CATHODOLUMINESCENCE STUDIES OF THE 1.4 eV BANDS IN CdTe (*)

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Résumé. — On a effectué des mesures de luminescence dans la bande voisine de 1,4 eV par cathodoluminescence à 80 K, sur divers types de cristaux de tellurure de cadmium : purs, stœchiométriques, compensés par un donneur sous excès de tellure. Ce travail constitue la première approche tenant compte à la fois de l'influence du niveau d'injection, de la réponse transitoire et de la coupure sous l'effet de la température. Nous avons établi que cette bande de luminescence possède les caractéristiques suivantes : la forme de la bande et la position du pic sont indépendants du niveau d'injection tant que les bandes ne se chevauchent pas ; la transition est lente avec des constantes de temps de l'ordre de 1 à 5 μ s ; ce temps de transition est indépendant du niveau de dopage lorsque celui-ci varie de trois ordres de grandeur ; l'intensité de la luminescence croît avec la concentration en donneurs ; la luminescence présente un phénomène de coupure avec la température avec une énergie d'activation relativement importante. L'ensemble de ces résultats ne peut-être expliqué à l'aide des mécanismes de transitions classiques, qui sont bien établis. Comme chacun de ces résultats est en accord avec certaines données de la littérature, nous devons supposer que cette transition est plus complexe que ce qui était supposé jusqu'ici, plutôt que de considérer l'existence de plusieurs transitions dans les divers matériaux.

Abstract. — Using cathodoluminescence at 80 K, we have studied the 1.4 eV luminescence bands in nominally undoped, nominally stoichiometric CdTe and in donor-compensated, Te-rich CdTe. The present work represents the first combined measurements of injection level dependence, transition response and thermal quenching for these materials. We find that the 1.4 eV luminescence has the following characteristics : 1) the band shape and peak position are independent of injection level, except for those samples having overlapping bands, 2) the transition is slow, with characteristic times on the order of 1-5E-6 s, 3) the transition response time is approximately constant over three orders of magnitude in doping level, 4) the luminescence intensity increases with donor doping level, and 5) the luminescence shows thermal quenching with a relatively large activation energy. This combination of characteristics is not explicable in terms of well-understood transition mechanisms. While the results of our individual measurements are similar to results from corresponding measurements in the literature, it is clear from the present work that the contradictory conclusions of previous investigators regarding the nature of the 1.4 eV transitions in CdTe arose from the fact that this transition is of a more complex nature than generally appreciated rather than from the appearance of different types of transitions in different CdTe samples.

1. Introduction. — Observations of broad emission bands centered near 1.4-1.45 eV were noted in the earliest investigations of luminescence in CdTe [1-3]. These bands, which can be seen in CdTe samples prepared in practically every laboratory [1-24], have appeared so persistently that they have sometimes been discussed [3] in conjunction with the edge emission of CdTe, which occurs between 1.5 and 1.6 eV. After two decades of research on CdTe, which has seen great improvements in material quality, the 1.4 eV bands still appear in all but the purest specimens. The origin of these bands is the subject of the present paper.

Certain basic aspects of the 1.4 eV bands in CdTe are understood. From the published investigations of many workers [4-16] it can be concluded that the bands

are enhanced by addition of impurities and by deviation either way from nominal 1 : 1 stoichiometry. Therefore, it is generally accepted that the 1.4 eV bands involve both impurities and native defects of some sort. It is also believed that the transitions responsible for these bands terminate on moderately deep acceptor levels that are the order of 0.1 eV from the valence band [4-22]. Lastly, generally similar bands in the range 1.4 to 1.45 eV have been observed in CdTe whether the material is Cd-rich, Te-rich, or nominally stoichiometric. The results of a literature survey on the 1.4 eV bands in CdTe are summarized in table I.

Despite the prominence of the 1.4 eV bands and their long history of observation, the possible origins of these bands remain a subject of much controversy. As shown in table I, there are a variety of apparent contradictions between results and conclusions of various groups who have studied the 1.4 eV bands. One problem is that the bands may have different

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TABLE I

Summary of prior work on the 1.4 eV bands in CdTe. The results are grouped according to whether the majority of samples studied were Cd-Rich (CdTe), Te-Rich (CdTe) or nominally stoichiometric or unspecified (CdTe). Assignments into these categories, as well as interpretations and conclusions, are sometimes our own. Abbreviations and symbols used : « il » = injection level ; « T » = temperature ; « D » = donor ; « A » = acceptor ; « NN » = nearest neighbor ; « CC » = configurational coordinate ; « + » = temperature of 20 K ; « o » = phonon structure not resolved.

[Ref.] Author (Date)	Material	Peak at 80 K (eV)	No-phonon peak at 4 K (eV)	Measure I. L. D.	Dynamic response	Thermal quenching (ϵ_A , eV)	Remarks	Conclusion as to nature of 1.4 eV band
[8-13] Taguchi, <i>et al.</i> (1972-1975)	CdTe	1.42	1.451- 1.455	×	×	0.16	1.4 eV band enhanced by Cd excess ; suppressed by Cd loss. Band very strong when both Cl donors and excess Cd are present. Time-resolved spectra shift to lower energies at longer times, but samples used have overlapping bands. Cd firing at 900 °C lowers peak energy of 1.4 eV band. In sample fired in low P_{Cd} and quenched, band is very weak ; band is now enhanced by e^- or n irradiation and 100 °C anneal.	Transitions between spatially separated donors (ϵ_c -0.02 eV) and acceptors ($\epsilon_v + 0.16$ eV). Donors are possibly Cd_i ; acceptors are complexes involving V_{Te} . Mean D-A separation must be 100-200 Å to explain slow time decay ; this seems inconsistent with stability of 1.4 eV band under Cd-firings or n-irradiations that severely quench edge emission. Il shift is used as evidence for D-A pair nature of band but shift is only 4.5 meV for $800 \times$ increase in il.
	CdTe : Cl CdTe : Ga		1.40 ₀ 1.377 ₀	×	×	0.16		
[4] Vavilov, <i>et al.</i> (1967)	CdTe	1.43	1.45 ⁺				Intensity of 1.4 eV band increases with In or Al or excess Cd content, decreases with vac annealing .	Transitions between spatially separated shallow donors and deep acceptors.
	CdTe : In CdTe : Al CdTe	1.42 1.42	1.47 ⁺					
[14] Rud' <i>et al.</i> (1971)	CdTe : A CdTe CdTe	1.41 No No	Band Band				1.4 eV band increases with excess Cd and with unknown acceptor conc. Band quenched by firing in vac or Te vapor. Slow cooling rate enhances band ; quenching destroys it.	Intracenter transitions in D-A complex of Cd_i -impurity type. Donor level is shallow and acceptor level is deep ($\epsilon_v + 0.15$ eV). Centers appear unaffected by change from p-type to n-type CdTe.
[18] Panossian, <i>et al.</i> (1969)	CdTe	1.42	1.453 ⁺				Phonons interact strongly with acceptor and weakly with donor.	Transitions between spatially separate donors ($\epsilon_c - 0.015$ eV) and acceptors ($\epsilon_v + 0.14$ eV).
[23] Noblanc and Durauffourg (1971)	CdTe		1.451				Some samples show sharp lines on the broader phonon replicas of the 1.451 eV band at 4 K. Lines result from recombination at oxygen isoelectronic trap.	There is no apparent explanation for 1.4 eV band in terms of recombination at oxygen iso-electronic traps.
[22] Barnes and Kikuchi (1975)	CdTe		1.45				Selective displacement of Cd by thermal neutron irradiation enhances 1.4 eV band in some samples, and decreases band in other samples, relative to edge emission.	Transitions to acceptor level arising from complex composed of Cd defect and donor impurity.
Present Work	CdTe	1.44	1.44 ₀	×	×	0.103	Samples are nominally stoichiometric and undoped but show overlapping bands.	As described for our work on Te-rich CdTe.
[15] Bryant and Totterdell (1972)	CdTe CdTe	1.42	1.451 (8 K) 1.451 (8 K)			0.13	1.4 eV band enhanced by 300 K e^- irradiation capable of displacing Cd only. Band is enhanced by vacuum firing but unaffected by firing for unspecified time at low P_{Cd} .	Transitions to acceptor levels at approx. $\epsilon_v + 0.15$ eV resulting from complex center containing V_{Cd} and possibly impurity atoms. Complexes are insensitive to firing treatments that affect edge emission. Thermal quenching suggests CB-A transitions.

TABLE I (Suite)

[Ref.] Author (date)	Material	Peak at 80 K (eV)	No-phonon peak at 4 K (eV)	Measure I. L. D.	Dynamic response	Thermal quenching (ϵ_A , eV)	Remarks	Conclusion as to nature of 1.4 eV band
[17] Bryant, <i>et al.</i> (1972)	CdTe	1.41	1.42 ₀ (8 K)			0.106	Thermal quenching data suggests CB-A transition. Peak shifts with T ; 4 K phonon structure not well resolved.	CB-A transitions. Acceptor level produced by complex involving Cd defect.
[16] Bryant and Webster (1968)	CdTe	1.40				0.24	Firing in Cd vapor at moderate time and P_{Cd} suppresses 1.4 eV band. Further firing causes similar band to appear; this band increases with firing time and P_{Cd} . Firing changes CdTe to $\overline{\text{CdTe}}$.	CB-A transitions. Acceptor levels are associated with a complex involving V_{Cd} . Acceptor level assigned at $\epsilon_v + 0.16$ eV, despite thermal quenching activation energy of 0.24 eV.
	CdTe	1.40						
[24] Bryant <i>et al.</i> (1968)	CdTe	1.44	1.457				Electron irradiations at 15 K producing isolated V_{Cd} or V_{Cd} and V_{Te} suppress 1.4 eV band while inducing higher-energy bands.	1.4 eV band involves complex defects rather than isolated V_{Cd} or V_{Te} .
[6] Agrinskaya, <i>et al.</i> (1970)	CdTe : In CdTe : Cl	1.42	1.45 1.47	$\times$ $\times$			1.4 eV band grows on firing in vac or Te vapor. No peak shift with il or T. Half-width increases strongly with T . No FC shift between lum and abs. $\Delta\epsilon$ between In and Cl doping suggests NN V_{Cd} - D complexes.	Transitions from CB to acceptor levels at $\epsilon_v + 0.15$ eV resulting from compact or NN V_{Cd} - D complexes. Gaussian band shape at 80-300 K, half-width variation, and absence of peak shift suggest CC model for V_{Cd} -D complex. However, absence of FC shift not discussed.
[7] Agrinskaya, <i>et al.</i> (1971)	CdTe : In	1.42	1.44	$\times$		0.155 0.13	Thermal activation energies nearly agree with acceptor depth assuming transition from CB or states close in energy. Peak shifts only 2 meV for $100 \times$ increase in il, < 10 meV with T from 77 K to 300 K. PC peak appears ~ 0.05 eV above lum peak.	Transitions within compact or NN V_{Cd} -D complexes. Acceptor-like ground state at approx. $\epsilon_v + 0.15$ eV. Donor-like excited state near ϵ_c . Characteristics of complex consistent with CC model, but abs. not measured.
	CdTe : Al CdTe : Cl CdTe : In	1.42	1.446 1.43 ₀ 1.42 ₀	$\times$ $\times$ $\times$				
[5] Agrinskaya, <i>et al.</i> (1971)	CdTe : In (Ion impl.)		1.457				1.4 eV band appears after In implantation. Annealing enhances band with little change in spectrum.	CB-A transitions. Acceptor level associated with V_{Cd} -In complexes.
[10, 12, 13] Taguchi, <i>et al.</i> (1973-1975)	CdTe CdTe CdTe : Cl	1.42	1.45 1.427 1.43				Participation of complex defects in 1.4 eV band is supported by fact that 77 K e^- irradiation suppresses band, while 300 K n irradiation enhances band. THM growth suppresses band, possibly because of higher purity.	Implied that 1.4 eV band arises from randomly-distributed shallow donors and deep acceptors. Possible origins of these levels in CdTe are not discussed.
[19, 20] Furgolle, <i>et al.</i> Marfaing, <i>et al.</i> (1974-1975)	CdTe : In CdTe : Al CdTe : Cl CdTe		1.457 1.451 ? 1.478 1.477				Optical abs shows transitions of holes bound to deep acceptors at $\epsilon_v + 0.13$ eV. Strong coupling to vibronic mode with energy $< TA$ phonon energy indicates compact V_{Cd} -D complex.	Transitions to acceptor levels, resulting from V_{Cd} -D complexes, at $\epsilon_v + 0.13$ eV. Implication that transitions originate on shallow donor levels ($\epsilon_c - 0.01$ eV that are spatially separated from acceptor complexes.
[2] Fatehally (as quoted) (1959)	CdTe	~ 1.3					No Franck-Condon shift between emission and excitation bands. Relatively impure samples.	Transitions from CB to acceptor level, associated with V_{Cd} , at $\epsilon_v + 0.15$ eV.
[3] Halsted <i>et al.</i> (1961)	CdTe CdTe : Ga CdTe : Ag		1.451+ 1.415 ₀ 1.49+				Spectra depend on identity of impurity on defect. 1.4 eV bands in these samples suppressed with increased P_{Cd} .	Transition terminating on acceptor levels attributed to V_{Cd} or impurities.

TABLE I (Suite)

[Ref.] Author (Date)	Material	Peak at 80 K (eV)	No-phonon peak at 4 K (eV)	Measure I. L. D.	Dynamic response	Thermal quenching (ϵ_A , eV)	Remarks	Conclusion as to nature of 1.4 eV band
[1] De Nobel (1959)	CdTe : In	1.41- 1.43					Peak shift of ~ 0.02 eV noted depending on Cd-vapor firing conditions. V_{Cd} has acceptor level at $\epsilon_v + 0.15$ eV	Data presented appear consistent with CB-A or D-A transitions terminating on V_{Cd} acceptor level.
[22] Barnes and Zanio (1975)	CdTe : In		1.454				Closely-compensated samples. lum intensities scale well with defect chemistry calc. of V_{Cd} -In complex concentration.	Transitions to acceptor levels produced by NN V_{Cd} -In complexes.
Present Work	CdTe : In	1.42- 1.45	1.455	×	×	0.09- 0.103	Closely compensated samples. No band shift with i_l or T . Half-width increases with T . Frequency response is independent of doping level. Band shape unaffected by severe quenching from implant damage introduction. $\Delta\epsilon$ between In and Cl doping suggests NN V_{Cd} -D complexes in both cases.	CB-A or intracenter transitions involving compact, probably NN V_{Cd} -D complexes. Acceptor levels, at approx. $\epsilon_v + 0.1$ eV, normally coupled to VB. Donor levels, IF present, weakly coupled to CB.
	CdTe : Cl	1.45	1.475	×	×	0.137		

origins in Cd-rich and Te-rich CdTe, and in some cases the stoichiometry of the material investigated has not been known. Another problem is that comprehensive luminescence studies, that is, studies involving a variety of methods such as injection level dependence, dynamic behavior, and thermal quenching, are lacking except for the work of Taguchi, *et al.* [8-13] on Cd-rich CdTe. Even in the latter case, where the injection level behavior and time dependence of the 1.4 eV luminescence are consistent with distributed donor-acceptor pair transitions, the conclusion that D-A transitions are responsible for the 1.4 eV band is not convincing because the measured thermal quenching behaviour [10] shows a large activation energy that is not consistent with D-A transitions involving shallow donors but can readily be explained in terms of conduction-band-to-acceptor transitions.

The thermal quenching results of Taguchi, *et al.* [10] are similar to those of Bryant and Totterdell [15] and Bryant and Webster [17] for Te-rich CdTe. In refs. [15] and [17] the quenching results were interpreted as definite evidence that the 1.4 eV band resulted from conduction-band-to-acceptor transitions. In addition, it has been suggested by Agrinskaya, *et al.* [7] that the 1.4 eV band results from intracenter transitions that occur within compact defect-dopant complexes, similar to the complexes shown to exist in defect chemistry calculations used to explain self-compensation in intentionally donor-compensated CdTe. However, the experimental evidence behind this conclusion is rather limited.

In reviewing the literature [1-24] we are unable to find any single case where, in our estimation, the ori-

gin of a 1.4 eV band in CdTe has been convincingly explained. In this paper we describe comprehensive cathodoluminescence measurements intended to clarify this puzzling situation. We will show that, in the samples studied, the 1.4 eV band results from a more complex type of transition than has generally been appreciated by previous investigators, and that in no case does the transition appear to be of a simple conduction-band-to-acceptor or donor-acceptor pair nature.

2. Experiment. — We have studied both nominally stoichiometric, nominally undoped CdTe obtained from the late R. E. Halsted at General Electric Co. and Te-rich, donor-compensated CdTe, with either In or Cl doping and widely-varying dopant concentrations, obtained from K. R. Zanio at Hughes Research Labs. The known characteristics of the samples studied are given in table II. On each of the samples we measured injection level dependence and frequency response using cathodoluminescence at 80 K. We also measured thermal quenching of the cathodoluminescence from 80 K to 200 K. In addition, on some samples we used photoluminescence to measure injection level dependence at 4 K and to measure thermal quenching from 4 K to 100 K. The spectra to be presented have been corrected for the wavelength response of the optical detection system using computer processing.

The injection level behaviour of the 1.4 eV band has been measured in two ways. The first way is simply the classical method of increasing the injection level and noting the shift, if any, in the peak location

TABLE II
CdTe sample parameters

Sample	Material	Doping level	Other data
CTG-50	CdTe	Nom. undoped	Resistivity ~ 1 ohm-cm ; n-type, high mobility
CTH-111	CdTe : Cl	$1.5E16/\text{cm}^3$	Resistivity $\sim 1E4$ ohm-cm, p-type
CTH-12B1	CdTe : Cl	$1.5E17/\text{cm}^3$	Resistivity $\sim 1E8$ ohm-cm
CTH-12B2	CdTe : Cl	$1.5E17/\text{cm}^3$	Same wafer as CTH-12B1
CTH-20A	CdTe : In	$3E15/\text{cm}^3$	Resistivity $\sim 1E8$ ohm-cm
CTH-26	CdTe : In	$3E16/\text{cm}^3$	Resistivity $\sim 1E8$ ohm-cm ; $\mu\tau$ product $\sim 1E3 \text{ cm}^2/\text{V}$
CTH-22	CdTe : In	Unknown	Resistivity $\sim 1E8$ ohm-cm ; $\mu\tau$ product $\sim 1\text{-}2E\text{-}5 \text{ cm}^2/\text{V}$
CTH-24D	CdTe : In	$1E18/\text{cm}^3$	Resistivity = $1E2\text{-}1E3$ ohm-cm, n-type

and band shape as a function of injection level. The second method, which gives more graphic results, involves exciting cathodoluminescence with a sinusoidal, harmonic-free electron beam and then recording both the fundamental and harmonic-frequency spectra. If a second-harmonic signal is detected, then the luminescence band has a non linear injection level dependence. If the sign of the second harmonic signal is negative, the injection level dependence is sublinear. If the sign of the second harmonic signal is positive, the injection level dependence is superlinear. If it happens that the shape of the second harmonic spectrum matches that of the fundamental frequency luminescence spectrum after appropriate amplitude normalization, then the band center and shape are independent of injection level.

The dynamic behavior of the 1.4 eV transitions in CdTe was measured using the frequency response of the luminescence under excitation by a sinusoidally-modulated electron beam under conditions of constant beam energy, injection level, and sample temperature. The frequencies of beam modulation and photomultiplier signal detection were varied in decade increments from 50 Hz to 50 MHz. At 50 kHz and below, the carrier was unmodulated and phase-sensitive detection was employed at carrier frequency. From 500 kHz to 50 MHz, the carrier signal was modulated at 400 Hz. At these frequencies the signal detection was asynchronous but the 400 Hz modulation was synchronously detected to enhance the signal-to-noise ratio.

3. Results and discussion. — Combined fundamental and harmonic spectra were taken on all the samples studied, with results typically similar to those shown in figure 1. Since the fundamental and second harmonic spectra virtually coincide for the 1.4 eV band in figure 1, we conclude that both the shape and peak location of the 1.4 eV band are independent of injection level. This behavior, which is confirmed by parallel injection level studies using 4 K photolumi-

nescence where the no-phonon peak is clearly resolved, is inconsistent with distributed donor-acceptor pair transitions. Although the spectra in figure 1 should

FIG. 1. — Typical fundamental (heavy line) and second harmonic (light line) spectra for donor-compensated CdTe. The phases of the second harmonic signal indicate that the 1.4 eV band is sublinear, while the near-bandedge luminescence at 1.57 eV is superlinear. This sample does not show an injection level shift of the 1.4 eV band.

be regarded as typical, it is important to note that it is not difficult to find anomalous samples in which there are overlapping bands or other effects that lead to an apparent injection level shift. An example of this behaviour is shown in figure 2.

In figure 2 the shape and peak energy of the 1.4 eV band shift with injection level because the fundamental and harmonic spectra do not coincide in this case. Since the high-energy side of the unresolved band is less sublinear than the low energy side, the 1.4 eV band in this sample will shift to higher energy as the injection level is increased. The presence of overlapping bands in the sample characterized in figure 2 is confirmed by frequency-resolved cathodoluminescence, in which the component bands show somewhat different frequency response ; by thermal quenching measure-

FIG. 2. — Fundamental and second harmonic spectra for a nominally undoped CdTe sample. In this case there is an apparent injection level shift of the 1.4 eV luminescence arising from overlapping bands.

ments, in which the component bands show slightly different quenching behavior ; and by 4 K photoluminescence measurements, in which the component no-phonon peaks and their phonon replicas can be resolved. Other effects which can lead to an injection level shift are impurity banding and band waviness, which occur at high concentrations of impurities and/or defects. The 1.4 eV band in the most heavily In-doped sample (CTH-24 D) shows a large injection level dependence which we ascribe to one or both of these effects. In fact, it appears that the $\epsilon_v + \sim 0.1$ eV impurity band has tailed into the valence band in this sample since the edge emission is orders of magnitude weaker than in other samples. Of the total of eight samples studied, three samples showed injection level shifts. Although it is clear that the basic 1.4 eV transition is characterized by a lack of injection level shift, the frequent occurrence of anomalous samples which exhibit injection level shifts is one possible explanation for the contradictory injection level results that have been reported in the literature for the 1.4 eV bands.

Next, we discuss the results of the frequency-resolved cathodoluminescence measurements. These measurements give information on the transition dynamics analogous to that obtained from the more familiar time-resolved luminescence methods. However, the frequency-resolved measurements can be carried out at a constant average injection level, and significantly greater sensitivity is often possible. Figure 3 shows a sequence of cathodoluminescence spectra taken under identical conditions of sample temperature, injection level, and electron beam energy, but using frequencies of electron beam modulation and photomultiplier signal detection ranging from 50 Hz to 50 MHz. Qualitatively speaking, slow transitions will not be visible in the high-frequency spectra because the response of the transition is not

FIG. 3. — Sequence of cathodoluminescence spectra for CdTe taken at frequencies of beam modulation and photomultiplier signal detection ranging from 50 Hz to 50 MHz. These spectra are normalized using the band-edge peak as reference. It is apparent that the transition responsible for the 1.4 eV luminescence is considerably slower than that responsible for the band-edge luminescence.

able to follow the rapidly-varying modulation. Thus, in following the sequence of spectra in figure 3 from low to high frequencies, it is apparent that the response of the 1.4 eV band is considerably slower than that of the band-edge luminescence.

Figures 4-6 show the frequency dependence of luminescence quantitatively, in the form of plots of log luminescence intensity vs. log modulation fre-

FIG. 4. — Frequency response plot for bands in nominally undoped CdTe. The response of the 1.4 eV band indicates a non-exponential time decay with a characteristic time of the order of $1E-6$ s.

quency at constant injection level, for all the samples investigated. Figure 4 shows frequency response for the bands in nominally stoichiometric, nominally undoped CdTe. The solid lines show the frequency response of the 1.4 eV band, and the dashed lines show the frequency response of the 1.57 eV band-edge emission. Since figure 4 is a log-log presentation, it is clear that the response of the 1.4 eV band falls off dramatically at high frequencies, as shown qualitatively in figure 3.

FIG. 5. — Frequency response plot for bands in Cl-doped CdTe. The response of the 1.4 eV bands indicates a non-exponential time decay with a characteristic time of the order of $5E-6$ s.

FIG. 6. — Frequency response plot for bands in In-doped CdTe. The response of the 1.4 eV band indicates a non-exponential time decay with a characteristic time on the order of $5E-6$ s.

Figure 5 shows frequency response data for three samples of Cl-doped CdTe. The frequency response of the bands in the Cl-doped CdTe is qualitatively similar to that in the nominally-undoped material. However, by comparing figures 4 and 5 it may be seen that the 1.4 eV transitions in the donor-compensated material are somewhat slower than in the nominally

undoped material. In addition, figure 5 shows that the transition response in the Cl-doped CdTe is unaffected by a tenfold change in doping level. The transition response is also unaffected by introduction of ion implantation damage that results in a tenfold quenching of the 1.4 eV luminescence.

Figure 6, which shows corresponding frequency response data for four samples of In-doped CdTe, also reveals a similar pattern of results. Now, however, we are able to verify that the frequency response of the 1.4 eV transition is practically unaffected by indium concentration over a thousand-fold range. This result argues against any distributed donor-acceptor pair interpretation of the 1.4 eV luminescence because the mean pair separation, and thus the transition response, would be expected to vary significantly over such a wide range of dopant concentrations if the transitions involved isolated donors. However, it is clear that the donor species must somehow be associated with the luminescence transition, because of the fact that the relative strength of the 1.4 eV luminescence increases with donor concentration, as can be seen in figures 5 and 6. Thus the relative invariance of the transition response in the donor-compensated CdTe argues in favor of the luminescence transition being associated with a compact center involving donors.

In addition, we find that there is a shift of approximately + 20 meV in the no-phonon peak of the 4 K photoluminescence spectrum between In-doped and Cl-doped CdTe (see table I). The corresponding shift expected on the assumption that the center is a nearest-neighbor V_{Cd} -donor complex has been estimated to be + 30 meV by Agrinskaya *et al.* [7]. The shift we observe argues that the 1.4 eV luminescence transition in donor-compensated CdTe involves donor-defect associates that are at least compact, and probably of nearest-neighbor configuration.

The thermal quenching behaviour of the Cl-doped, In-doped, and nominally-undoped CdTe samples is shown in figure 7 for temperatures of 80 K-200 K. The undoped and In-doped samples show quenching activation energies of 0.09-0.103 eV. The Cl-doped samples show a somewhat higher activation energy of 0.137 eV. As is customarily done, we assume that quenching of the luminescence occurs because of thermal population of the participating acceptor level. In terms of relating the thermal quenching results to energy levels and the band edges, it is well known that thermal and optical activation energies are expected to differ somewhat, with the optical activation energy generally being greater than the thermal activation energy. The expected difference between these energies in CdTe has been calculated and found to be less than one percent [17]. If we assume that the thermal activation energy of the acceptor level is approximately the same as the energy of a hypothetical radiative transition from acceptor

level to valence band, then we can estimate the energy of the donor levels, if any, involved in the 1.4 eV luminescence. For this estimate we use the quenching activation energies determined from 30 K-80 K photoluminescence measurements (the data are similar to those of figure 7), together with the energies of the

FIG. 7. — Thermal quenching behavior of all types of CdTe samples studied.

no-phonon peaks in the 4 K photoluminescence spectrum, which occur at approximately 1.455 eV for In-doped CdTe and 1.475 eV for Cl-doped CdTe. We find that in all cases the donor levels, if present, must lie within hundredths of an eV above or below the conduction band, whereas the acceptor levels are approximately a tenth of an eV from the valence band. Therefore the assumption of donor levels leads to a paradox because of the fact that the deeper accep-

tor levels are dominating the thermal quenching. Thus, if any donor levels are involved in the 1.4 eV transition, the quenching results indicate that these levels are not in normal thermal equilibrium with the conduction band. It should be mentioned that there is precedence for the existence of thermally disconnected levels near the conduction band in results from photoconductivity and thermally stimulated current measurements on CdTe [25, 26]. However, there is no direct evidence that such levels are participating in the 1.4 eV transition.

3. Conclusion. — It is not clear that donor levels of any kind are necessarily involved in the 1.4 eV luminescence. The proximity of the initial state to the conduction band may also be taken to suggest that there is, in fact, no discrete donor level involved and that instead the conduction band continuum is the initial state. In this case, the injection level dependence and thermal quenching behavior would be consistent with our experimental results, and the relatively slow transition response must be explained. Possibly this transition is slow because it is partially forbidden. The absence of a donor level in the known presence of donors could be accounted for by the close association of singly ionized donors and double acceptors, such as cadmium vacancies.

There is also the possibility that the 1.4 eV luminescence in CdTe is the result of an intracenter transition in compact donor-cadmium vacancy complexes [7] similar to those known by EPR measurements to be involved in the self-activated luminescence in ZnS [27]. At the present time, it appears that this proposal and the forbidden conduction-band-to-acceptor hypothesis are the most promising candidates for explaining the unusual characteristics of the 1.4 eV luminescence in CdTe. Additional experiments will be necessary to decide between the two hypotheses. At any rate, it is now clear that at least some of the confusion regarding the 1.4 eV luminescence in CdTe has arisen because the transition is of a more complex nature than generally anticipated.

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References

- [1] DE NOBEL, D., *Philips Res. Repts.* **14** (1959) 361 and 430.
- [2] GARLICK, G. F. J., *J. Phys. & Chem. Solids* **8** (1959) 449.
- [3] HALSTED, R. E., LORENZ, M. R. and SEGALL, B., *J. Phys. & Chem. Solids* **22** (1961) 109.
- [4] VAVILOV, V. S., GIPPIUS, A. A. and PANOSSIAN, J. R. in *II-VI Semiconducting Compounds*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967), pp. 743-754.
- [5] AGRINSKAYA, N. V., ARKAD'EVA, E. N., GUSEVA, M. I., MASLOVA, L. V., MATVEEV, O. A., RYVKIN, S. M., SLADKOVA, V. A. and STARININ, K. V., in *Proc. International Symp. on Cadmium Telluride*, edited by P. Siffert and A. Cornet (1971), paper XVI-1.
- [6] AGRINSKAYA, N. V., ARKAD'EVA, E. N. and MATVEEV, O. A., *Sov. Phys. Semicond.* **4** (1970) 347.
- [7] AGRINSKAYA, N. V., ARKAD'EVA, E. N. and MATVEEV, O. A., *Sov. Phys. Semicond.* **55** (1971) 767.
- [8] TAGUCHI, T., SHIRAFUJI, J. and INUISHI, Y., in *Radiation Damage and Defects in Semiconductors* (The Institute of Physics, London, 1972), pp. 407-415.
- [9] TAGUCHI, T., SHIRAFUJI, J. and INUISHI, Y., in *Luminescence of Crystals, Molecules, and Solutions*, edited by F. Williams (Plenum Press, New York, 1973), pp. 258-261.
- [10] TAGUCHI, T., SHIRAFUJI, J. and INUISHI, Y., *Japan. J. Appl. Phys.* **12** (1973) 1558.

- [11] TAGUCHI, T., SHIRAFUJI, J. and INUISHI, Y., *Japan. J. Appl. Phys.* **13** (1974) 1003.
- [12] TAGUCHI, T., SHIRAFUJI, J. and INUISHI, Y., *Japan. J. Appl. Phys.* **13** (1974) 1169.
- [13] TAGUCHI, T., SHIRAFUJI, J. and INUISHI, Y., *Inst. Phys. Conf. Ser.* No. 23 (1975) 272.
- [14] RUD', Y. V., SANIN, K. V. and SHRETER, Y. G., *Sov. Phys. Semicond.* **5** (1971) 573.
- [15] BRYANT, F. J. and TOTTERDELL, D. H. J., *Phys. Stat. Sol. (a)* **10** (1972) K 75.
- [16] BRYANT, F. J. and WEBSTER, E., *Brit. J. Appl. Phys. (J. Phys. D)*, **1** (1968) 965.
- [17] BRYANT, F. J., TOTTERDELL, D. H. J. and HAGSTON, W. E., *Phys. Stat. Sol. (a)* **14** (1972) 579.
- [18] PANOSSIAN, J. R., GIPPIUS, A. A. and VAVILOV, V. S., *Phys. Stat. Sol.* **35** (1969) 1069.
- [19] FURGOLLE, B., HOCLET, M. and VANDEVYVER, M., *Solid State Commun.* **14** (1974) 1237.
- [20] MARFAING, Y., TRIBOULET, R., FURGOLLE, B., HOCLET, M. and VANDEVYVER, M., *Inst. Phys. Conf. Ser. No. 23* (1975) 288.
- [21] BARNES, C. E. and ZANIO, K., *J. Appl. Phys.* **46** (1975) 3959.
- [22] BARNES, C. E. and KIKUCHI, C., *Radiat. Effects* **26** (1975) 105.
- [23] NOBLANC, J. P. and DURAFFOURG, G., *Phys. Stat. Sol. (b)* **46** (1971) 705.
- [24] BRYANT, F. J., COX, A. F. J. and WEBSTER, E., *J. Phys. C (Proc. Phys. Soc.)* **1** (1968) 1737.
- [25] BARNES, C. E. and ZANIO, K., *IEEE Trans. Nucl. Sci.* **NS-23** (1976) 177.
- [26] URLI, N. B., in *II-VI Semiconducting Compounds*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967), pp. 1335-1347.
- [27] See, for example, CURIE, D. and PRENER, J. S., in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (American Elsevier, 1967), pp. 445 ff.
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