E_g VERSUS x RELATION FROM PHOTOLUMINESCENCE AND ELECTRON MICROPROBE INVESTIGATIONS IN p-TYPE $Hg_{1-x}Cd_xTe$ ($0.35 \leq x \leq 0.7$)

P. GILLE, K.H. HERRMANN, N. PUHLMANN, M. SCHENK, J.W. TOMM and L. WERNER

Sektion Physik der Humboldt-Universität zu Berlin, Invalidenstrasse 110, DDR-1040 Berlin, German Dem. Rep.

Combined photoluminescence (at $10 \leq T \leq 300$ K) and electron microprobe investigations have been carried out with HgCdTe samples grown from the melt or from solution. By exciting the samples through metallic masks with 200 μm diameter holes fixed with respect to the sample care was taken to pick-up both characteristic X-ray radiation as well as the photoluminescence from the same sample area. The E_g versus x relation determined in this way at $T = 30$ K has been compared with data from the interband absorption edge by other authors.

1. Introduction

Photoluminescence (PL) spectra are widely used as a method for studying alloy compounds, among them narrow-gap semiconductors such as the lead salts and $Hg_{1-x}Cd_xTe$ (MCT).

The aim of the experiments reported in this paper was to find a relation between the chemical composition x of the material as determined by electron microprobe, and the PL emission spectrum. Care was taken to ensure that both measurements were made in the same area of the sample. Such a calibration of PL allows us to use the PL signal for the purpose of absolute x determination with an error as low as 0.005. By comparing the relation found with empirical $E_g(x, T)$ relations by other authors, and with the temperature dependence of the PL signal, arguments are derived concerning the nature of the luminescence in small-gap MCT.

2. Experiment

In our experiments the PL behaviour of THM-grown samples of p-type $Hg_{1-x}Cd_xTe$ with $0.35 \leq x \leq 0.7$ was investigated. From Hall-effect measurements the carrier concentration p and the mobility μ were found to be $p = 10^{15}-10^{16}$ cm^{-3} and $\mu = 200-300$ cm^2 V^{-1} s^{-1} at 77 K. In some cases the Hall-effect sample was directly used in the PL experiment.

For preparing samples, the following technique was used: After etching the samples in a 0.1% Br$_2$/methanol solution aluminium masks with holes of about 200 μm diameter were fixed with respect to the surface. After that the PL spectra were measured through the holes. The diameter of the Nd-YAG laser beam at the sample surface plane was chosen to exceed 200 μm. Because excitation of MCT by a YAG laser is deep in the fundamental absorption band, the depth from which luminescence is being received, should be of the order of diffusion length (several micrometers). After that the area of the hole was examined with the electron microprobe. The diameter of the area excited by the electron beam was of the order of 1–2 μm, and the depth was 1.5–2.5 μm. Thus the depth investigated was nearly of the same order in both chemical (X-ray) and optical (PL) investigations. About 20 points were investigated within every hole. With extended integration time the standard error usually was found to be of the order of 0.002. The same value was found for 20 measurements at one and the same point without any shift of the sample. From that we conclude that the compositional homogeneity within a sample area of 200 μm diameter is better than 0.002.

The absolute x value determined is considered to be true within the same error limits. The

calibration was done using standard samples. This kind of sample preparation allows us to determine a relation between the spectral position of the PL signal and the chemical composition of the sample investigated. Another advantage of the technique described is that it is possible to take temperature dependent PL spectra without any error due to misalignment during temperature cycling. It is known that all cryogenic equipment introduces sample movement if the temperature changes. Therefore sample inhomogeneities produce an additional uncertainty in temperature dependent measurements. This effect is completely excluded in our experiments.

A description of the experimental arrangement for the YAG-laser excited PL was given earlier [1]. The Q switch delivers pulses with t_{FWHM} of about 80 ns. By combining cw PL with pulsed (pw) PL it becomes possible to vary the extinction level over more than five orders of magnitude under identi-cal conditions, and with limited heating effects. It can be assumed that within an 80 ns pulse, nearly steady-state conditions are established. For samples with $x = 0.4$ as well as $x = 0.6$, no shift of the main PL-peak position $\hbar\omega_p$ at 1 mW (cw) and at 300 W (pw) was found within an error below 2 meV.

In this paper pulsed PL was used only for determining the temperature dependence $\hbar\omega_p(T)$ in the range 80–300 K which led to the slope $d\hbar\omega/dT$ for the $x = 0.354$ (dashed cross) sample in fig. 3. For all other PL experiments the method of cw PL was used. The excitation power was about 10 mW for cw PL. First, it should be emphasized that both cw PL as well as pulsed PL lead to the same peak position for the main line. Second, note that pulsed PL allows MCT PL spectra (for $0.35 \leq x \leq 0.7$) to be measured at room temperature.
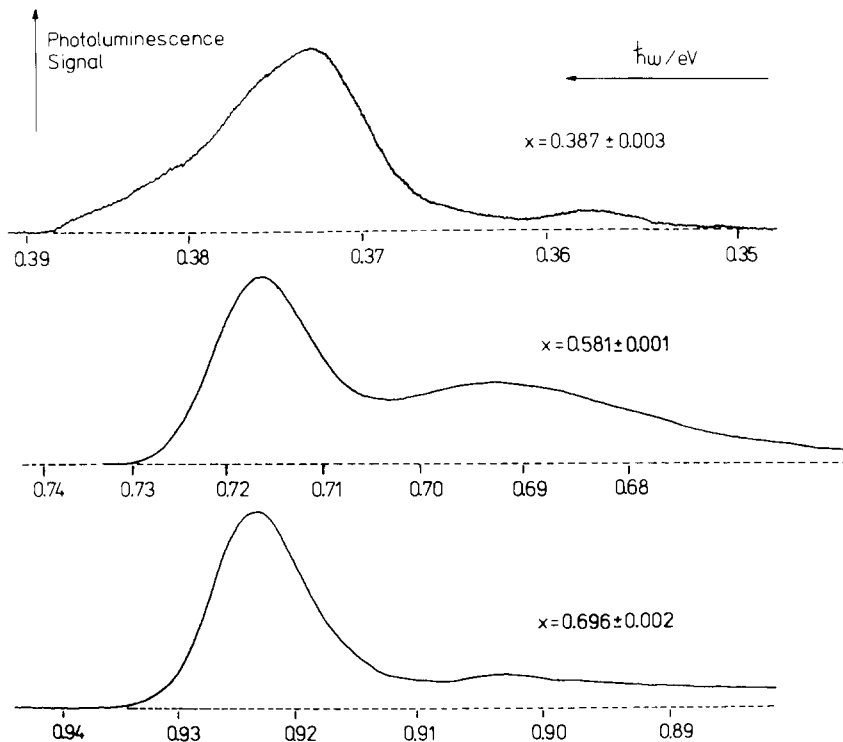

Fig. 1. Photoluminescence spectra of MCT with various compositions at 10 K.

3. Results and discussion

3.1. PL spectra and their temperature dependence

All spectra observed exhibit a main line (A) which is closely related to E_g. At temperatures below 15–30 K (dependent on the sample) a second line (B) at energies below the A line was observed. The separation between the peaks of the A and B lines, was found to be between 8 and 72 meV. In most cases values between 21 and 28 meV were obtained. In fig. 1 typical spectra measured

at 10 K are shown.

At $T = 30$ K, both the A and the B line begin to merge into an asymmetric spectrum, and from 80 K to room temperature only one nearly symmetric line was observed.

In fig. 2, the temperature dependences of the peaks and the halfwidths of both lines are plotted. The dashed lines are the slopes dE_g/dT for the given x value. The dE_g/dT values were calculated from the empirical relations given by Hansen et al. [2], Chu et al. [3] and Finkman and Schacham [4] (compare with fig. 3). Independent
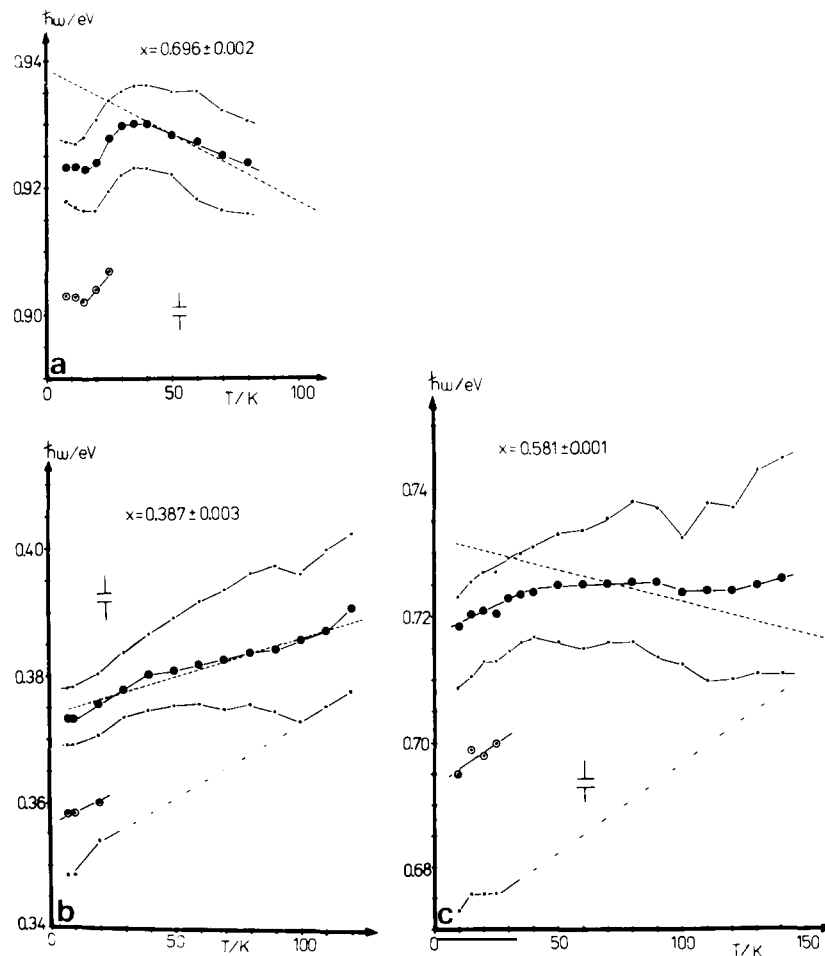

Fig. 2. Temperature dependence of the spectral position of the PL spectra: (●) A peak; (○) B peak; (·) spectral position of the point where the luminescence intensity equals half A or B peak intensity. The dashed lines represent the slope dE_g/dT calculated from refs. [2–4] for the corresponding x value (-2.1×10^{-4} eV K^{-1} for $x = 0.696$; -1×10^{-4} eV K^{-1} for $x = 0.581$; 1.2×10^{-4} eV K^{-1} for $x = 0.387$).
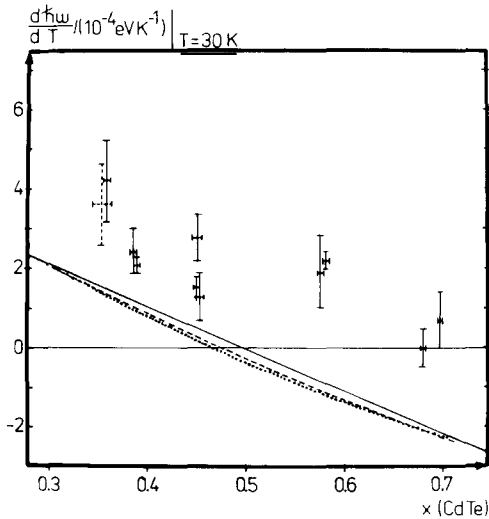
Fig. 3. Slope $d\hbar\omega/dT$ versus x at $T = 30$ K as compared with dE_g/dT, taken from ref. [2] (———), ref. [3] (— —) and ref. [4] (······). The dashed cross is a slope $d\hbar\omega/dT$ in the temperature range 80–300 K.

of the composition, the slope $d\hbar\omega/dT$ is positive for $T < 30$ K and generally larger (for exceptions see fig. 2b between 40 and 90 K) than dE_g/dT calculated from the empirical relations. If the slopes of the B line are extrapolated towards higher temperatures, it may be seen that interference between both A and B lines takes place and influences both the slope $d\hbar\omega/dT$ and the FWHM. We think that the exceptions mentioned should be seen in the framework of this interference and should not be attributed to a weaker $E_g(T)$ dependence in this x and T range. Such exceptions of the $E_g(T)$ are found in the absorption measurements, too [5].

In fig. 3, $d\hbar\omega(x)/dT$ of the A line taken at 30 K is plotted. The $dE_g(x)/dT$ curves calculated according to refs. [2–4] are added.

The temperature of $T = 30$ K was chosen because it is the highest one where interference between the A and B peaks is excluded. Note the x-independent shift of the experimental points at 1–3 k_B ($k_B = 0.86 \times 10^{-4}$ eV K^{-1}) as compared with the calculated values for dE_g/dT. This is in agreement with Hunter and McGill [6,7]. The dashed cross in fig. 3 indicates the slope in the 80–300 K range. It underlines that the observation

of an additional contribution to the slope is not limited to low temperatures.

For a non-degenerate semiconductor using the model of direct interband transitions (see, e.g., Anderson [8] for MCT) an energetic difference of $0.5k_B$ between $d\hbar\omega/dT$ and dE_g/dT is predicted, whereas with k-conservation broken (see, e.g., Lasher and Stern [9]) a value of $2k_B$ may be explained.

On the one hand, the results of fig. 3 are a further argument for the unique nature of optical transitions in MCT with compositions x varying from 0.3 to 0.7. On the other hand, it can be concluded that indirect band-to-band transitions could also explain the nature of recombination radiation in $0.3 \leq x \leq 0.7$ MCT.

3.2. $\hbar\omega$ versus x relation

In determining the relationship between the chemical composition and the spectral position of the PL signal, the temperature $T = 30$ K was chosen. This temperature is more convenient than 4.2 K from a practical point of view, and the FWHM is not significantly larger than at lower temperatures. At 30 K the FWHM of all samples investigated was between 10 and 16 meV. From the PL spectra at 30 K (peak of the A line) and the x values determined by the electron microprobe, the relation

$$\hbar\omega_p = -0.1044 + 0.5909x + 1.9483x^2 + 0.1087x^3$$
$$-2.364x^4 + 1.212x^5 \qquad (1)$$

was obtained.

The point at the low energy side of the A peak as defined by extrapolation of the largest slope was attributed to E_g. For E_g it was found:

$$E_g = -0.780 - 0.5762x + 1.401x^2 + 1.2686x^3$$
$$-2.995x^4 + 1.19x^5. \qquad (2)$$

3.3. Comparison of the spectra with empirical $E_g(x, T)$ relations

In order to test eqs. (1) and (2) in fig. 4a, the differences between the position of the maximum
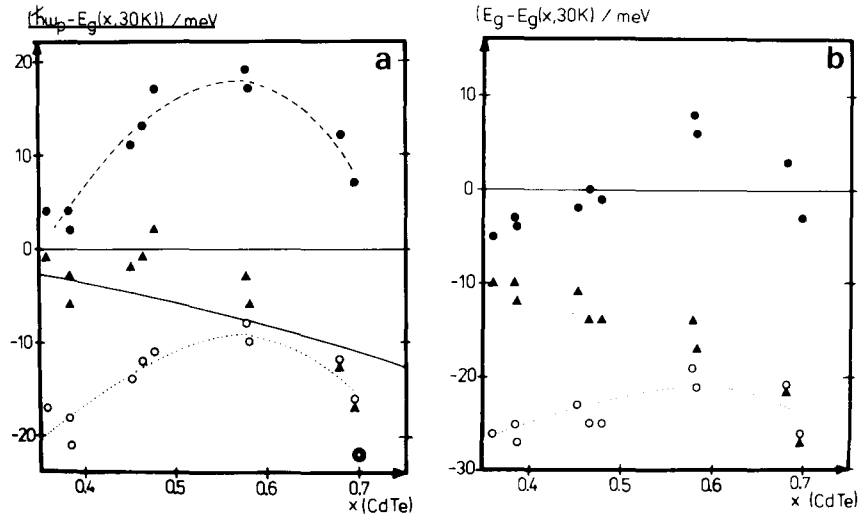
Fig. 4. Difference between the spectral position of the A peak and the E_g point defined in our spectra and empirical $E_g(x, T)$ relations at 30 K versus x value: (●) $E_g(x, T)$ from Hansen et al. [2]; (▲) $E_g(x, T)$ from Finkman and Schacham [4]; (○) $E_g(x, T)$ from Chu et al. [3]. The full line in (a) represents the binding energy of a free exciton (plotted with negative sign) calculated from hydrogen-like model using composition dependent dielectric constants, energy gaps and momentum matrix elements. The single point at $x = 0.7$ in (a) is the difference between eq. (1) and the $E_g(x, T)$ relation after ref. [10].

of the A line peak (this paper) and the empirical E_g values from refs. [2–4] at 30 K were plotted. The uncertainty in the points is below 10 meV (7–8 meV due to the ±0.002 composition error, plus spectral slit width of the monochromator). In this plot the full line describes the binding energy of a hydrogen-like free exciton in MCT calculated from the effective masses. Assuming that the E_g versus x relation by Finkman and Schacham [4] reflects the real value of the gap, the free exciton model explains the recombination radiation in 0.35–0.7 MCT very well. This hypothesis is in good agreement with that by Legros and Triboulet [10]. The single point at $x = 0.7$ in fig. 4a represents the difference between $\hbar\omega_p$ ($x = 0.7$) taken from eq. (1) and E_g ($x = 0.7$, $T = 30$ K) taken from fig. 2 in ref. [10]. It shows the coincidence of both their and our experiments and also with the $E_g(x, T)$ relations in refs. [4] and [10] within the error limits of their and our x determination. From this point of view our experiments can be considered as a continuation of the experiments by Legros and Triboulet towards smaller x values. We consider these facts as further hints for the excitonic nature of the recombination radiation in

MCT with $0.35 \le x \le 0.7$. Fig. 4b describes the difference between the E_g point defined in our spectra and the $E_g(x, T)$ relations of the authors mentioned. The weak distortion of the curves as compared with fig. 4a is due to the non-uniformity in the FWHM.

From fig. 4b it may be seen that the $E_g(x, T)$ relation by Finkman and Schacham does not apply to our results in the framework of interband transitions.

Then, it may be seen that the $E_g(x, T)$ relation by Hansen et al. is in good agreement with the interband model. The same statement is true with respect to the formula by Chu et al. if the fact is taken into account that these authors determined E_g from absorption measurements, and that from their definition of E_g (the 2000 cm^{-1} point) a difference from the results by Hansen et al. is automatically obtained. This fact is being considered to be an additional argument for the interband nature of the optical transitions in MCT. Unfortunately, only a very limited temperature range is covered by the PL experiment reported in this paper.

4. Conclusions

The lineshape of the PL spectra in MCT observed in the 0.35–0.7 composition range at temperatures between 10 and 300 K is nearly uniform for different x values. Therefore a unique nature of recombinative transitions in this composition range is assumed.

The slope $d\hbar\omega/dT$ of the PL signal is between 1 and 3 times k_B larger than dE_g/dT taken from empirical relations; the difference is independent of x. Such behaviour is typical of interband transitions without k conservation; one possible explanation is within a free-exciton model.

The dependence of the PL signal on the composition was compared with empirical $E_g(x, T)$ relations [2–4]. Assuming that Hansen et al. [2] or Chu et al. [3] have found the true $E_g(x, T)$ relation our experiments may be explained in the framework of a model which assumes that interband transitions create the A peak of the PL signal observed. Assuming that Finkman and Schacham gave the true $E_g(x, T)$ relation also, recombination via free excitons could create the A line. For $x = 0.7$ our experimental results agree with those by Legros and Triboulet [10] who made PL measurements in the 0.7–1.0-compositional range and attributed their spectra to excitonic transitions.

As to the nature of recombination radiation in MCT in the 0.35–0.7 range, further experiments are needed, but interband transitions without k conservation are promising candidates.

The relations (1) or (2) may be used for determining the composition x from PL spectra with an error not exceeding 0.005.

Acknowledgements

The authors wish to thank Dr. I. Rückmann for stimulating discussions, and T. Fleischer and F. Posniak for their help.

References

[1] L. Werner and J.W. Tomm, Phys. Status Solidi, in press.
[2] G.L. Hansen, J.L. Schmit and T.N. Casselman, J. Appl. Phys. 53 (1982) 7099.
[3] J. Chu, S. Xu and D. Tang, Appl. Phys. Letters 43 (1983) 1064.
[4] E. Finkman and S.E. Schacham, J. Appl. Phys. 56 (1984) 2696.
[5] M.W. Scott, J. Appl. Phys. 40 (1969) 4077.
[6] A.T. Hunter and T.C. McGill, J. Appl. Phys. 52 (1981) 5779.
[7] A.T. Hunter and T.C. McGill, J. Vacuum Sci. Technol. 21 (1982) 205.
[8] W.W. Anderson, Infrared Phys. 20 (1980) 363.
[9] G. Lasher and F. Stern, Phys. Rev. 133 (1964) A553.
[10] R. Legros and R. Triboulet, J. Crystal Growth 72 (1985) 264.