## Shallow donors in CdTe

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Photoluminescence and high-resolution selective excitation of luminescence have been used to study shallow donors in non-intentionally-doped Te-rich or nearly stoichiometric CdTe crystals and their evolution after controlled thermal annealings (specifically under Cd overpressure). It has been shown that there are at least six native donors. For each of these donors, the  $(1s \rightarrow 2s)$  and  $(1s \rightarrow 3s)$  transition energies, the ionization energy, and the exciton localization energy have been determined. The ionization energies range from 13.71 to 14.79 meV and the localization energies obey Haynes's rule. Doping experiments clearly identify the chemical nature of three donors (Ga, In, and Cl), and two other native donors are tentatively ascribed to Al and F. This study clearly indicates that the conversion to *n*-type behavior induced by the annealing under Cd overpressure does not involve stoichiometric defects like interstitial Cd but is essentially related to a modification of the solubility of the residual contaminants of the ingots.

## I. INTRODUCTION

The last ten years have produced a much better understanding of the physical properties of donor impurities in II-VI compounds. Studying optical properties of crystals doped with appropriate impurities, several authors have determined the chemical identity of donors and their energy levels in the band gap. In CdS crystals, six substitutional donor impurities have been identified, with binding energies ranging between 32.1 and 35.1 meV.<sup>1</sup> In ZnSe, five donor impurities were observed,<sup>2</sup> with their binding energies (26.3-29.3 meV) all close to the effective-mass value. In ZnTe, which is always p type, only two donors have been identified until now,<sup>3</sup> with ionization energies of 18.5 and 20.1 meV.

The first studies of *n*-type CdTe did not allow separation of the contribution made by the various donor impurities to the luminescence spectra.<sup>4,5</sup> The existence of several different donor impurities was first pointed out by Simmonds *et al.*<sup>6</sup> using far-infrared photoconductivity experiments. They separated five different donors with chemical shifts between 1 and 8 cm<sup>-1</sup>.

In CdTe crystals, the only precise chemical identification to date is that of the chlorine donor, due to Neu.<sup>7</sup> Therefore, in this material, most of the physics of donors has to be clarified including the nature of the residual donors and their associated energy levels. Particularly intriguing is the observation of the systematic conversion to *n* type which is obtained after annealing under Cd vapor. This has been known since the early work of De Nobel<sup>8</sup> and has been attributed to isolated cadmium interstitials (Cd<sub>i</sub>) acting as donors. Indeed, electrical measurements on such samples indicate an *n*-type behavior.<sup>9</sup> However, the existence of stable isolated Cd interstitials at room temperature has not been established. We recently reported some partial spectroscopic identification of donors in CdTe.<sup>10</sup> The present paper

deals with a more complete and detailed study of (i) the donors present in non-intentionally-doped material; (ii) the donors which are produced by annealing in a Cd environment; (iii) the thermal diffusion of donors from elements of column III or VII of the Periodic Table; (iv) the identification of some of the donors by doping experiments.

#### **II. EXPERIMENTAL**

#### A. Crystal preparation

The aim of this work was to get a general understanding of the donors in CdTe. Therefore numerous samples of various purity and grown in different ways have been studied.

CdTe samples are sliced from ingots grown by the Bridgman method by Schaub.<sup>11</sup> The samples used for the present experiments were grown from melts of various composition to obtain either stoichiometric or Te-rich ingots (designated ST and TR, respectively). The starting materials are commercially available 99.99999% purity cadmium and tellurium. The shape of the CdTe phase diagram indicates a maximum melting point at 1092 °C. The growth temperature is fixed by the Te concentration in the melt. Nearly stoichiometric crystals are obtained for an initial Te content close to 50 at. % and a solidification temperature of 1092°C. For the crystals grown with a Te excess, the initial Te content is 60 at. % and the solidification begins at 967°. The ingots grown in this way are thought to be slightly nonstoichiometric. Although the Te excess in the CdTe lattice is unknown, it does not in any case exceed  $10^{-5}$ .<sup>12</sup>

Four CdTe ingots were used in this investigation: three Te-rich (TR1 to TR3) and one stoichiometric (ST). The samples were cut from the central part of each ingot. Some pieces of the slices were analyzed by the spark

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TABLE I. Results of mass spectroscopy analysis of three typical slices taken in the central part of the ingots used (TR ingots are grown from a tellurium-rich melt, ST ingot is from a nearly stoichiometric melt). (*i*) indicates a high heterogeneous value; a surface pollution is suspected (cf. text).

	Concentration $(10^{16} \text{ cm}^{-3})$				
Impurity	TR1	TR2	ST		
Li	≤0.5	< 0.5	< 0.2		
F	$\approx 15(i)$	< 0.6	< 0.5		
Na	$\approx 200(i)$	5	15		
Mg	$\leq 0.7$	< 1.5	1		
Al	< 0.8	< 0.8	< 0.5		
Si	< 5	6	7		
Р	< 0.6	< 0.3	< 0.3		
S	< 6	< 6	<4		
Cl	1,5	5	3		
K	$\approx 100(i)$	10	10		
Ca	< 0.5	< 0.5	< 0.4		
Cr	≤0.5	3.5	≤0.5		
Zn	< 1	< 1	< 0.45		
Se	< 0.6	< 0.6	< 0.5		
Br	≤0.6	< 0.6	< 0.5		
Ag	0.7	< 0.6	< 0.5		
In	≤0.5	0.6	≤0.5		

source mass spectrometry technique. The results are presented in Table I for TR1, TR2, and ST. The results for TR1 show a contamination with F, Na, K. The contamination level is different in different pieces of the slices analyzed and is presumed to be due to the handling of the starting materials. The comparison of ingots TR2 and ST does not show any marked difference between the impurity content produced by the two growth techniques (except possibly for the Cr content). The ingot TR3 has not been analyzed but the starting materials and the growth method were identical to those used for TR2 ingot.

The carrier concentration of the crystals were deduced from capacitance-voltage measurements at room temperature on Schottky diodes with either In or Au electrodes, depending on the conductivity type of the sample. The Te-rich crystals are p type  $(N_a - N_d \simeq 5 \times 10^{14} \text{ cm}^{-3})$ , the near stoichiometric ingot is n type  $(N_d - N_a \simeq 10^{15} \text{ cm}^{-3})$ .

The slices (diameter 50 mm), which contained only a few monocrystalline grains, were mechanically and chemically polished in a bromine-methanol solution (2%). In some cases, after annealing or diffusion treatment, the samples were mechanically beveled with an angle of 3° so that depth profiling of the carrier concentration or the luminescence spectra is possible. The last operation before the photoluminescence analysis is always a chemical etch in the bromine-methanol solution.

The annealing treatments were performed in several different furnaces. In the range 500-650°C we used a quartz tube furnace under a continuous (90%  $N_2$ -10%  $H_2$ ) gas flow. For annealing temperatures between 700 and 900 °C the annealings were performed under a cadmium overpressure using a quartz ampoule loaded with cad-

mium as pure (99.99999% purity) as the starting material used for the crystal growth. Before the annealing, the quartz ampoule is carefully cleaned, baked at 350 °C and evacuated down to  $10^{-7}$  Torr using an ion pump. During the annealing treatment, the Cd pressure induced by the Cd source can be adjusted using an argon counterpressure, a technique described in Ref. 13. After the treatment the ampoule is quenched by immersing in cold water.

For the doping experiments, the samples were coated with a thin metallic layer of the element to be diffused (Al, Ga, or In) before loading them in the quartz ampoule. For these annealing or doping experiments, the slices were cut into several pieces. One was kept untreated and used as a reference and the other submitted to the various treatments indicated.

### **B.** Photoluminescence measurements

Photoluminescence (PL) experiments are performed at 1.8 K. The samples are mounted in an immersion-type cryostat. For above band-gap excitation, the red lines of a krypton laser are used as the excitation source; the power incident on the sample is 20 mW (spot size about  $0.5 \times 0.5 \text{ mm}^2$ ). Selective excitation of luminescence is performed using a dye laser (oxazine 750). The laser beam is mechanically chopped and the luminescence is focused on the entrance slit of a grating monochromator having a dispersion of 12 Å/mm. The signal is detected by a cooled, GaAs or  $S_1$  cathode photomultiplier and analyzed by a lock-in amplifier.

In these experiments, care must be taken to get the best possible energy resolution in the PL spectra. This is achieved by reducing the monochromator slit width (to 15  $\mu$ m) and by using a very low scanning speed (5-10 Å/min). With these conditions, a shift of 0.2 Å between two PL lines can be resolved.

Also, we have performed PL studies of uniaxially stressed CdTe crystals. The results will be published in a forthcoming paper but it can be pointed out that the stress experiments show that the multiple resolved lines we report here do not result from stress effects.

#### C. Electrical measurements

Schottky diodes have been fabricated by evaporating dots ( $\phi = 0.4 \text{ mm}$ ) of indium (on *p*-type material) or gold (on *n*-type material) through a metallic mask. The Ohmic contacts to the crystals were performed either by electroless gold plating (AuCl<sub>3</sub>) on *p* type or by evaporating indium on the back face of the crystals. The *C*-*V* characteristic of the reverse biased diode is measured at room temperature at frequencies ranging between 1 and 100 kHz.

#### **III. RESULTS**

#### A. General description of the luminescence spectra

Figure 1 shows the luminescence spectrum of a typical as-grown sample, taken from the central part of a Te-



Energy (eV)

Wavelength (Å)

FIG. 1. Photoluminescence spectra of an as-grown good quality crystal of CdTe near the band gap: sample TR2.

rich-type CdTe crystal (TR2), in the high-energy region. The recombination of excitons bound to neutral donors or acceptors gives the set of lines labeled D and A, respectively, also referred to as principal bound-exciton (PBE) lines.<sup>14</sup>

The lines, due to acceptor-bound excitons, have been previously identified;<sup>15</sup> thus each line is labeled with the name of the corresponding acceptor impurity.

The lines due to donors show a more complicated structure. The spectral scale of Fig. 1 does not allow separation of the contribution of the various chemical species; the various lines  $D_1^i$  are, in fact, the fundamental and excited states of this neutral donor-bound exciton complex. After the exciton recombination, the neutral donor is in its ground state.

The intensity ratio of the lines due to donor- and acceptor-bound excitons reflects the relative concentrations of the various types of impurities. However this ratio is not proportional to the ratio of the concentration of both kinds of impurities and cannot be use for a precise measurement. In a ST-type sample, the donor-bound excitons are almost as intense as the acceptor-bound excitons. The acceptor impurities are mainly copper, lithium, and sodium.<sup>15</sup>

At lower energies (1.581-1.585 meV) a complex set of lines is identified as the two-electron transition (TET) replica of the  $D_1^i$  lines. They are labeled  $D_2^i$ ,  $D_3^i$ , as they correspond to a situation where the electron bound to the donor is left in the 2s,3s state, respectively, after the exciton recombination. Detailed photoluminescence excitation spectroscopy has proved the validity of the attribution of such lines and allowed detailed studies of the donors in ZnTe (Refs. 16 and 17) and in ZnSe (Ref. 18), for instance.

Thus the  $D_2^1 - D_1^1$ ,  $D_3^1 - D_1^1$ , and  $D_4^1 - D_1^1$  energy differences taken from Fig. 1 give, respectively, the excitation energies  $1s \rightarrow 2s$ ,  $1s \rightarrow 3s$ , and  $1s \rightarrow 4s$  of the donor. The  $D_2^1$ line is relatively well resolved, but lines  $D_3^1$  and  $D_4^1$  are broad and structureless. This technique can, in principle, be extended to the other exciton lines  $D_1^i$  (i=2,3,4). In order to separate the excitonic spectra due to various donor species, the spectra must be recorded with a much better resolution since the expected chemical shift does not exceed 1 meV on the TET lines and 0.1 meV on the PBE lines, as shown by Simmonds *et al.*<sup>6</sup>

#### B. Photoluminescence (PL) studies of residual donors in as-grown CdTe crystals

In this section we present systematic PL studies of asgrown crystals. The high-resolution PBE spectra obtained on representative ingots are shown in Fig. 2. From these spectra, it is possible to identify several different PBE lines  $D_1^1$  labeled S, A, (B,C), E, and (F). The precise energy positions of these lines are listed in Table II. The lines B and C are not clearly separated in Fig. 2 but resonant excitation of the luminescence clearly shows that there are two distinct lines. The PBE lines  $D_1^1$ of the ST ingot appear relatively less resolved. This could result from the *n*-type conductivity of this ingot and from a higher donor concentration. Figure 2 clearly confirms the simultaneous existence of several native donors as already reported by Simmonds *et al.*<sup>6</sup>

As shown in Fig. 1, there are various replicas of the PBE lines, and we can expect that replicas of different donors might be better separated in the TET spectra, due



FIG. 2. High-resolution PL spectra recorded on the  $D_1^1$  line for several samples cut from different ingots grown from a nearly ST or Te-rich melts (TR1, TR2, and TR3).

TABLE II. Energy of the  $D_{n=1,2,3}^{1}$  lines associated with each donor.  $E_{loc}$  is the binding energy of the exciton. The ionization energies are either calculated  $[E_{\alpha}(1s)]$  or obtained by extrapolation from Fig. 4  $[E_{\beta}(1s)]$ . The wavelengths are determined with respect to the copper bound exciton lines  $A_{1}^{Cu}$  (1.589 56 eV). The asterisk denotes tentative identification.

	$D_1^1$ (eV)	$\begin{array}{c} D_2^1 \\ (\pm 2 \times 10^{-2}) \end{array}$	$D_3^1$ $\delta eV)$	E <sub>loc</sub>	$\frac{E(1s)-E(2s)}{(\text{meV})}$	R₀ ±0.02 m	$E_{\alpha}(1s)$ neV)	$E_{\beta}(1s)$	Chemical species
S	1.593 39			3.11					
Ī	1.593 14	1.582 86	1.580 97	3.36	10.28	12.85	13.71	13.67	F*
A	1.593 09	1.582 72	1.580 76	3.41	10.37	12.96	13.83	13.88	Ga
B	1.593 05	1.582 52	1.580 56	3.46	10.53	13.16	14.04	14.05	Al*
С	1.593 02	1.582 46	1.580 44	3.48	10.56	13.20	14.08	14.15	In
E	1.592 96	1.582 10	1.58006	3.54	10.86	13.58	14.48	14.48	Cl
F	1.592 84	1.581 75	1.579 79	3.66	11.09	13.86	14.79	14.60	

to their different central-cell corrections. However, the TET are sometimes difficult to observe, especially on Terich samples. In these ingots, the relatively high-acceptor doping induces acceptor-bound exciton lines with a low-energy tail which can dominate the TET lines. As already outlined, the TET lines can be enhanced by selectively pumping in the  $D_1^1$  line.<sup>14</sup> The result of selective excitation experiments with different excitation energies  $L_1, L_2, L_3$  on TR samples is shown in Figs. 3(a) and 3(b).

The following two remarks have to be taken into account when discussing on selective excitation PL experiments.

(i) As the excitation energy is on  $D_1^1$ , the higher-energy PBE lines are not excited and the corresponding TET replica do not appear; in fact, due to the finite width of the excitation line,  $D_2^2$  is excited simultaneously to  $D_2^1$ .

(ii)  $D_1^1$  is a composite line containing the excitonic transition associated to several donors. By tuning the exact position of the pumping line, it is possible to reinforce the TET replica of one particular component and thus to associate a given PBE position and a TET line or a TET set.

The spectra obtained on a sample sliced from crystal TR2 [Fig. 3(a)] show two main TET lines, which are labeled  $B_2^1$  and  $E_2^1$ : the relative intensity of each line depends on the excitation energy, designated  $L_1, L_2$  in the inset. There are also two main TET lines in selective excitation spectra obtained on a sample sliced from crystal TR3 [Fig. 3(b)]. These lines are designated  $E_2^1$  and  $F_2^1$ . The presence of these TET lines  $B_2^1$ ,  $E_2^1$ , and  $F_2^1$  depending on the excitation energy shows that we are dealing with three different donors whose PBE lines are B, E, and F. In the upper spectrum of Fig. 3(b) we can observe a line labeled R which is an electronic Raman-scattering line, shifted from the excitation energy by the quantity E(1s) - E(2s) [or E(2p)]. Such lines are seen clearly when the pumping energy is selected near the n=2 free exciton. These transitions could be used to deduce the inelastic excitations of the bound electron. Their intensity varies strongly with the excitation energy.<sup>19</sup>

For the ST ingot, the identification of the PL lines is easier since the intensity of the donor related PBE lines is strong enough with above band-gap excitation. Figure 3(c) shows three spectra obtained using samples sliced at different positions in the central part of the ST ingot: we can observe a variation of the relative strength of the various components of the PL spectra. Four TET lines  $A_2^1$ ,  $B_2^1$ ,  $C_2^1$ , and  $E_2^1$  can be detected and are ascribed to four donor species, inhomogeneously distributed in the ingot; two of them coincide with the TET lines of Fig. 3(a).

In summary, from the PL spectra of Fig. 3, five

FIG. 3. TET lines recorded at 1.8 K with the various resonant excitations shown in the inset for Te-rich samples (a) TR2 and (b) TR3 and with above band-gap excitation for three stoichiometric samples (c) ST. These spectra give evidence of five different "native" donors (A, B, C, E, and F). The line R on spectrum (b) is a Raman line.



different TET lines are observed and presumed to be associated with five different donors.

Examination of the impurity content of the investigated samples (Table I) shows that there are various candidates which have been detected in sufficient quantities: C1 (ST ingot) or In and C1 (TR2 ingot). This is only a first clue to help the future identification since other donors may be present in amounts too small to be revealed by the chemical analysis. On the other hand, chemically detected impurities may be partially or totally inactive due to chemical reaction or associations (precipitation, complexes, etc.).

The energies of the  $D_{n=1,2,3}^{1}$  lines associated with each donor are reported in Table II. The identifications listed in the last column will be justified in Sec. III E below. No emission of TET lines has been observed when pumping on the S line [inset of Figs. 3(a) and 3(b)]. We do not have any clue for the identification of this line.

# C. Ionization and localization energies of the residual donors in as-grown CdTe

In the effective-mass theory, modified to account for the polaron effect, the donor energy levels  $-R_0/n^2$  are shifted by a corrective term  $\Delta E$  so that the energy of the *n*th level becomes<sup>20</sup>

$$E(n) = -\frac{R_0}{n^2} + \Delta E(n)$$

with

$$-\frac{\Delta E(n)}{\alpha} = \frac{R_0}{6n^2} , \qquad (1)$$

 $R_0$  being the modified Rydberg and  $\alpha$  the polaron coupling constant. It must be noticed that  $\alpha$  cannot be deduced from the Frohlich formula<sup>21</sup> since the static and high-frequency dielectric constants which appear in this formula are very difficult to determine accurately. Direct experimental determination on CdTe (Ref. 22) leads to  $\alpha = 0.40 \pm 0.03$ . This value can be used to determine the energy levels E(ns) as a function of  $R_0$  taken as a parameter. From relations (1), it can be deduced that

$$E(1s) = 1.067R_0,$$
  

$$E(2s) = 0.267R_0,$$
  

$$E(3s) = 0.119R_0,$$
  
(2)

etc.

In particular, the ionization energy E(1s) can be obtained if a precise value of  $R_0$  is available. However the uncertainty on  $R_0$  is generally large if a theoretical formula is used (due to the uncertainties related to the dielectric constants and the electron effective mass).

We propose a direct empirical determination of  $R_0$ , for each of the native donors, by comparing the experimental shift E(1s)-E(2s) as shown in Fig. 1 to the difference deduced from relations (2):

$$E(1s) - E(2s) = 0.800R_0$$
 (3)

The  $R_0$  values obtained by this method range between 12.85 meV for donor I and 13.86 meV for donor F (the existence of this donor is shown later) as indicated in Table II. These values must be compared to  $R_0 = 106\pm 2$ cm<sup>-1</sup> $\approx$ 13.25 meV already proposed for  $R_0$  in CdTe crystals (6). From such a direct evaluation of  $R_0$ , the ionization energy E(1s) can be deduced using Eq. (2). These values are listed in Table II [column  $E_{\alpha}(1s)$ ]. With this method, within the effective-mass approximation, the only inaccuracy in the ionization energy comes from the evaluation of the coupling constant  $\alpha$  and the determination of the  $(1s \rightarrow 2s)$  energy on a PL spectrum.

Another more direct determination of E(1s) can be done by assuming a pseudoacceptor model for the  $(D^0X)$ complex.<sup>23</sup> For each donor, we plot the experimental splittings E(ns) - E(1s) versus  $1/n^2$  and, extrapolating to  $n \to \infty$ , we obtain E(1s). Figure 4 illustrates this method. It must be pointed out that only two transitions [(1s-2s) and (1s-3s)] are available for all five donors. The transition (1s-4s) is observed only for donors A and E, and with a rather large incertainty. Nevertheless, the values of E(1s) can be obtained and are listed as  $E_{\beta}(1s)$ in Table II. It can be seen that both experimental determinations lead to very comparable results, within 0.07 meV.

Table II shows that the difference between the extreme values of the ionization energies for the different donors is only 1 meV. This is consistent with the values obtained earlier by Simmonds *et al.*<sup>6</sup> who reported that the E(1s)-E(2p) energies for the different native donors extend from 10.01 to 10.84 meV.







FIG. 5. Exciton localization energy vs the ionization energy for the various donors detected in CdTe. The slope value is 0.246. The letters A, C, and E stand for gallium, indium, and chlorine, respectively, according to further identification.

From the PBE line  $D_1^1$  the localization energy  $E_{loc}$  of the exciton on the donor can be deduced

 $E_{\rm loc} = D_1^1 - E_x$ 

 $E_x$  being the energy of the free-exciton line. Experimental values of  $E_{\rm loc}$  for the native donors are listed in Table II if the value  $E_x = 1.5965$  eV is used.<sup>15</sup> Figure 5 is a plot of  $E_{\rm loc}$  versus E(1s). A linear relationship is obtained with an average value of 0.246 for the slope, in approximate agreement with Haynes's rule. This value is comparable to that obtained for donors in other II-VI compounds.<sup>23</sup> In contrast, it has been shown previously<sup>15</sup> that Haynes's rule does not work for acceptors in CdTe and in ZnTe.

## D. Photoluminescence studies of thermally annealed CdTe crystals

#### 1. General remarks on annealing of CdTe materials

Heat treatments under tellurium or cadmium overpressure are of particular interest because the overall stoichiometry of the crystal can be changed. The cadmium vapor anneals convert CdTe to n type, even for materials with a high-acceptor impurity content, provided high Cd overpressures are used.<sup>8,24</sup> Tellurium vacancies<sup>8,25</sup> or Cd interstitials are generally invoked to explain this conversion. Moreover, annealing in a liquid metallic phase is thought to purify the crystal because of the higher solubility of the impurities in the liquid.

#### 2. Annealing in liquid or vapor-phase cadmium

In this section we study the effect of thermal annealing in molten cadmium or under cadmium vapor pressure. The annealing temperature is 700 °C and the duration is 1 h. Figure 6 presents typical PL spectra of TR2 and ST samples (initially p and n type, respectively) before (lower spectra) and after (upper spectra) the annealing treatment. These spectra are recorded using identical conditions: excitation energy above the band gap; excitation



FIG. 6. Comparison between near-band-gap PL spectra of (a) a Te-rich sample and (b) a stoichiometric sample, before (lower spectra) and after (upper spectra) annealing in molten cadmium (700 °C, 1 h).

power, 20 mW; temperature, 1.8 K. We make the following remarks.

(i) As pointed out before, there are some variations in the PL spectra from slice to slice within a given ingot, but the modifications we observe after annealing are considerably stronger and irrespective of the location of the slice on each ingot. Furthermore the comparison is always done for each ingot with unannealed samples of the same slice.

(ii) Electrical measurements (C-V measurements on Schottky diodes) after the thermal annealing indicate conversion to n type for all slices from the three TR ingots.

(iii) There is a systematic relative enhancement of the PBE line associated with the donors. This enhancement is larger for a larger initial departure from the stoichiometric condition: the  $I(D_1)/I(A_1^{Cu})$  ratio of the PBE line intensities ( $A_1^{Cu}$  is the PBE line related to the residual Cu acceptor) increases from 0.03 to 2.5 for all of the TR ingots, but only from 0.6 to 1 for the ST ingot. On beveled samples, this enhancement appears to be larger at the surface ( $\sim 80-100 \ \mu m$ ) than in the bulk of the slice, indicating that the duration of the treatment is too short to establish the equilibrium throughout the sample. Such results indicate either an increase of the donor concentration or a purification of the crystal by eliminating acceptor impurities (like Li or Cu).

(iv) There is an intensity enhancement of the replica of the free-exciton line (X-1 LO) after the thermal treatment. This result can be explained by a decrease of the concentration of exciton trapping centers related to some purification process.

Because of the relative width of the PBE line  $D_1^1$ , we cannot decide by direct examination of this line whether the annealing has induced an increase of the concentration of the initially present donor or if a specific donor has been introduced by the treatment. Resonant excitation of the TET lines was done to investigate this point.

Spectra shown in Fig. 7 are for the stoichiometric sample of Fig. 6(b) (sample ST annealed at 700 °C for 1 h in molten cadmium). No new TET line is observed but the TET lines that were already present in the sample before annealing are much more intense and can be more easily enhanced selectively: depending on the excitation energy, TET lines  $B_2^1$ ,  $E_2^1$ , or  $F_2^1$  (spectra *a*, *b*, and *c*) are successively enhanced. The spectra are for the surface of the sample where the TET line  $F_2^1$  appears stronger than in the bulk.

We have performed 1 h annealings at T = 700 °C under various overpressures:  $P_{Cd} = 50$ , 80, 150, and 400 Torr. The general trends are the following.

(i) For TR ingots, an enhancement of the PBE line associated with the donors occurs if  $P_{Cd}$  is lower than 400 Torr. However for  $P_{Cd} = 50$  Torr this enhancement is too weak and thus irregularly observed.

(ii) For the ST ingot, a broadening of the excitonic luminescence lines associated with donors or acceptors is observed if the overpressure  $P_{Cd}$  is higher than 150 Torr.

(iii) For all ingots, annealing under a high Cd overpressure introduces a broad band at 1.586 eV already reported.<sup>26</sup> The presence of this band is generally related to a

FIG. 7. TET lines detected at 1.8 K on the stoichiometric sample of Fig. 6(b). (ST sample annealed at 700 °C for 1 h in molten cadmium.) The excitation energies are successively set on the  $D_1^1$  components (cf. Fig. 1) to reinforce the TET lines  $B_2^1$ ,  $E_2^1$ , and  $F_2^1$  [spectrum (a), (b), and (c), respectively]. The spectra are recorded at the surface of the sample.

compensation of the material but there is presently no identification of the transition involved.<sup>26</sup>

(iv) Figure 8 shows typical TET lines observed on a slice from ingot TR1, the annealing conditions being  $P_{Cd}$  = 400 Torr, 700 °C, 20 min. Spectrum (b) is obtained on an unannealed piece of the slice, while the two other spectra are recorded at the surface (a1) or in the bulk (a2)of a piece of this slice which has been annealed. The marked feature here is the appearance of a new TET line  $I_2^1$ . This new TET line  $I_2^1$  is observed even with nonresonant excitation. It can be associated with a new PBE line  $D_1(I)$  at 1.593 14 eV. From the excitation energy (10.28 meV) this new donor appears to be the shallowest of the detected donors. This line  $I_2^1$  is observed with various intensities for annealed samples sliced from different Te-rich ingots but is never detected in annealed samples extracted from the ST ingot. The best annealing conditions to obtain the well-resolved  $I_2^1$  line are  $80 < P_{Cd} < 400$ Torr with a annealing duration between 20 min and 1 h.

## E. Chemical identification of the donors

We have carried out the identification of the donors using diffusion-doping experiments. The samples were covered with thin layers of the metal to diffuse (Ga, In, or Al) and annealed in the conditions detailed later. For chlorine, such a diffusion process was impracticable due





Wavelength (Å)

FIG. 8. TET lines detected at 1.8 K for an annealed Te-rich sample (TR1 ingot) (700 °C, 20 min,  $P_{Cd}$  = 400 Torr) at the surface (a1) and in the bulk (a2). Spectrum (b) is for an unannealed sample. The treatment induces a new TET line labeled  $I_{2}^{1}$ .

to the lack of a convenient source. Thus we have used ingots grown by the traveling-heater method (THM) which were purposely doped during growth by adding  $CdCl_2$  into the melt.

From physico-chemical considerations, the solubility of donors on Cd sites should be enhanced by thermal diffusion under Te overpressure. Unfortunately such anneals can induce the formation of Cd vacancies and complex acceptors like  $V_{Cd}$ - $D_{Cd}$ . Defects of this kind have indeed been observed in ZnTe crystals:  $V_{Zn}$ -Al<sub>Zn</sub> and  $V_{Zn}$ -Cl<sub>Te</sub>.<sup>27</sup> Thus, we attempted to diffuse Ga, Al, and In donor impurities under a Cd overpressure, even if the solubility is not optimum. Moreover, we have shown in the preceding section that thermal annealing of as-grown crystals under a cadmium overpressure reveals at least six shallow donors. The point now is to separate the effects related to the thermal treatment itself from those induced by the thermal diffusion of a specific donor impurity.

Typical thermal diffusion conditions are 1 h, 700 °C,  $P_{Cd} = 50$  or 150 Torr. In some cases, a double diffusion technique has been used<sup>28,29</sup>: the metal source is evaporated onto the surface of the sample and a short preheating is first performed ( $T \simeq 400$  °C) under a N<sub>2</sub>-H<sub>2</sub> atmosphere. Then, the metallic layer is removed to control the impurity source and to prevent the excessive formation of complex centers during the more extended thermal treatment which is given afterwards.

After the thermal diffusion, a clear enhancement of the intensity of line  $D_1$  compared to that of line  $A_1$  is observed. As already stated, the most pronounced effect occurs for the crystal ST, with  $P_{Cd} = 150$  Torr. In this case, the  $I(D_1)/I(A_1)$  ratio reaches 10 at the surface of the sample. Such a result has never been obtained in thermal annealing of the same as-grown samples; this indicates that a significant diffusion of the impurities from the source has occurred. Moreover, such treatments induce a large increase  $(\times 4)$  of the linewidth of the PBE line  $D_1^1$  and a shift of this line toward lower energies  $(\sim 0.5 \text{ meV})$ . This increase of the exciton localization energy could be due to the simultaneous binding of excitons to a pair of donors; such an effect has already been reported for high concentration of acceptors in ZnTe crystals.28

The spectra shown in Fig. 9 illustrate these various points. They were recorded on an aluminum-diffused ST sample annealed at 700 °C under  $P_{Cd} = 150$  Torr and subsequently beveled. The spectrum (1) was taken at the surface, spectrum (2) at a position corresponding to a depth of 100-200  $\mu$ m and spectrum (3) or on the back side of the sample. The increase of the ratio  $I(D_1)/(A_1)$  on going closer to the diffusion source as well as the broadening and shift due to the higher donor concentration are clearly observed. Such strong effects have never been observed in nondiffused annealed test samples.



FIG. 9. PL spectra recorded at 1.8 K on aluminum diffused ST samples. Anneal 700 °C,  $P_{Cd} = 150$  Torr. The spectra are recorded at the surface (1), about 100-200  $\mu$ m below the original surface (2) and on the back side surface (3) of the sample.

#### 1. Identification of gallium and indium donors

Table III summarizes the thermal-diffusion conditions in the case of diffusion doping with Ga and In, and the electrical measurements obtained on a beveled sample are listed in the last column. The cadmium overpressures are limited to the 50-150 Torr range because the PL lines broaden for a higher overpressure.<sup>30</sup>

As broadening of the PBE line  $D_1$  is observed after thermal diffusion; a study of the TET lines is necessary to identify the donor impurity. Figure 10 summarizes the TET lines recorded on samples doped with Ga [spectrum (a)] or In [spectrum (b)], when the same material (TR2) is used (Table III). In the same figure, in order to clarify the following discussion, we also present the spectrum obtained for chlorine doped material [spectrum (c)] (cf. below). The spectra (d) and (e) were obtained on control samples of the same TR2 crystal, nondiffused, annealed at 700 °C under cadmium overpressure of, respectively, 400 and 80 Torrs.

Independently of the treatment conditions (Table III) the spectra of the Ga-diffused samples are essentially made up of the TET replica of donor A [spectrum (a)] and the In-diffused samples spectra present TET replicas of donor C with a small component E [spectrum (b)]. Thus it can be concluded that the donor A, which only appears in Ga-diffused samples is related to Ga<sub>Cd</sub>. There are two components C and E in the spectra obtained for the In-diffused sample: component E is observed in nondiffused samples while component C is introduced by the diffusion process. Furthermore, we will show in the next paragraph that E is probably associated with chlorine. We are thus lead to identify the donor C with In.

## 2. Tentative identification of chlorine, fluorine, and aluminum donors

#### a. Chlorine

The energy levels of the chlorine donor have already been obtained by Neu<sup>7</sup> by the comparison between pure material and chlorine-doped CdTe crystals. Several slices of the same chlorine-doped crystal were kindly supplied to us by Triboulet. This crystal had been doped with  $CdCl_2$  in the melt by the THM. After annealing (700 °C,  $P_{\rm Cd} = 150$  Torr), the TET spectrum of such a sample, shown in Fig. 10 [spectrum (c)], is particularly simple being made up of a single line  $E_2^1$  and of its higher energy satellites. By comparison with the spectra (a) and (b) of Fig. 10, we conclude that the TET line  $E_2^1$  is due to a chlorine-related donor in agreement with the previous identification by Neu.<sup>7</sup> Due to the high mobility of excitons between donor impurities, the large amount of chlorine donors reduces the recombination probability of excitons bound to other donors. This explains the disappearance of the lines related to other donors.

In fact, donor E is also observed in control (Fig. 8) and in In-diffused [Fig. 10(b)] samples, a result which accounts for the relatively large amounts of chlorine detected in the various undoped crystal by chemical analysis (1.5-5 ppm) as well as for the fact that the annealing treatments with a cadmium overpressure are expected to favor the solubility of the residual chlorine on Te sites. Thus, the only argument for the identification is the much larger TET line E obtained for deliberately doped crystals.

b. Aluminum

The diffusion of aluminum impurities (700 °C, 1 h,  $P_{Cd} = 150$  Torr) from a source made of an evaporated metallic aluminum layer has been attempted using samples extracted from ST and TR1 ingots. Such a treatment produces a relative enhancement of the  $B_2^1$  line with respect to the other TET lines while a similar treatment



FIG. 10. PL spectra recorded with above band-gap excitation for (a) a gallium diffused crystal, (b) an indium diffused crystal, (c) a crystal doped in the melt with chlorine, and (d) and (e) for control samples of the same TR2 crystals. The diffusion conditions for spectra (a) and (b) are indicated in Table III. Spectra (d) and (e) are obtained using nondiffused samples which were annealed at 700 °C under cadumium overpressure  $P_{Cd}=400$  and 80 Torrs, respectively. The spectra are recorded under identical experimental conditions. Lines  $A_2^1$ ,  $C_2^1$ , and  $E_2^1$  refer to gallium, indium, and chlorine related donors, respectively.

					Elect	rical
				measurements $(200 - 3) \times 10^{16}$		
			Doping conditions		$n(\text{cm}^{-1}) \times 10^{10}$	
Sample	Impurity	Ingot	Anneal	P <sub>Cd</sub> (Torr)	Surface	Bulk
	Ga	ST	700 °C-1 h	150	2	0.2
	Ga	TR1	Prediffusion 400 °C-1 h + 700 °C-1 h	150	4	0.2
( <i>a</i> )	Ga	TR2	Prediffusion 500 °C-1 h + 700 °C-1 h	50	10	0.001
	In	TR1	Prediffusion 400 °C-1 h + 700 °C-1 h	150	0.10	0.005
( <i>b</i> )	In	TR2	Prediffusion 400 °C-1 h + 700 °C-1 h	50	0.4	0.02
		CdTe:In-doped	Without treatment			0.001
		in the bath	700 °C-1 h	150		1

TABLE III. Gallium and indium diffusion doping experimental conditions and electrical measurement results. Samples (a) and (b) have been used to obtain the spectra (a) and (b) in Fig. 10.

does not produce any similar enhancement of line  $B_2^1$  on the control sample. Such results are illustrated in Fig. 11(a) for the ST sample: spectrum (1) and (2) correspond to Al diffused and control sample, respectively. Identical Al-diffusion treatment on a TR1 sample leads to the spectra of Fig. 11(b), which are recorded at the original surface (1), about 100-200  $\mu$ m below the original surface (2) far from the original surface (3) of the sample. No clear information can be deduced from the spectrum recorded



FIG. 11. TET lines recorded at 1.8 K on aluminum diffused samples (700 °C, 1 h,  $P_{Cd}$ =150 Torrs). The starting material was taken from the ST crystal (a) [surface of the Al-diffused sample: spectrum (1), control sample; spectrum (2), annealed without the aluminum source] or (b) from the TR1 crystal [the spectra were recorded at the surface (1), 100-200  $\mu$ m below the surface (2), and far from the original surface (3)].

near the diffusion source, as we have already stated. However, far from the diffusion source an enhancement of the  $B_2^1$  line can be observed [spectrum (3) in Fig. 11(b)].

In fact, the line  $B_2^1$  is always present in as-grown samples. This would mean, according to our tentative identification, that the Al impurity would be systematically present in the as-grown samples in small quantities. Indeed the segregation coefficient of this impurity is very low (k = 0.1); thus, during the growth of the crystal, it remains in the solid phase and there is no purification by the growth process itself. Moreover the very close proximity of the line  $C_2^1$  makes this identification more uncertain.

#### c. Fluorine

As already stated, the donor called I is the shallowest of the donors detected in CdTe. The impurity which produces such a small central-cell correction has certainly a small mass number, in agreement with the wellestablished trends for the central-cell corrections.

After an annealing under Cd overpressure, an increase of the solubility on Te sites can be assumed. The examination of the results of a mass spectroscopy analysis (Table I) suggests that this donor could be fluorine in a Te site. Such an assumption is also supported by the irregular observation of the TET line  $I_2^1$  and the variation in a large range of the observed fluorine concentrations (Table I). The fact that donor I is irregularly observed rules out any attribution of donor I to isolated cadmium interstitials. To sum up, the identification of chlorine, aluminium, and fluorine donors is speculative only and should be supported by complementary experimental results.

## **IV. DISCUSSION**

The experiments reported in this paper have confirmed that several donors exist in CdTe. Three of them have been related to impurities introduced by diffusion experiments. The identification is sometimes made uncertain by the fact that many impurities preexist in normally undoped materials. The donor activity is assumed to come from isolated substitutional impurities: uniaxial stress experiments clearly suggest that the donors occupy a high-symmetry site, very probably a substitutional  $T_d$  site.<sup>31</sup>

In the past, the role of intrinsic defects as donor or acceptor species in CdTe has often been invoked.<sup>8</sup> However, the main conclusion of a detailed study of acceptors in CdTe was that isolated intrinsic defects do not have any direct role in the conductivity while they control the solubility of the active impurities.<sup>15</sup>

Thus, it was of great interest to check if some of the donor species detected could in fact be intrinsic defects like  $Cd_i$ . Indeed, the general trend is that thermal annealing under Cd overpressure increases the donor activity and sometimes converts the crystal to *n* type.<sup>32</sup> However, very long-term anneals under Cd overpressure do not systematically enhance the donor content. Also, some species (like donor *I*), which are revealed by the Cd annealing, can be observed only in some kinds of crystals and not in others. This is just the opposite of what would be observed if intrinsic defects related to stoichiometry were directly active.

Our interpretation of the experiments is the following: the treatment of the crystal in the metal-rich atmosphere changes the stoichiometry of the crystal since the growth usually occurs in Te-rich conditions. The following consequences can be envisaged.

(i) Tellurium precipitates are dissolved. They release the impurities which have been segregated in the molten Te phase during growth. So acceptor and donor impurities diffuse out from the location of the precipitate. This mechanism has been studied in detail in ZnTe (see Ref. 12 and earlier work quoted therein) and CdTe.<sup>26</sup>

(ii) The solubility of some impurities on tellurium sites is increased. This could be the case for fluorine, chlorine, or even bromine while the solubility of Cd-site impurities is decreased.

(iii) During growth in tellurium-rich conditions, there are Cd vacancies in equilibrium. If donor-type impurities and charged vacancies (with two negative charges) are simultaneously present there is a Coulombic attraction between them which leads to the formation of singly charged acceptors. Complex centers (A center) of this type have been observed in ZnS, ZnSe, and ZnTe.<sup>27</sup> A subsequent thermal treatment in metal-rich conditions allows the complex to react with metal ions: the donor impurities are then revealed.

All of these processes are expected to increase the concentration of active donor-type impurities, particularly if they are on tellurium sites. The resulting effect is less clear for Cd-site impurities whose solubility could decrease under heat treatment in Cd-rich atmospheres.

## V. SUMMARY AND CONCLUSIONS

We have presented detailed luminescence studies of native shallow donors in CdTe crystals, their evolution after thermal annealing under conditions of excess cadmium and the chemical identification of some of the donors.

Photoluminescence and high-resolution selective excitation of the luminescence experiments for as-grown crystals clearly indicate that there are at least six donors present in as-grown CdTe. Precise studies of the PBE and the TET lines allow the determination of the  $(1s \rightarrow 2s)$  and  $(1s \rightarrow 3s)$  transition energies, the ionization, and the exciton localization energies for each donor (Table II). The ionization energies all range between 13.71 and 14.79 meV and the exciton localization energies obey Haynes's rule.

From doping experiments, we have clearly identified two donor impurities indium and gallium, while the identification of the chlorine and the aluminum donor is less definitive and that of the fluorine donor is speculative only.

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