-Impurity Elements in Cadmium Telluride*: Preprint of the NAS of Ukraine (Institute of Physics, Kyiv, 1983) (in Russian).
6. I. Stefaniuk, M. Bester, I.S. Virt, M. Kuzma, EPR spectra of Cr in CdTe crystals // *Acta phys. polonica* **108**, p. 413-418 (2005).
7. K. Zanio, Cadmium Telluride // *Semicond. and Semimet.* **13**, p. 235 (1978).
8. M.K. Sheinkman, A.Ya. Shik, Long-term relaxation and residual conductivity in semiconductors // *Fizika Tekhnika Poluprovodnikov* **10**(2), p. 209-215 (1976) (in Russian).