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## DETERMINATION AND CHARACTERIZATION OF DEEP LEVELS IN p-CdTe(Cl) (\*)

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**Résumé.** — On a préparé des monocristaux de tellure de cadmium par la méthode de Bridgman en vue d'étudier leurs propriétés physiques et de réaliser des détecteurs de rayonnements nucléaires. Les cristaux sont compensés au chlore en cours de tirage par addition de  $\text{CdCl}_2$  à des concentrations de 100-5 000 ppm.

Afin de déterminer la distribution des niveaux donneurs et accepteurs présents dans ces matériaux, nous avons entrepris des mesures d'effet Hall, de photoconductivité, de courants thermostimulés, de mobilité, de courants de charge d'espace. Les résultats obtenus sont ensuite confrontés à un modèle considérant un effet de pairage donneur-accepteur convenablement placé dans le réseau.

En détection nucléaire, nous obtenons typiquement les résolutions en énergie suivantes : des largeurs à mi-hauteur de raies de 7 keV pour des photons de 122 keV ( $^{57}\text{Co}$ ) et de 5 keV pour des photons de 59 keV ( $^{241}\text{Am}$ ).

**Abstract.** — CdTe single crystals grown from Te solvent have been used for both evaluation of physical parameters and preparation of nuclear radiation detectors. Ingots were doped with  $\text{Cl}(\text{CdCl}_2)$  in the range of 100-5 000 ppm.

For the experimental determination of the distribution of the donor and acceptor levels in CdTe(Cl) the Hall effect, photoconductivity, drift mobilities, thermo-stimulated currents (TSC) and space charge limited currents (SCLC) were employed. The results are compared with a model based on acceptor-donor pairs separated by distinct distance within the crystal lattice.

For a typical detector produced from p-CdTe(Cl) the total resolution was approximately 7 keV (FWHM) for the 122 keV gamma  $^{57}\text{Co}$  and 5 keV (FWHM) for 59 keV gamma  $^{241}\text{Am}$ .

**1. Introduction.** — Nuclear radiation spectrometers made from chlorine doped CdTe single crystals grown from tellurium solvent have a good resolution for gamma-rays, when operating at room temperature. Recent work on CdTe(Cl) detectors has indicated the importance that charge transport and trapping effects have in limiting detector performance.

In an effort to understand the trapping in CdTe(Cl) detectors the distribution of energy levels in band gap was studied in some detail.

The investigation of the energy levels system of charged centres in CdTe, as well as in other II-VI compounds, presents a complicated problem not yet well understood.

In section 2 the method of preparation is described, including the growing techniques. In section 3 is presented a model of self-compensation and distribution of energy levels in the band gap of CdTe. The experimental results, determined from the Hall effect, photoconductivity, drift mobilities, thermo-stimulated currents and space charge limited currents, are summarized in section 4, including a comparison

between theory and experimental data. The parameters of CdTe(Cl) gamma-ray detectors are presented in section 5.

**2. Crystal growth.** — The vertical Bridgman method was used to grow CdTe single crystals by directional cooling of a Te — rich solution of the composition 30 at % Cd and 70 at % Te.

A charge of Cd : 6 N and Te : 6 N redistilled in a stream of pure hydrogen put in a quartz tube, coated with a layer of pyrolytic graphite which was evacuated ( $10^{-5}$  torr). Synthesis of CdTe and homogenization of the charge was realized by heating the tube in a direct flame. After synthesis the tube was inserted into furnace and was pulled through the temperature gradient (Fig. 1a). Dependence of solid CdTe fraction during pulling on the temperature of growing interface is given in figure 1b.

Ingots were prepared, both undoped and doped with chlorine, which was added, in the form of anhydrous salt  $\text{CdCl}_2$  to the charge. The concentration of chlorine in the total charge was varied from 100 to 5 000 ppm.

In agreement with results obtained in Tyco Laboratories [1], CdTe crystals grown from tellurium

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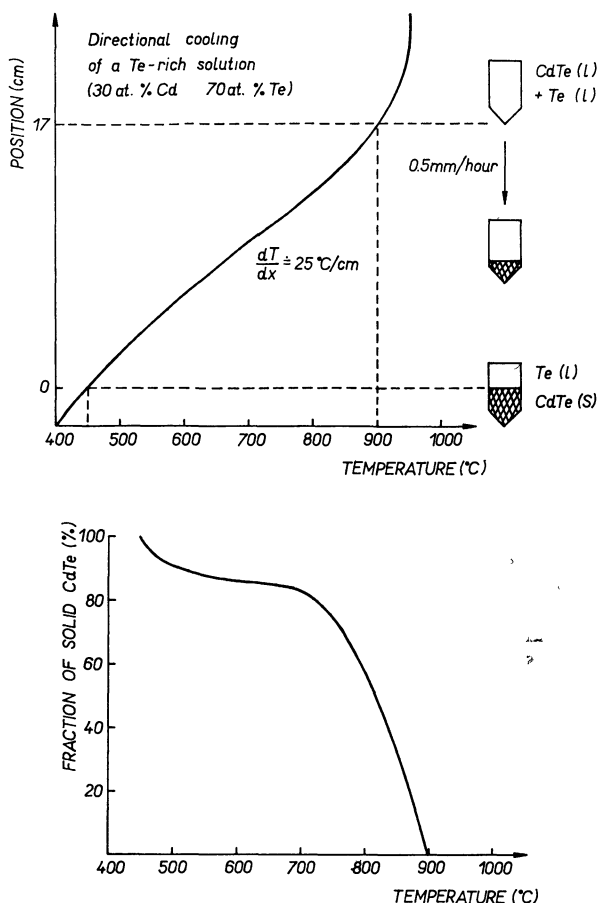


FIG. 1. — *a*) Temperature distribution and positions of ampoule in the furnace during pulling the CdTe single crystals from tellurium melt. *b*) Fraction of solid CdTe, calculated from phase diagram of the system Cd-Te [12].

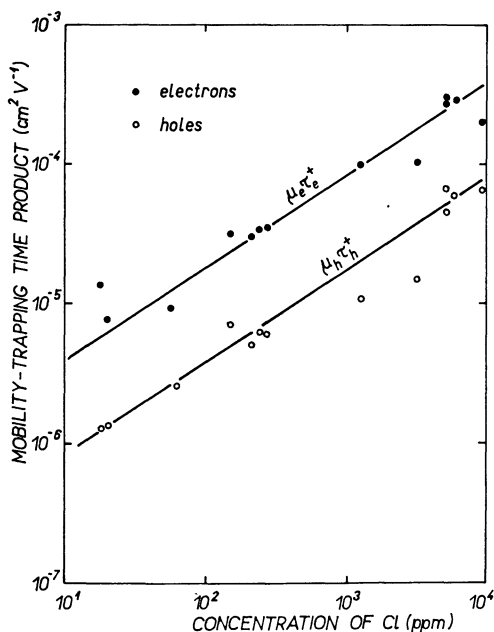


FIG. 2. — Mobility-trapping time products  $\mu\tau^+$  for both electrons and holes as function of total concentration of chlorine in the charge.

solution and doped with chlorine appear to be the most promising for the preparation of gamma-ray detectors. For that reason we have carried out measurements of mobility-trapping time products  $\mu\tau^+$  for both electrons and holes as a function of the total concentration of chlorine in the charge (Fig. 2). We have used a method in which  $\alpha$ -particles ( $^{241}\text{Am}$ ) generate carriers close to one of the contacts, and charge collection efficiency is measured for electrons or holes (Hecht relation).

From figure 2 it can be seen that in proceeding from low to high concentration of chlorine the mobility-trapping time product increases jointly for electrons and holes. The optimum chlorine concentration for radiation detection is around 5 000 ppm in the charge.

**3. Model and theory.** — In CdTe crystals, both foreign atoms and native point defects of Frenkel-type ( $V_{\text{Cd}}$ ,  $\text{Cd}_i$ ) and Schottky-type ( $V_{\text{Cd}}$ ,  $V_{\text{Te}}$ ), determine the electrical properties of crystals. The concentrations of the dopant atoms and defects are not independent on each other. (Kröger's notation [2] for defects will be used throughout this section.) The introduction of electrically active impurities into a host crystal induces the formation of electrically active defects and neutral complexes, which tend to compensate the material. Therefore the process of self-compensation is usually used for the preparation of semi-insulating CdTe.

For CdTe(Cl), where  $\text{Cl}_{\text{Te}}$  acts as shallow donor ( $\text{Cl}_{\text{Te}}^*$ ) there are three possibilities of self-compensation.

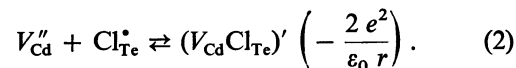
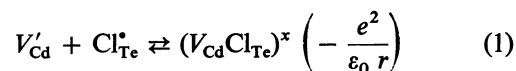
(a) The first mechanism is compensation by cadmium vacancies singly or doubly ionized  $V_{\text{Cd}}'$ ,  $V_{\text{Cd}}''$  (acceptors).

(b) The second is compensation by complexes  $(V_{\text{Cd}}\text{Cl}_{\text{Te}})'$  separated by a distinct distance  $r$ .

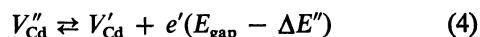
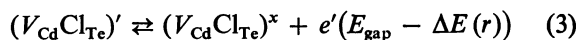
(c) Finally a neutral complex consisting of one  $V_{\text{Cd}}''$  and two  $\text{Cl}_{\text{Te}}^*$  is considered  $(V_{\text{Cd}} 2 \text{Cl}_{\text{Te}})^x$  [3].

In all cases during compensation the difference  $|N_A - N_D|$  decreases; only in the last case individual components  $N_A$ ,  $N_D$  decrease too.

Donor-acceptor pairs  $(V_{\text{Cd}}\text{Cl}_{\text{Te}})$  and associated electronic states play an important role in the investigation of deep acceptor levels in CdTe(Cl). In this case association takes place according to the quasi-chemical reactions :



Acceptors  $V_{\text{Cd}}'$  and  $(V_{\text{Cd}}\text{Cl}_{\text{Te}})^x$  can be ionized; thus :



where  $\Delta E(r)$ ,  $\Delta E''$  are the ionization energies of complex  $(V_{\text{Cd}}\text{Cl}_{\text{Te}})'$  and doubly ionized cadmium vacancy,  $\epsilon_0$  is the low frequency dielectric constant and  $e$  is the electronic charge. We can easily see that

$$\Delta E(r) = \Delta E'' - \frac{e^2}{\epsilon_0 r}. \quad (5)$$

Corrections to simple coulombic considerations which are important for small  $r$  will be neglected here.

For acceptors on cation sites —  $V_{\text{Cd}}$  and donors on anion sites —  $\text{Cl}_{\text{Te}}$ , the possible distance between acceptors and donors in the zinc blende structure are given by :

$$r_j = a \left( \frac{1}{2}j - \frac{5}{16} \right)^{1/2} \quad j = 1, 2, \dots, k \quad (6)$$

where  $a$  is a lattice constant. Discrete values of  $r_j$  range up to a maximum value  $r_{\text{max}}$ , equal to  $\frac{1}{2} C^{-1/3}$  ( $C$ ... donor and acceptor concentration). Thus, for activation energies of the acceptors  $(V_{\text{Cd}}\text{Cl}_{\text{Te}})_j$  we obtain :

$$\Delta E^{(j)} = \Delta E'' - \frac{e^2}{\epsilon_0 r_j} \quad (7)$$

Prener [4] adapted previous considerations of ion pairing in solution to the case of discrete sites in a three-dimensional lattice. For a pair concentration, separated by the distance  $r_j$ , be found :

$$N_j \approx ACZ_j \exp\left(\frac{e^2}{\epsilon_0 r_j k_0 T}\right) \exp\left(-C \sum_{i=1}^j Z_i\right) \quad (8)$$

where  $A$  is a normalization constant

$$\left( \sum_{j=1}^k N_j = 1 \right),$$

$k_0$  is the Boltzman constant,  $T$  is temperature and  $Z_j$  is the number of sites available to a positively charged defect —  $\text{Cl}_{\text{Te}}^+$  at a distance  $r_j$ , from a negatively charged defect —  $V_{\text{Cd}}'$ . From eq. (8) is possible to see, that with increasing  $j$ , the concentration of pairs decreases.

Hall effect measurements in undoped CdTe crystals demonstrate that the concentration of free holes is governed by a level lying  $\approx 0.15$  eV above the valence band [5]. The hydrogenic value for the acceptor — binding energy can be written as

$$\Delta E = 13.6(m_{\text{hh}}^*/m_0)/\epsilon_0^2.$$

With an effective mass of heavy holes

$$m_{\text{hh}}^*/m_0 = 0.89 [6]$$

we then obtain  $\Delta E \approx 0.13$  eV. For this reason we assume that the activation energy for singly ionized Cd vacancy is  $\approx 0.15$  eV.

From the temperature dependence of carrier concentration in p-type samples we identified an acceptor level  $\approx 0.85$  eV above the valence band [5]. We assume, that this is the second ionization level of Cd vacancy.

Values  $r_j$ ,  $\Delta E^{(j)}$  obtained by eq. (6), (7) with

$$\epsilon_0 = 9.65, a = 6.48 \times 10^{-8} \text{ cm}$$

and  $\Delta E'' = 0.85$  eV are summarized in the table I.

TABLE I  
Activation energies of levels in semi-insulating CdTe(Cl)

Identity	Model		Experiment — $E_D, E_A$ (eV)					
	$j$	$r_j 10^8$ (cm)	$E_D, E_A$ (eV)	HE	TFT	PC	TSC	SCLC
donors	$\text{Cl}_{\text{Te}}^+$				0.025	0.02		
	?				0.050	0.05		
	$V_{\text{Cd}}'$		0.15	0.15 (*)	0.15	0.16		
acceptors	$(V_{\text{Cd}}\text{Cl}_{\text{Te}})'_1$	1	2.81	0.32	$\approx 0.30$	0.32	0.30 ; 0.34	
	$(V_{\text{Cd}}\text{Cl}_{\text{Te}})'_2$	2	5.37	0.57	0.57		0.5	$\approx 0.45 ?$
	$(V_{\text{Cd}}\text{Cl}_{\text{Te}})'_3$	3	7.06	0.64	0.65 (**)			0.65
	$(V_{\text{Cd}}\text{Cl}_{\text{Te}})'_4$	4	8.42	0.67			$\approx 0.7$	
	$(V_{\text{Cd}}\text{Cl}_{\text{Te}})'_5$	5	9.57	0.69				
	$V_{\text{Cd}}''$			0.85	0.85 (**)			
?	?					0.12		

(\*) Undoped crystal CdTe.

(\*\*) Different crystals CdTe(Cl).

4. **Experimental results.** — For the detailed study of distribution of energy levels in the band gap, a CdTe crystal doped with Cl in amount  $\approx 5\,000$  ppm was selected, characterized at room temperature by the following parameters : p-type,

$$\sigma = 6.4 \times 10^{-9} \Omega^{-1} \text{ cm}^{-1}, \mu_H = 35 \text{ cm}^2/\text{V} \cdot \text{s},$$

$$p = 1.14 \times 10^9 \text{ cm}^{-3},$$

$$\mu_e \tau_e^+ = 2 \times 10^{-4} \text{ cm}^2/\text{V}$$

and

$$\mu_h \tau_h^+ = 7 \times 10^{-5} \text{ cm}^2/\text{V}.$$

Materials Evaluation.

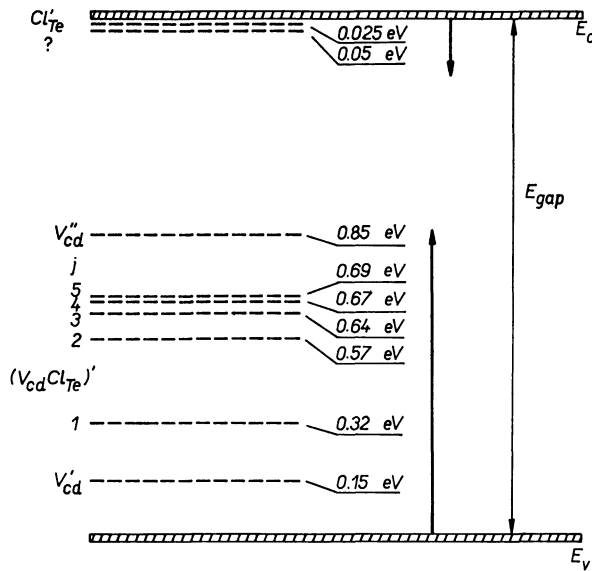


FIG. 3. — Energy levels in the forbidden gap of CdTe (calculated values).

4.1 **HALL EFFECT (HE).** — An activation energy of  $\Delta E = 0.57$  eV denoting an acceptor level was determined on the basis of the measurements of temperature dependence of the Hall constant ( $r_H = 1$ ). Measurements were performed in a relatively narrow-temperature range since they could not be carried out at low temperatures for which the resistance of samples exceed  $10^{12} \Omega$ . In undoped samples an activation energy for an acceptor level  $\Delta E \approx 0.15$  eV was determined.

4.2 **TIME-OF-FLIGHT TECHNIQUE (TFT).** — Drift velocity measurements for both electrons and holes have been performed as a function of electrical field and temperature, with charge carriers generated by a pulsed electron beam. From reduced mobility we have obtained the following levels : 0.025 eV below conduction band and 0.15 eV above valence band. The activation energies of traps :  $E_C - 0.05$  eV,  $E_V + 0.15$  eV and  $E_V + 0.3$  eV were also obtained by measuring the 0-85 % voltage pulse rise-time of

the waveforms (two components) and changing the temperature. A more detailed discussion is found in [7]. All these measurements were performed in the laboratory of prof. G. Ottaviani at Modena University during the fellowship stay of one of the authors.

4.3 **PHOTOCONDUCTIVITY (PC).** — Photoconductivity spectra were recorded in the 0.1 eV-1.6 eV region at the temperatures 15 K and 80 K. Impurity photoconductivity was measured with and without additional illumination. The illumination with energy  $h\nu = E_{\text{gap}}$  was employed in order to shift the positions of quasi-Fermi levels within the forbidden gap of CdTe. The amplitude and phase shift of photocurrent were investigated. The energy of the impurity levels was determined according to Bube [8] and Ryvkin [9]. Obtained impurity levels are following :

$$E_C - 0.025 \text{ eV} ; E_C - 0.055 \text{ eV} ; E_V + 0.7 \text{ eV} ;$$

$$E_V + 0.36 \text{ eV} ; E_V + 0.32 \text{ eV} ;$$

$$E_V + 0.16 \text{ eV and } E_C - 0.12 \text{ eV or } E_V + 0.12 \text{ eV} .$$

4.4 **SPACE CHARGE LIMITED CURRENTS (SCLC).** — The D. C. measurements of currents have been performed on samples CdTe(Cl) with platinum contacts as a function of the applied voltage for different temperatures in the range 100 K-300 K. From the temperature dependence of the quadratic portions of the voltage-current characteristics a discrete level at  $E_V + 0.65$  eV with a fair accuracy could be identified. Another one at approx.  $E_V + 0.45$  eV was found with lower accuracy [10].

4.5 **THERMO STIMULATED CURRENTS (TSC).** — TSC measurements were performed with a standard technique in the range between 100 K and 300 K after optical, electrical or combined excitations, both at low temperatures or during the cooling process. Where possible, the « cleaning » of the TSC-curves by interrupted heating was applied to separate the individual maxima. Five levels most probably associated to hole traps were identified by means of the initial rise method

$$\left( E_t = k \frac{d(\log I)}{d(1/T)} \right)$$

and from the temperature at maximum current

$$\left( \text{Bube's method, } E_t = kT_{\text{max}} \log \frac{N_V}{p} \right)$$

respectively.

A fairly good agreement ( $\sim 1.5\%$ ) between both values indicates a strong recapture of holes on these levels.

The averaged trap energies obtained were the following ; 0.30 eV ; 0.34 eV ; 0.37 eV ; 0.40 eV ; 0.5 eV. There is an indication of a level at  $E_t > 0.5$  eV. The details will be published elsewhere [11].

All obtained results are summarized in table I.

5. **Radiation detector characteristics.** — Detectors of gamma radiation were prepared from the same CdTe(Cl) single crystal used for material evaluation.

Detectors were fabricated in the forms of plates  $5 \times 5 \times 1 \text{ mm}^3$ , whose faces were lapped and mechanically polished to optical quality. The electrodes were deposited by chemical precipitation of gold ( $\text{AuCl}_3$ ).

The quality of the detectors was tested with  $^{57}\text{Co}$  and  $^{241}\text{Am}$  sources. In the  $^{57}\text{Co}$  spectrum (Fig. 4), low noise is demonstrated by the presence of 14 keV

peak and good resolution  $\approx 7 \text{ keV}$  (FWHM) is evident from the separation of 122 keV and 136 keV peaks. In  $^{241}\text{Am}$  spectrum (Fig. 5) both peaks  $L_\alpha$  14 keV and  $L_\beta$  18 keV are well resolved. The CdTe(Cl) detectors are stable with time; they exhibit no polarization.

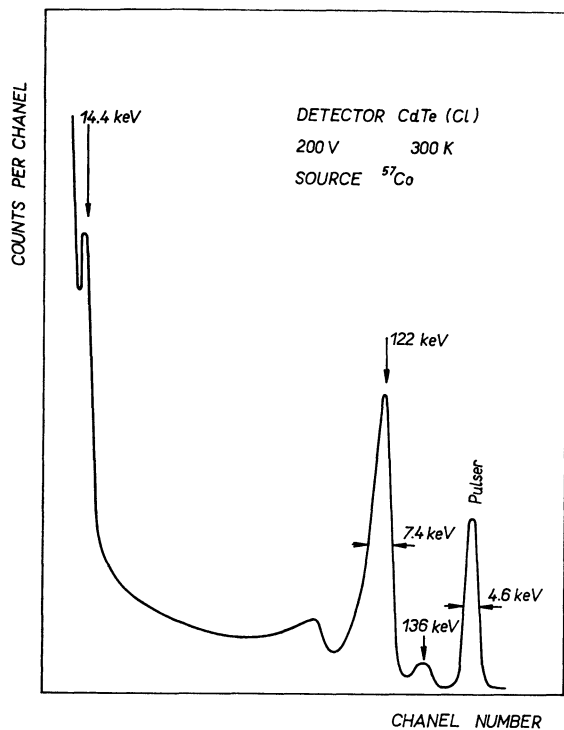


FIG. 4. —  $^{57}\text{Co}$  gamma-ray spectrum at room temperature.

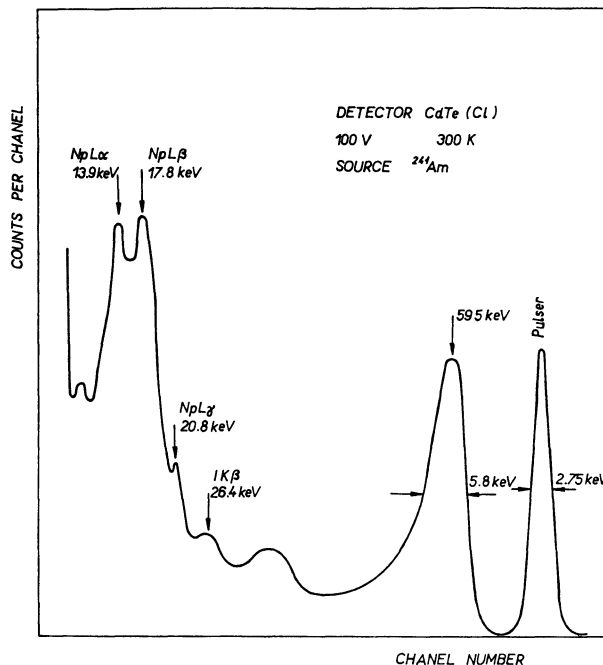


FIG. 5. —  $^{241}\text{Am}$  gamma-ray spectrum at room temperature.

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