

# Does the low-temperature Arrhenius plot of the photoluminescence intensity in CdTe point towards an erroneous activation energy?

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Several experimental photoluminescence (PL) bands of different energies for variously prepared CdTe samples are compared. Temperature variation of the PL intensity is modeled with two nonradiative thermal activation energies, of which  $E_{T1}$  is dominant for about  $T \leq 60$  K, and  $E_{T2}$  for the upper temperature range of the measurement. The size of  $E_{T1}$  is invariably of the order of a few meV and, although of unclear origin, its magnitude is usually interpreted as an electronic energy level difference over which the carriers escape by thermal excitation. In CdTe the existence of such a small energy level difference  $E_{T1}$  is not easy to explain. On the contrary, we find clear evidence that, at low temperature, the PL intensity reduction with increasing temperature in fact results from the approximately  $T^{-2}$  temperature dependent capture cross sections of the carriers at the recombination centers, and not from a genuine thermal activation energy  $E_{T1}$ . © 1997 American Institute of Physics. [S0021-8979(97)07503-8]

## I. INTRODUCTION

The temperature dependence of the photoluminescence (PL) spectrum, intensity in particular, has been used to obtain information about electronic gap levels in various semiconductors. It is recognized that a host of different processes contribute to the reduction of the PL intensity as temperature increases.<sup>1</sup> In CdTe, thermal release of trapped carriers, followed by capture in a nonradiative recombination center, is proposed as the principal mechanism of thermal quenching. In some cases the thermal quench is pictured as being essentially due to a transition from the excited state directly to the ground state via the so-called internal mechanism.<sup>2</sup>

## II. DISCUSSION

Irrespective of the specific quenching mechanism, the temperature dependence of the integrated intensity  $I(T)$  of PL bands in CdTe is most often described by the expression

$$I(T) = \frac{I_0}{1 + \alpha \exp(-E_T/kT)} \quad (1)$$

with the process rate parameter  $\alpha$  and activation energy  $E_T$ . As a rule, expression (1) does not fit the experiment data correctly over a large temperature range. Although, in the high-temperature range of a measurement, a well defined value for  $E_T$  is obtained, there may still be some ambiguity in the low-temperature region. To manage this situation, a ‘‘better’’ fitting function has been introduced, with two different activation energies, of which  $E_{T1}$  is dominant for the low-temperature region ( $T \approx 5-60$  K) and  $E_{T2}$  for the high-temperature region ( $T > 60$  K).<sup>3-5</sup>

$$I(T) = \frac{I_0}{1 + \alpha_1 \exp(-E_{T1}/kT) + \alpha_2 \exp(-E_{T2}/kT)} \quad (2)$$

In CdTe quite detailed PL quenching studies have been reported for the 1.4 eV PL band.<sup>2-4</sup> Recently thermal PL quenching experiments were done also for deeper PL bands in CdTe.<sup>5</sup> The results obtained for the various bands are summarized in Table I.

It is clear from Table I that the two quenching processes are characterized with entirely different parameters. The low-temperature quenching, with a small value of  $E_{T1}$ , always has an extremely low value of the parameter  $\alpha_1$ , and it is intriguing to ask why this is so. There is general agreement in the literature that the donor-acceptor pair (DAP) model is the best model for the 1.4 eV PL band, although the precise nature of the DAP defects may not be quite the same in different samples. The deep donor–deep acceptor model also finds good experimental support for the PL bands in the 1.1 eV spectral region.<sup>5</sup> It would seem natural to assume that the low values of  $\alpha_1$  and  $E_{T1}$  should be explained as a result of donor ionization.<sup>3,4</sup> The high-temperature quenching is then due to the thermal release of trapped holes from the acceptors. Unfortunately all the available data do not support this explanation. First of all, there is similar magnitude of the low-temperature parameters  $\alpha_1$  and  $E_{T1}$  for different PL bands. It has been shown that the 1.1 eV PL bands in CdTe are related to deep donor levels<sup>5</sup> and 1.4 eV band to shallow donor levels. Therefore, it is hard to understand why the resulting activation energy  $E_{T1}$  for both bands should be the same. The second problem is the absence of the so-called free-to-bound emission features in the PL spectra within the quenching temperature region. After donor ionization, the resulting free electron may be captured by the same acceptor which is a member of a donor-acceptor pair, and as a result of new PL band should appear at higher energy. These kinds of bands are well known in other II–VI compounds and they

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TABLE I. Thermal quenching parameters  $\alpha_1$ ,  $\alpha_2$ , and  $E_{T1}$ , and  $E_{T2}$  of the PL intensity in CdTe, obtained from fitting experimental  $I(T)$  with Eq. (2).

Sample (PL band)	$\alpha_1$	$E_{T1}$ (meV)	$\alpha_2$	$E_{T2}$ (meV)	Ref.
CdTe:Cl (1.08 eV)	1.57	$4.0 \pm 2.5$	$2.0 \times 10^8$	$174 \pm 7$	a
CdTe:Cl (1.17 eV)	3.6	$5.7 \pm 2.5$	$2.2 \times 10^6$	$113 \pm 5$	a
CdTe:In (1.4 eV)	$3 \pm 0.2$	$5 \pm 1$	$(1.5 \pm 0.1) \times 10^6$	$95 \pm 10$	b
CdTe:I (1.4 eV)	8	15	$1.4 \times 10^6$	125	c
CdTe:Cu:Cl (1.4 eV)	$22 \pm 7$	$18 \pm 2$	$(4.5 \pm 3.5) \times 10^{10}$	$206 \pm 7$	a

<sup>a</sup>J. Krustok, V. Valdna, K. Hjelt, and H. Collan, J. Appl. Phys. **80**, 1757 (1996); the data for CdTe:Cu:Cl (1.4 eV) are from our own previously unpublished measurements.

<sup>b</sup>W. Stadler, D. M. Hofmann, H. C. Alt, T. Muschik, B. K. Meyer, E. Weigel, G. Müller-Vogt, M. Salk, E. Rupp, and K. W. Benz, Phys. Rev. B **51**, 10619 (1995).

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are quite easily detected. As far as we know, the free-to-bound band corresponding to the 1.1 eV DA bands in CdTe has not been detected.

The third problem is the low value of the parameter  $\alpha_1$ . In an electronic transition from a localized donor level to a delocalized band the transition probability is expressed as

$$\omega = \nu_D \Phi_D \exp(-E_D/kT), \quad (3)$$

where  $\nu_D$  is the escape frequency,  $\Phi_D$  is a parameter which takes into account the probability of finding an empty level, and  $E_D$  is the donor depth. For a continuous band, as an order of magnitude,  $\Phi_D \approx 1$  and at 10 K  $\nu_D \approx 3 \times 10^{11} \text{ s}^{-1}$ .<sup>6</sup> The parameter  $\alpha_1$  is proportional to  $\omega$  and quite high values of  $\alpha_1$  are expected—but are not found experimentally. To overcome this problem a two-acceptor-levels model was proposed by Cotal *et al.* in Ref. 6. In this model the low-temperature quenching was explained as a thermal transition of holes from one level to another. The transition between two localized levels may indeed have a very small transition probability because of a low value of the parameter  $\Phi_D$ . There were also two PL bands visible in the spectra of Cotal *et al.*<sup>6</sup> thus, additionally, giving justification to the assumption of two different activation energies. It is worth noticing, however, that in the low-temperature region activation energies generally of the order of  $E_T \approx 10$  meV have been found in widely different materials, such as ZnSe,<sup>7</sup> CdS,<sup>8</sup> and GaP.<sup>9</sup> It is not likely that a transition between two localized acceptor states would be the right explanation for the low-temperature quenching of the PL intensity in all these materials.

We focus our attention on the low-temperature quenching of the PL in CdTe and show that the temperature dependence of  $I(T)$ , reminiscent of an activation energy  $E_{T1}$  of a few meV and a low value for the rate parameter  $\alpha_1$ , is quite easily explained if we take into consideration the temperature dependence of the capture cross sections of both the donor and the acceptor defects, in a way similar to that suggested by Maeda.<sup>9</sup>

In II–VI semiconductors the recombination via DA pairs involves three steps:

- (1) capture of a free hole by an acceptor level,
- (2) capture of a free electron by a donor level, and
- (3) recombination of a bound electron with a bound hole.

Accordingly, we have to consider three types of center:

- (1) empty DA pairs with concentration  $N_E$ ,
- (2) DA pairs with a trapped hole with concentration  $N_h$ ,
- (3) DA pairs with both an electron and a hole with concentration  $N_{eh}$ .

The total concentration of DA pairs  $N_0$  is then

$$N_0 = N_E + N_h + N_{eh}. \quad (4)$$

According to this model we can write down the following kinetic equations:

$$\frac{dN_E}{dt} = C_{DA}N_{eh} - pC_{pE}N_E + \omega_A N_h = 0, \quad (5)$$

$$\frac{dN_{eh}}{dt} = -C_{DA}N_{eh} - \omega_D N_{eh} + nC_{nh}N_h = 0. \quad (6)$$

Here  $C_{DA}$  is the radiative recombination probability within DA pairs,  $C_{pE}$  is the probability of hole capture on the empty DA pair ( $C_{pE} = v\sigma_{pE}$ ),  $C_{nh}$  is the probability of electron capture on a DA pair with a previously captured hole ( $C_{nh} = v\sigma_{nh}$ ),  $v$  is the thermal velocity,  $\sigma_{pE}$  and  $\sigma_{nh}$  are the capture cross sections,  $\omega_D$  and  $\omega_A$  are the thermal ionization probabilities of electrons and holes, and  $n$  and  $p$  are the concentrations of free electrons and holes, respectively. The DA emission intensity is then proportional to  $N_{eh}C_{DA}$ . At low temperatures  $\omega_A \approx 0$  and, solving Eqs. (4)–(6), we get

$$I = N_{eh}C_{DA} = \frac{N_0 C_{DA}}{1 + \frac{C_{DA}}{nC_{nh}} + \frac{C_{DA}}{pC_{pE}} + \frac{\omega_D}{nC_{nh}}}. \quad (7)$$

To somewhat simplify the analysis, in the following  $n$  and  $p$  are assumed to be independent of temperature; i.e., the lifetimes of free electrons and holes are determined by the non-radiative recombination centers. This is equivalent of assuming a low luminescence efficiency, the assumption of which is further supported by our direct observation that when the intensity of a luminescence band is reduced, none of this intensity appears to be carried over to some other luminescence band. This indicates that the nonradiative recombination mechanisms play a dominant role. In addition, CdTe is known to have a lower luminescence efficiency than other II–VI materials, so this assumption appears to be justified. We also take  $C_{DA}$ , the radiative recombination probability within DA pairs, to be independent of temperature in the low temperature limit. The temperature dependences of  $C_{nh}$  and

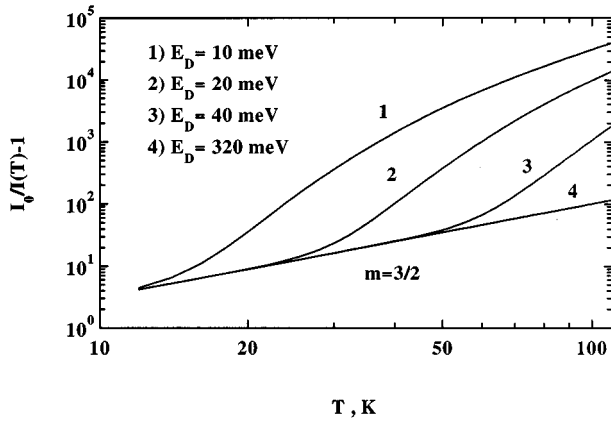


FIG. 1. Theoretical temperature dependence of the PL intensity calculated using Eq. (9) with  $\phi_1=0.1$  and  $\phi_2=100$  and with the donor activation energy varying from  $E_D=10$  to  $320$  meV.

$C_{pE}$  in Eq. (7) are essentially determined by the thermal velocity  $v$  of free carriers ( $v \sim T^{1/2}$ ) and by the temperature dependence of the capture cross sections of the defects. As found by a detailed calculation of Ascarelli and Rodriguez<sup>10</sup> for  $n$ -type Ge, and supported by experimental data on CdS by Colbow and Nyberg,<sup>11</sup> it is a reasonable approximation to write  $\sigma_{pE}, \sigma_{nh} \sim T^{-2}$ , so we have

$$C_{nh} \sim C_{pE} \sim T^{-3/2}. \quad (8)$$

Finally, for  $I(T)$  we get

$$I(T) = \frac{I_0}{1 + \phi_1 T^{3/2} + \phi_2 T^{3/2} \exp(-E_D/kT)}. \quad (9)$$

It is obvious that if we are dealing with relatively deep donor levels, i.e., if  $\exp(-E_D/kT) \ll 1$ , then the temperature dependence of the PL intensity is essentially determined by the capture cross sections  $\sigma_{pE}$  and  $\sigma_{nh}$ . In this case the measured PL intensity, presented as  $\log[I_0/I(T) - 1]$  vs  $\log(T)$ , should result in a straight line with a slope  $m=3/2$  [see curve (4) in Fig. 1]. If, on the other hand, the donor depth is small,

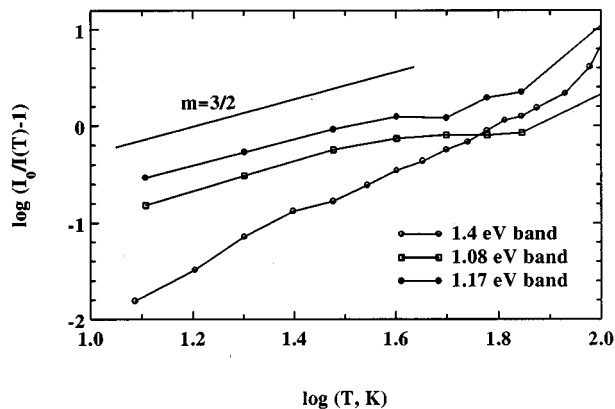


FIG. 2. Measured temperature dependence of the PL intensity of the 1.08 eV, 1.17 eV (see Ref. 5) and 1.4 eV (see Ref. 4) PL bands in CdTe, plotted as  $\log[I_0/I(T) - 1]$  vs  $\log(T)$ . The lines through the experimental points are drawn as visual aids only. The straight line with the slope  $m=3/2$  is included for comparison.

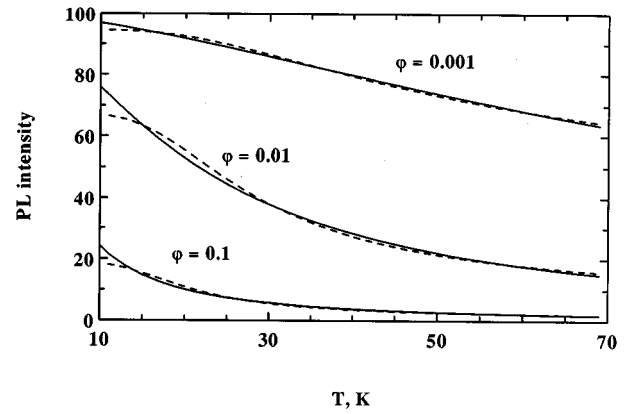


FIG. 3. Presentation of the function  $I(T) = I_0 / (1 + \phi T^{3/2})$  with different values of parameter  $\phi$  (solid curves) over the temperature range  $10 \text{ K} < T < 70 \text{ K}$ , shown together with the corresponding least-square fits using the function  $I(T) = I_0 / [1 + \alpha \exp(-E_T/kT)]$  (dashed curves; see also Table II). Apart from the low temperature end of the graph,  $10 \text{ K} < T < 20 \text{ K}$ , these two functions do not differ appreciably.

i.e., if  $\exp(-E_D/kT) \sim 1$ , then the ionization of donors will remarkably affect the intensity of the PL emission but, nevertheless, the slope will again be  $m=3/2$ . In between these two limiting cases there is a transition region, and within this temperature region a steeper dependence with  $m > 3/2$  should be detected [see curves (1)–(3) in Fig. 1]. Just these general features seem to be observed in the low-temperature region of the PL intensity of CdTe and, in fact, of various other semiconductor materials.

To compare the agreement between the theory presented above and recent experimental observations, the measured temperature dependence  $I(T)$  for three different PL bands in CdTe<sup>4,5</sup> are shown in Fig. 2 as  $\log[I_0/I(T) - 1]$  vs  $\log(T)$ . Comparison of Fig. 2 with Fig. 1 shows that Eq. (9) appears to fit experimental data quite well.

To clarify our case further, the theoretical function  $I(T) = I_0 / (1 + \phi T^{3/2})$  [cf. Eq. (9)], with various values of parameter  $\phi$ , was least-square-fitted with the more commonly applied function  $I(T) = I_0 / [1 + \alpha \exp(-E_T/kT)]$ . The results are plotted in Fig. 3, and show that in practice it is quite difficult to draw a distinction between these two functions. An intercomparison of the resultant fitting parameters is given in Table II.

Thus this kind of analysis seems to give just the same numerical range for parameters  $\alpha_1$  and  $E_{T1}$  as has been reported in the literature [cf. Table I], supporting the notion that the particular (low) values of these parameters, usually obtained when the fitting formula (2) is used, may be just an artifact without genuine physical significance. Accordingly,

TABLE II. The least-squares fitting parameters  $\alpha$  and  $E_T$ , obtained by fitting the theoretical function  $I(T) = I_0 / (1 + \phi T^{3/2})$  with the function  $I(T) = I_0 / [1 + \alpha \exp(-E_T/kT)]$ ; see also Fig. 3.

$\phi$	$\alpha$	$E_T$ , meV
0.001	1.61	7.37
0.01	9.94	6.63
0.1	25.03	6.08

to account for the slow reduction of the PL intensity with increasing temperature—in the low temperature end of the measurements, i.e., for  $T < 80$  K—the present analysis obviates the need to assume an activation energy of the order of a few meV, and of dubious origin.

### III. CONCLUSION

To sum up, the common usage of two different thermal activation energies  $E_{T1}$  and  $E_{T2}$  [cf. Eq. (2) and Table I] for fitting the measured temperature dependences of PL intensity in CdTe below  $T \approx 80$  K probably lacks the basis it is supposed to have. Rather than being due to a true energy level difference, at the low-temperature end, the slow reduction of the PL intensity with increasing temperature is shown to be consistent with the approximately  $T^{-2}$  dependence on temperature of the defect capture cross sections. Thus, any interpretation of an experimentally observed slow thermal decay of PL intensity in terms of a small activation energy, of the order of a few meV's difference between two closely lying levels, should definitely be corroborated with additional evidence—such as observation of some specific features in the measured PL spectrum, which directly correspond to the stipulated energy level difference.

### ACKNOWLEDGMENTS

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<sup>2</sup>See, for instance, I. B. Ermolovich and V. V. Milenin, *Phys. Status Solidi* **133**, 611 (1986); J. Krustok, J. Mädasson, K. Hjelt, and H. Collan, *J. Mater. Sci.* (to be published).

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