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## Photoluminescence Properties of Z-Bands in CdTe

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We have studied the photoluminescence band shape of the 1.36 eV (Z-band) and the 1.32 eV (Z'-band) PL bands in high purity low-temperature-grown n-type bulk polycrystalline CdTe as a function of the excitation power and temperature. Both bands have a nonsymmetrical shape with a gradual decrease on the high-energy side but the variation of the shape with temperature and excitation power is different for Z- and Z'-bands. Both bands have the same temperature quenching activation energy  $E_T = 35$  meV. On the basis of our investigations we assign the 1.32 eV emission to a free-to-bound recombination near dislocations and the 1.36 eV emission to a DA emission near the same dislocation. Both bands are related to a shallow acceptor  $E_A = 35$  meV (probably Li or Na), whose concentration in the bulk is quite low. The Z-band is also related to a deep donor ( $E_D \geq 200$  meV), probably of intrinsic origin.

### 1. Introduction

Cadmium telluride has received persistent attention for several decades as a possible candidate for thin film solar cells and other optoelectronic devices. Photoluminescence (PL) is proved to be the most powerful technique for evaluating the quality of CdTe films. A great number of shallow and deep PL bands have been identified mostly in CdTe single crystals. Besides these well-known PL bands there exist also several bands, which were detected only in particular samples. One of these PL bands is the 1.47 eV band (Y-band) and its phonon sidebands with very weak electron-phonon coupling properties ( $S \approx 0.2$ ) [1 to 4]. It is shown that this band originates from vicinity of dislocations [4]. The second "unusual" PL band is located at 1.36 eV and is called Z-band and it is almost always accompanied by the subpeak at 1.32 eV with lower intensity [2, 4 to 8]. We call this band as Z'-band. Both bands were first detected in MOCVD-grown CdTe films on (111) orientated substrates [2]. Later they have been observed also in high purity low-temperature-grown bulk polycrystalline CdTe [8]. The origin of Z- and Z'-bands is still unresolved and several hypotheses exist. It is noticed that there is a certain type of correlation between Z-bands and dislocations, but the Z-recombination mechanism cannot be related to the dislocation core itself but to the impurity cloud near the dislocation [7]. In [6] the Z-band is related to the radiative recombination of electrons and holes trapped at a localized center associated with a less-common structural defect. The localized center model was also proposed in [8] and the authors suggest that the Z-center originates from a 3d impurity on a Cd site, most probably Cu. It is obvious that these bands have really unusual properties and in order to make further

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progress more experimental data are needed. In the present work we have made for a first time a detailed PL analysis of the Z- and Z'-band shapes in polycrystalline CdTe samples and we propose an alternative model for the Z-bands.

## 2. Experimental Details

The initial gaseous phase synthesized 5N CdTe powder was previously annealed at 650°C for 80 h in static vacuum to remove possible nonreacted components. About 2 g of vacuum heat-treated CdTe powder was put in an 8 mm diameter U-form quartz tube into the furnace. Through the quartz tube a 3N purity H<sub>2</sub> flow with speed about 3mm/s was blown. The CdTe temperature was kept at 645 °C for 80 h. The CdTe layer grew in the temperature region between 120 and 580 °C. At higher temperatures (350 to 580 °C) a polycrystalline layer with crystal diameter up to 30 μm was formed. For PL measurements we took a little piece of n-type layer from a temperature region  $T \approx 260$  °C, where the thickness of the layer was about 10 to 15 μm, the grain size being 10 μm and less.

Photoluminescence spectra measurements were carried out at 8 to 110 K using closed-cycle He cryostat. A He–Cd laser with a wavelength of 441.6 nm was used for excitation and a computer controlled 0.4 m single grating monochromator for PL measurements. The chopped signal was detected by a S1 photomultiplier using the conventional lock-in technique. For the purpose of analysis, the emission spectra were corrected for grating efficiency variations and for the spectral response of the detector.

## 3. Results and Discussion

A typical PL spectrum of our sample at 8 K is shown in Fig. 1. The whole spectrum consists of a neutral-donor bound exciton ( $D^0-X$ ) line at 1.593 eV, the  $(e-A^0)$  line at 1.549 eV with the acceptor being probably a singly ionized cadmium vacancy [9], the Y-band near 1.474 eV, followed by several replicas due to LO phonons and the Z- and Z'-bands at 1.36 and 1.327 eV, respectively. We did not observe an usually intense PL

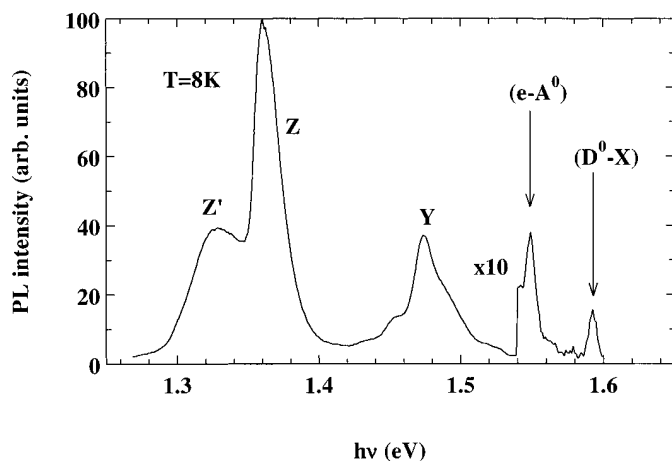


Fig. 1. Photoluminescence spectrum of our CdTe sample measured at 8K

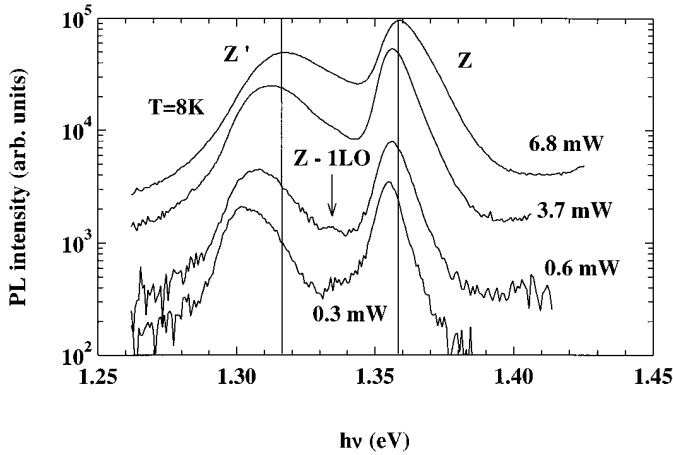


Fig. 2. PL spectra of Z-bands in CdTe, measured with varying excitation laser power

band near 1.42 eV. This fact may be considered as a sign of purity of our sample. At the same time the intensity of the exciton emission was quite low which on the contrary indicates a high concentration of structural defects. Approximately the same kind of PL spectra were recorded in as-grown MOCVD CdTe films [2, 5, 6]. It is known that Y- and Z-bands could be easily quenched after a low-temperature ( $T \approx 200$  °C) short ( $\approx 15$  min) annealing [2, 5]. There is no doubt that these bands are somehow associated with structural defects like dislocations. A direct evidence of that was given in [7], where it was found that the Z-band intensities correlate with the dislocation etch pits but not with grain boundaries.

The closer look at Z-bands reveal that both bands have a nonsymmetrical shape with a gradual decrease on the high-energy side. Fig. 2 shows the PL spectra for different excitation intensities at 8K. At lower intensities the first LO phonon replica of the Z-band can be found at 1.3345 eV. As it can be seen from Fig. 2 both Z-bands shift towards higher photon energies with increasing excitation intensity (j-shift), but this shift is remarkably larger for the Z'-band. The peak shift is accompanied by the widening of both bands. This kind of behavior is characteristic of the donor–acceptor pairs (DAP) model and therefore in [2] the DAP transition was suggested for the Z-band. It is also interesting to note that the total spectral background in this region is increasing with excitation intensity.

In order to study the shape of Z-bands we fitted all spectra with the modified Gaussian function

$$I(h\nu) = \frac{I_0 \exp[-4 \ln 2(h\nu - \varepsilon_0)^2/W^2]}{1 + \exp[-\alpha(h\nu - \varepsilon_0)]}, \quad (1)$$

where  $I_0$ ,  $\varepsilon_0$ ,  $\alpha$ ,  $W$  are fitting parameters. It is obvious, that  $W$  and  $\alpha$  determine the shape of the PL band at the high- and low-energy sides, respectively. The result of this fitting is presented in Fig. 3. The fitting function (1) was chosen because it gave the best results, but obviously it does not have a direct physical meaning. The only purpose was to study the changes in the shape of these PL bands.

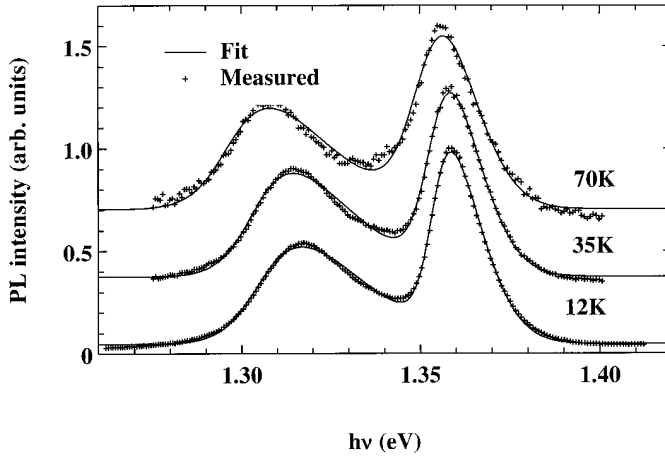


Fig. 3. A typical result of fitting of the normalized PL emission intensity of Z-bands with Eq. (1)

Fig. 4 represents the dependence of fitting parameters  $W$  and  $\alpha$  upon excitation intensity for both bands. We see, that both bands show a widening at the high-energy side, but the widening is much stronger for the Z'-band, see Fig. 4. At the same time the low-energy side of PL bands behaves differently for Z- and Z'-bands. The opposite dependence of parameter  $\alpha$  for both bands certifies that these bands must have a different origin.

The temperature dependence of the band shape is also a valuable tool in obtaining an information about PL-bands. Both bands show a gradual shift toward low energies with temperature, see Fig. 5. All temperature series were measured with laser power of 6.8 mW. For the Z'-band the peak position exactly follows the energy gap  $E_g$  but the peak position of the Z-band has a much slower shift. We may assume that Z-bands have also a different recombination process and that continuous band states are involved in Z'-band recombination.

Fig. 6 represents the temperature dependence of the parameter  $\alpha$ . It can be seen that the parameter  $\alpha$  for the Z-band has nearly linear dependence upon temperature while it

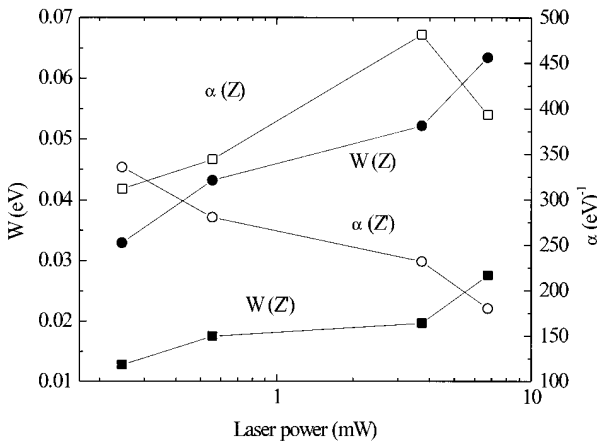


Fig. 4. The dependence of the parameters  $W$  and  $\alpha$  on laser power for Z-bands in CdTe

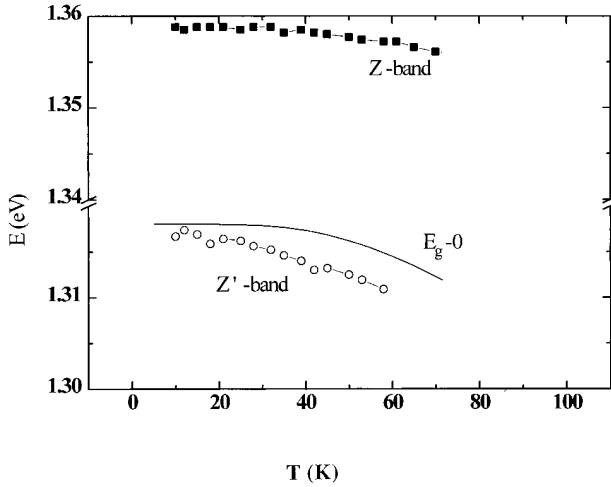


Fig. 5. Temperature dependence of the peak positions for Z-bands and  $E_g$  [15]

has practically a constant value for the Z'-band. Therefore we may assume that thermal processes play a significant role for the low-energy side of the Z-band. The nearly linear dependence of the parameter  $\alpha$  on temperature is rather surprising and indicates that the inhomogeneous broadening of the Z-band is not caused by ordinary reasons, which tend to give a  $1/T$  dependence for the parameter  $\alpha$ . Using the computer analysis of Eq. (1) we also found a total half-width  $H$  and the integral intensity  $\Phi$  for both bands, Fig. 7 and 8, respectively. It is really amazing that the half-width of the Z'-band seems to be independent of temperature. Therefore we must assume, that the recombination in the corresponding Z'-center happens with a very small electron-phonon interaction and the shape of the Z'-band is caused mainly by other processes. On the contrary, the half-width of the Z-band shows almost perfect theoretical dependence upon temperature. It is known that in case of wide PL bands without any phonon structure the temperature

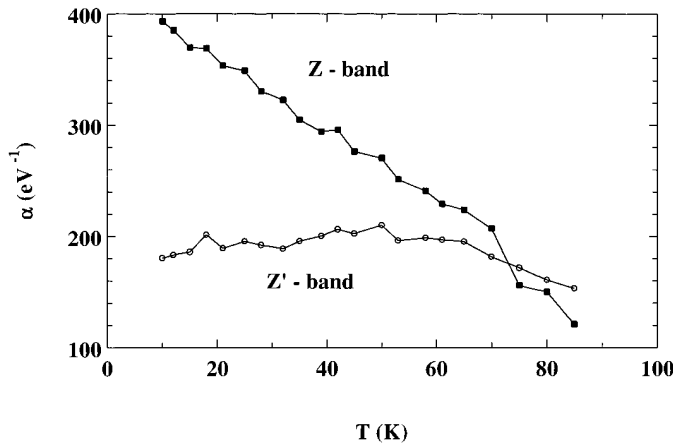


Fig. 6. Temperature dependence of the parameter  $\alpha$  for Z-bands

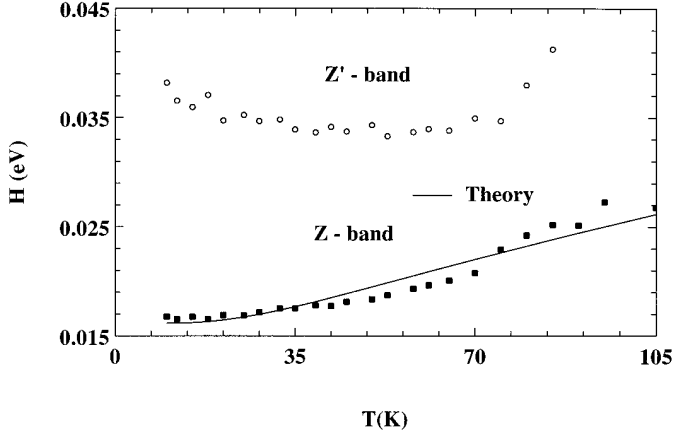


Fig. 7. Temperature dependence of the half-widths of the two Z-bands and the theoretical fit using Eq. (2) for the Z-band

dependence of the half-width  $H(T)$  can be presented as [10]

$$H(T) = H_0 \sqrt{\coth\left(\frac{\hbar\omega_e}{2kT}\right)}, \quad (2)$$

where  $\hbar\omega_e$  is the effective phonon energy of the excited state,  $H_0$  is the half-width at 0K. The fitting with Eq. (2) gives for the Z-band:  $H_0 = 16.16$  meV and  $\hbar\omega_e = 7.25$  meV. The latter value falls between the LA and TA phonon energies in CdTe [9] and therefore we may assume that the widening of the Z-band is caused by the electron-phonon interaction with acoustic phonons. It is also interesting to note that the H values obtained in [8] were remarkably smaller (4 and 8 meV for Z- and Z'-bands, respectively) than in this paper. This fact and our own PL spectra measured from various samples verify, that there is a tight connection between the shape of Z-bands and a sample preparation conditions.

The temperature dependence of the integral intensity  $\Phi$  of Z-bands was measured also in [5], where two or even three different activation energies were obtained for the low- and high-temperature regions re-

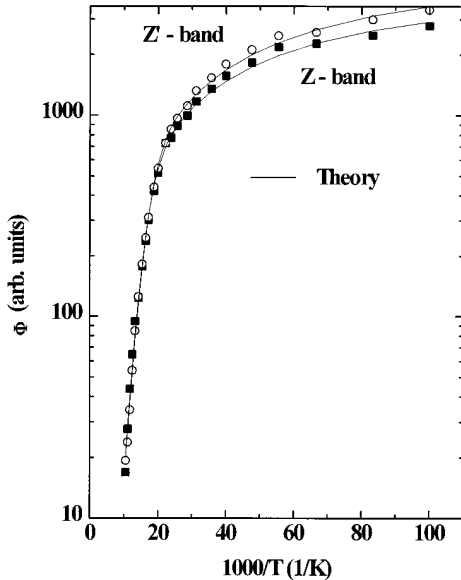


Fig. 8. Temperature dependence of the integral intensity of Z-bands. The fits using Eq. (3) are shown as continuous curves.

Table 1  
Fitting parameters for Z and Z' PL bands in CdTe

	Z-band	Z'-band
$\Phi_0$	$4380 \pm 460$	$5540 \pm 430$
$c_1$ ( $K^{-1.5}$ )	$0.016 \pm 0.003$	$0.018 \pm 0.002$
$c_2$ ( $K^{-1.3}$ )	$16 \pm 5$	$22 \pm 5$
$E_T$ (meV)	$35 \pm 2$	$35 \pm 1$

spectively. In [11] however it was shown that usually the low-temperature quenching is not really a thermal activation process with a certain activation energy, but is caused mostly by the temperature dependence of capture cross sections of a particular recombination center. According to this theory the temperature dependence of the integral intensity may be presented as

$$\Phi(T) = \frac{\Phi_0}{1 + c_1 T^{3/2} + c_2 T^{3/2} \exp\left(-\frac{E_T}{kT}\right)}, \tag{3}$$

i.e. with only one activation energy  $E_T$ . Both bands were fitted with Eq. (3) and the results of these fittings are presented in Fig. 8 and Table 1. As it can be seen from Fig. 8 and Table 1, both bands have nearly the same dependencies and also the same activation energy 35 meV. It is obvious that both bands must have a common quenching substance.

Taking into consideration all the experimental data obtained, we propose a new model for Z-bands, see Fig. 9. According to this model the Z'-band is caused by the recombination of a free electron near the dislocation with the hole captured by shallow acceptor in the dislocation core with  $E_A = 35$  meV. It is known that the dislocation causes a local deformation of the energy gap of CdTe and other semiconductors. As a result we have a local reduction of the energy gap near the dislocation and a spatial separation of elec-

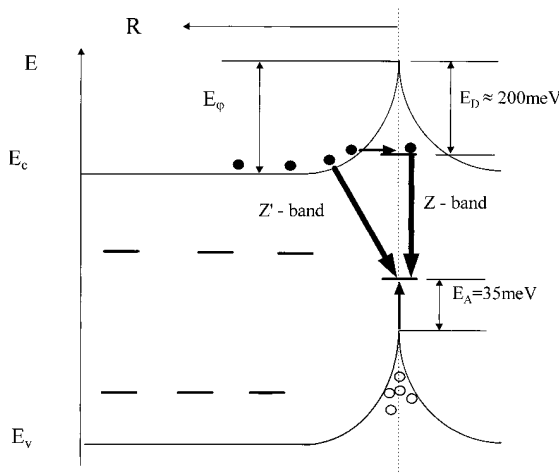


Fig. 9. Suggested model for Z-bands in CdTe

trons and holes. This is why the free-to-bound recombination near dislocations has properties very close to those for DA pairs. The recombination energy  $h\nu$  and the recombination probability  $W$  have a certain dependence upon the distance  $R$  of the electron from the dislocation,

$$h\nu(R) = E_g - E_A - E_\varphi + E(R) \quad (4)$$

and

$$W(R) = W_0 \exp(-\gamma R). \quad (5)$$

Both dependencies lead to the j- and t-shift of the  $Z'$ -band. Moreover, the recombination near dislocations must give a nonsymmetrical shape of the corresponding PL band and this band must widen more at the high-energy side with increasing excitation intensity. These features are typical for DA pairs, but in case of DA pairs the temperature dependence of the peak position must have a slower decline than the temperature dependence of the energy gap  $E_g$ . At the same time, if the excitation intensity is high enough, the temperature dependence of the peak position of the  $Z'$ -band may have the same decline as the energy gap.

According to our model the Z-band is formed as a DA recombination of a captured by a donor defect electron with a hole captured at the same shallow acceptor as for the  $Z'$ -band. The shallow acceptor with  $E_A = 35$  meV is below the effective-mass acceptor limit in CdTe. In the bulk CdTe with low concentration of dislocations this acceptor state must show a free-to-bound PL peak near 1.57 eV. In our case there was not any emission in this region and therefore we believe that the concentration of corresponding acceptors is quite low in the bulk and that these defects were segregated mostly into dislocations. The chemical nature of these acceptor defects is not known, but according to [9] the most probable candidates are Li and Na, which usually form shallow acceptor states in II–VI semiconductors. It is also important that, in principle, the segregation of defects into dislocations and their ability to show PL emission may be a sensitive tool to detect low concentrations of impurities. For example, in [8] PL bands at 1.268, 1.289, 1.295 and 1.338 eV were detected and these bands are a direct evidence of various defects and impurities near dislocations. If the concentration of impurities is relatively high also in the bulk, then there must exist a certain similarity between PL spectra in the Z spectral region (dislocations) and the edge emission spectral region (bulk). These similarities indeed have been found in [8].

We assume that before recombination electron penetrates the potential barrier and is captured by the relatively deep donor level within the dislocation core. In [12] several donor levels were detected with  $E_D \geq 220$  meV by DLTS measurements. According to authors, the level at  $E_D = 340$  meV may be related to cadmium interstitials or tellurium vacancies and it was found that the heat treatment at temperatures higher than 350 °C remarkably reduces the concentration of this level near the surface. It is known that the same kind of heat treatment also reduces the intensity of Z-bands in CdTe [5]. Therefore we assume that the deep donor defect included in Z-band recombination is related to an intrinsic defect such as  $Cd_i$  or  $V_{Te}$ . As it was shown in [13, 14] deep donor defects are also involved in deep PL bands in the 1.1 and 0.7 eV regions. As the Z-band shows less pronounced j-shift and according to [8] no t-shift, it is probable that we have relatively close DA pairs. It is not surprising because the electron has a quite localized wave function in this deep donor. Therefore the temperature dependence of the peak position of



the Z-band is so slow and the recombination in these DA pairs resembles the recombination between excited and ground states within a localized center.

The small difference between the peak positions of the Z and Z' PL bands in our model must cause a small increase of the relation  $\Phi_Z/\Phi_{Z'}$  with temperature and also with excitation power. Both dependencies are indeed apparent, see for example Fig. 8.

It is also obvious that the shape of the Z'-band is more strongly affected by the local structure of the potential curve near the dislocation than by the electron-phonon interaction and therefore we were not able to detect a theoretically correct temperature dependence of the half-width of the Z'-band.

#### 4. Conclusions

We have done a detailed analysis of the band shape for the 1.32 eV (Z'-band) and 1.36 eV (Z-band) PL bands in CdTe. On the basis of our investigations we assign the 1.32 eV emission to a free-to-bound recombination near dislocations and the 1.36 eV emission to a DA emission within a dislocation core. Both bands are related to a shallow acceptor  $E_A = 35$  meV (probably Li or Na), whose concentration in the bulk is quite low. The Z-band is also related to a deep donor ( $E_D \geq 200$  meV), probably of intrinsic origin.

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