Photoluminescence in Mercury Cadmium Telluride – a Historical Retrospective. Part I: 1966-1996

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Abstract. This work presents a historical retrospective on the studies of photoluminescence in mercury cadmium telluride (HgCdTe), one of the most important materials of infrared photoelectronics. The first part of the review considers the results of the studies performed during the early years of the development of the technology of this material (1966-1996). These studies were carried out mostly using samples of bulk crystals and epitaxial films grown by liquid-phase epitaxy. The results of the studies allowed for identification of the nature of optical transitions in HgCdTe, including excitonic emission, interband recombination, donor-acceptor pair recombination and recombination via shallow and deep levels, which greatly helped in maturing the material technology.

Mercury cadmium telluride (HgCdTe, MCT) was first synthesized at the end of 1950s [1], and quickly became one of the basic materials of infrared (IR) phototoelectronics, which position it has maintained for over 60 years. Binary HgTe and CdTe compounds form a continuous series of solid solutions (alloys) with a bandgap of up to 1.6 eV at 300 K. This makes it possible not only to manufacture, on the basis of one material, photodetectors covering the spectral range from 1 to 14 μm, but also to form on one semiconductor crystal, by changing the composition, multi-color IR detectors. The low effective mass of carriers and the low dielectric constant of MCT provide a high speed of operation of phototoelectronic devices [2].

MCT technology continues to evolve and improve in parallel with advances in instrument design. Currently, the most popular MCT photodetectors are those based on multi-element arrays of detector elements, integrated with signal processing systems [3]. There is also an interest in emitters based on MCT, especially for the mid-IR range (wavelength 3-5 μm), in which the characteristic absorption bands of many chemical compounds are located [4]. Sensors of these substances are in demand both for monitoring the state of the atmosphere and for instrumental control in industrial production.

MCT is a semiconductor alloy with a zinc blende structure. Properties of MCT change continuously with a change in the composition (CdTe molar fraction) x between the phases of binary compounds. Both HgTe and CdTe possess zinc blende structure and have similar lattice parameters $\alpha^{HgTe} = 6.42$ Å and $\alpha^{CdTe} = 6.48$ Å. CdTe is a direct gap semiconductor with bandgap $E_g = 1.6$ eV at $T = 300$ K and the spin-orbit splitting energy $\Delta = 0.8$ eV. HgTe has an inverted band structure with E_g of -0.3 eV and $\Delta = 0.94$ eV. Thus, in MCT the bandgap can vary from 1.6 eV to 0 depending on the composition x, while the energy of spin-orbit splitting changes very little.

The temperature dependence of the bandgap of MCT solid solutions is almost linear, and in $Hg_{1-x}Cd_xTe$ with $0.156 \leq x \leq 0.50$ the bandgap increases with temperature (x=0.156 corresponds to $E_g = 0$ eV). For $x \geq 0.5$, the temperature coefficient of E_g is negative (Fig. 1).

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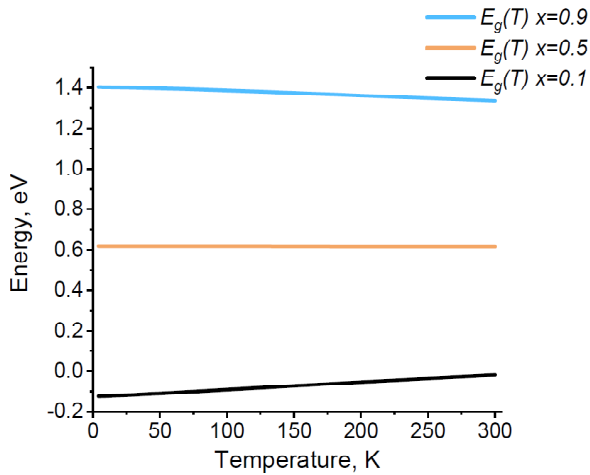
Fig. 1. Temperature dependences of the bandgap of MCT for the material with $x = 0.1$, $x = 0.5$, and $x = 0.9$. The dependences were calculated according to the $E_g(x,T)$ relation by Becker et. al, *Phys. Rev. B, vol. 62, pp. 10353-10363 (2000)*, which was the latest version of this relation for MCT at the time of the writing of this review.

An important feature of MCT is that depending on specific conditions, non-equilibrium charge carriers can recombine through any of the known mechanisms, e.g., interband ones, those involving trapping of the carriers at local levels in the bandgap, on a surface, etc. The dominating role of a specific process is determined by the bandgap value, carrier concentration, temperature, concentration and properties of local centers, etc. In addition to fundamental interest, the study of recombination processes is also of practical importance, since the lifetime of non-equilibrium carriers determines the sensitivity and speed of the detectors fabricated on the basis of a given material and, thus, is one of its most important characteristics. Because of this, interband recombination and the carrier lifetime in narrow-gap MCT has always been of interest. In MCT, three main types of carrier recombination are usually taken into account: radiative, Auger recombination, and Shockley-Reed-Hall recombination.

Historically, the main attention was paid to the study of crystals and epitaxial layers of MCT with $x \leq 0.3$, since they were used for the manufacture of IR detectors for the wavelength range of 8-14 μm, almost unattainable for interband photodetectors based on other materials. For these MCT compositions, interband recombination mechanisms indeed play an important role. With the bandgap decreasing, i.e., going over to narrow-gap MCT alloys, the probability of radiative recombination decreases and non-radiative (in particular, Auger) processes dominate, especially at high temperatures.

Photoluminescence (PL) spectroscopy is a powerful tool for investigation of optical and electronic properties of semiconductors. One advantage of this method is its non-destructive character. When investigating PL, it is often of interest to vary different parameters. The most common variations include the excitation power, sample temperature, and excitation wavelength. The most interesting are measurements at low temperatures (such as the liquid helium temperature). Measurement of the PL intensity as a function of temperature provides information on the recombination channels in semiconductors. At the same time, the change in the width of the PL peaks with temperature allows one to access the information on the distribution of charge carriers. PL can also provide some insight into structural properties of the material, its chemical purity, defects, presence of strain, etc. PL studies have been widely used for investigation of the properties of almost all semiconductor materials. As narrow-gap MCT has a small electron effective mass and a high dielectric constant, the exciton binding energy in narrow-gap MCT is very small, so that excitons were believed to be usually dissociated even at very low temperatures. In contrast to the PL spectra of many wide-bandgap materials, which are dominated by sets of exciton-related lines, narrow-gap MCT PL spectra could be very simple in structure [5]. PL studies in MCT have also been hindered by the high rate of non-radiative (mostly Auger) recombination and effect of thermal background radiation. Recently, however, it became possible to obtain high-quality PL spectra of narrow-gap MCT thanks to the development of high-sensitivity IR photodetectors (including those made of MCT) and advances in signal modulation techniques.

It has been over 10 years since the optical properties of MCT, including those revealed as a result of PL spectroscopy measurements, were reviewed, and on that occasion they were reviewed very briefly [5]. In this work, we attempt to present a more comprehensive review of the most prominent studies of PL in MCT. The review consists of two parts, which correspond to different time spans. As MCT was initially considered to be a material for defense applications, its science and technology experienced a strong boom during the cold war era. With the end of the cold war, in the early 1990s, the interest in this material strongly dwindled, also, it was believed at that time that MCT-based photodetectors, which were difficult to fabricate because of inherent properties of mercury-containing II-VI materials, would be replaced by the detectors based on much more technologically advanced III-V materials (superlattice-, quantum-well- or quantum-dot-based photodetectors, or, in the case of InAsSb alloys, interband photodetectors) [6]. Thus, the first part of the

review considers the PL studies of MCT performed in 1966-1996. The second, upcoming part of the review, will consider modern (2000-2020) works on PL in MCT. And though these two parts will consider PL studies performed nominally on the same material, yet technology of MCT has changed so drastically in these years [1] that the results of the earlier works must be used with caution when interpreting the data of recent stuides.

In this review, we shall mostly concentrate on optically pumped spontaneous emission from 'bulk' MCT samples, i.e., samples of bulk crystals and epitaxial films. Nanostructures, including superlattices, quantum-well structures, etc., and laser action in MCT will not be considered, and MCT 'sister' materials, such as HgMnTe, HgCdSe, HgCdZnTe, HgCdMnTe, etc., will not be considered either. The material under consideration in this part of the review would be mostly grown by 'classical' methods, such as the Bridgman method or the Traveler Heater Method (THM), and epitaxial films at that period would be mostly grown by Liquid Phase Epitaxy (LPE) on lattice-matched CdTe and ZnCdTe substrates. At the end of 1980s, other growth methods, such as Molecular Beam Epitaxy (MBE) or Metalorganic Chemical Vapor Deposition (MOCVD) started to be used more actively for the growth of MCT, also, 'alternative' substrates made of Si or GaAs came into use. These results will be also included in this part of the review.

One of the first works on PL in MCT was published back in 1966, when Melngailis and Strauss from Massachusetts Institute of Technology observed spontaneous emission at wavelengths from 3 to 15 μm and laser emission at 3.8 and 4.1 μm from MCT crystals grown by the Bridgman method [7]. Spontaneous emission was obtained from the samples with values of x between 0.18 and 0.37. A dependence of the photon energy at the peak of the spontaneous emission line on sample composition for temperature values 12 K and 77 K was obtained.

In 1972, Elliott et al. performed PL measurements on bulk p-type MCT samples with x values between 0.21 and 0.50 [8]. Two emission peaks were observed in the PL spectra, with a relative intensity of the peaks dependent on excitation power; the intensity of the short wavelength peak was increasing more rapidly with the power. The shorter wavelength (high-energy) peak was attributed to interband transitions, while the longer wavelength peak was attributed to transitions from the conduction band to an acceptor level (c-A). The authors of [8] believed that their PL data established acceptor ionization energy of the order of 20 meV (15 to 22 meV for different samples) for MCT with $x \approx 0.3$, consistent with their electrical observations.

The next series of experiments on PL in MCT started in 1980s, when Hunter et al. [9] from California Institute of Technology studied the low-temperature PL of the material with $x = 0.32$ and $x = 0.48$. Samples with $x = 0.32$ were grown by the float-zone-refining polycrystalline method and their PL spectra had two peaks. The high-energy peak was attributed to the interband (c-v) transitions due to linear dependence of its intensity on the excitation power, as well as to the shift of the peak towards higher energies with increase in temperature. The low-energy peak was broader and had a low-energy tail. The origin of this peak at low temperatures was explained by optical transitions of the carriers from the donor level to the acceptor level (recombination of donor-acceptor pairs, DAP). With temperature increasing, when donors became ionized, the origin of the peak was ascribed to recombination of a free electron and a bound hole. Samples with $x = 0.48$ were grown by solid-state recrystallisation and, similar to samples with $x = 0.32$, were annealed in mercury vapor to reduce the concentration of mercury vacancies. These samples also had high- and low-energy PL peaks with presumably similar (to those in sample with $x = 0.32$) origin. In addition, PL spectra of some samples contained an intermediate peak, which was attributed to the recombination of a bound exciton (BE).

Later, Hunter and McGill published more detailed work on the PL of MCT [10]. They partly re-considered their results obtained on the same samples with $x = 0.32$ and $x = 0.48$ and proposed an advanced model interpreting the origin of the high-energy PL peak corresponding to the 'interband transition'. Now the shape of the peak, the dependence of its intensity on the excitation power, and the shift of the peak with a change in temperature were found to be appropriate to an electron-hole plasma with recombination proceeding without conservation of the wavevector k. The presence in the PL spectrum of a low-energy peak corresponding to the recombination of a free (bound at low temperatures) electron and a bound hole made it possible to estimate the ionization energy of impurities in the material. The value for the acceptor binding energy of 14.0 ± 1.5 meV for the material with $x = 0.32$ and 15.5 ± 2 meV for the material with $x = 0.48$ were obtained. The authors believed that this acceptor was either an Au substitutional atom (some samples were Au-doped), or an alloy vacancy. Based on the current knowledge, we can assume that this acceptor was, indeed, a mercury vacancy, as its binding energy $E_a \sim 14$ meV was confirmed since then in numerous PL studies [11-13]. The presence of a BE peak in MCT samples with $x = 0.48$ was explained by the longer lifetime of Auger recombination than that of radiative recombination. The BE nature of this peak was suggested by the fact that its intensity did not depend on the excitation power; also, the peak maximum did not shift with temperature in the whole 4.8-20 K range where it was

observed. The full-width at half-maximum (FWHM) of this peak equaled 6 meV at 4.8 K. From DAP PL, the donor binding energies E_D of 1.0 ± 1.0 meV for the material with $x = 0.32$ and 4.5 ± 2.0 meV for the material with $x = 0.48$ were obtained, which was consistent with the values calculated within the frames of the hydrogenic model that predicts very low E_D for the materials with low electron effective mass, including narrow-gap MCT.

Feldman from the University of Missouri with co-authors from the Rockwell International Science Center [14,15] studied PL of 'wide-bandgap' MCT with $x \approx 0.7$ grown by LPE. In one set of experiments [14], they observed a single PL line with FWHM of 5-6 meV at 4.2 K, which, upon analogy of a similar line in the PL spectra of CdTe, was attributed to the recombination of electrons and holes bound to a neutral donor. In another set of experiments, also performed on films with $x = 0.69$ and $x = 0.71$, the authors of [15] observed two lines in the PL spectra. One of them was attributed to the recombination of a free exciton with binding energy at 77 K equaling 16 ± 6 meV. The other, much broader, line was attributed to recombination via deep levels with the energy of the level being of the order of 130 meV.

Polla and Aggarwal from the Massachusetts Institute of Technology [16] applied the technique of 'below band-gap' PL to MCT with $x \approx 0.33$ grown by LPE. A single peak observed has been interpreted as being due to a spontaneous transition from a deep donor level at approximately $0.4E_g$ to the valence band (at 94 K PL peak was centered at 0.12 eV with E_g being 0.3 eV). The energy associated with this peak corresponded closely to deep level activation energies obtained by optical modulation spectroscopy and thermally excited relaxation characterization techniques.

In a work by Legros et al. [17], the results of PL studies of MCT in a composition range $0.7 < x < 1$ were presented. Crystals grown by the THM and films grown by LPE on a CdTe substrate were studied. The obtained PL spectra contained a high-energy peak with FWHM of 12 meV at 12 K and its phonon replicas. This band was attributed to a mixing of excitonic lines broadened by the effects of alloy disorder. The authors have developed a relationship $E_g(x,T)$ specifically to analyze the PL spectra of MCT with $0.6 < x < 1$:

$$E_g(x,T) = -0.303 + 1.94x - 0.655x^2 + 0.579x^3$$

$$+(5.5 - 13.92x + 5.84x^2) \times 10^{-4} T.$$

The authors also recorded PL spectra of indium-doped $Hg_{0.3}Cd_{0.7}Te$ crystals grown by the THM method and possessing a low electron concentration ($n = 2 \times 10^{14}$ cm^{-3} at 300 K). In this case, they observed emission arising from both excitonic and DAP transitions. A relationship was used for calculating the energy of a DAP transition E_{DAP} at low temperatures:

$$E_{DAP} = E_g - (E_D + E_A) + \frac{q^2}{4\pi \in R},$$

where E_D is the donor energy, q is elementary charge, $\in$ is the dielectric permittivity, R is the pair separation. It was suggested that the donor in question was possibly arising from indium doping, while the nature of the acceptor remained unclear, one possibility being Cu_{Cd} (though now it is generally accepted that copper acceptors occupy interstitial positions in MCT; the same applies to gold atoms mentioned in [10], they are also believed to occupy interstitials [18]).

The paper by Lusson et al. published in 1990 [19] was also one of the first to attribute the features of the PL of MCT to the alloy disorder (composition fluctuations, which in MCT are generally understood as the random distribution of Hg and Cd atoms in the cation sublattice). The authors investigated PL in a wide composition range $0.2 < x < 1$ using samples grown by LPE (for $x < 0.5$) or THM (for larger compositions). In their opinion, local potential oscillations (on which free carriers or excitons can be "captured") caused by the alloy disorder were responsible for the localization of the exciton. Typical PL spectra obtained by the authors of this work are shown in Figs. 2 and 3.
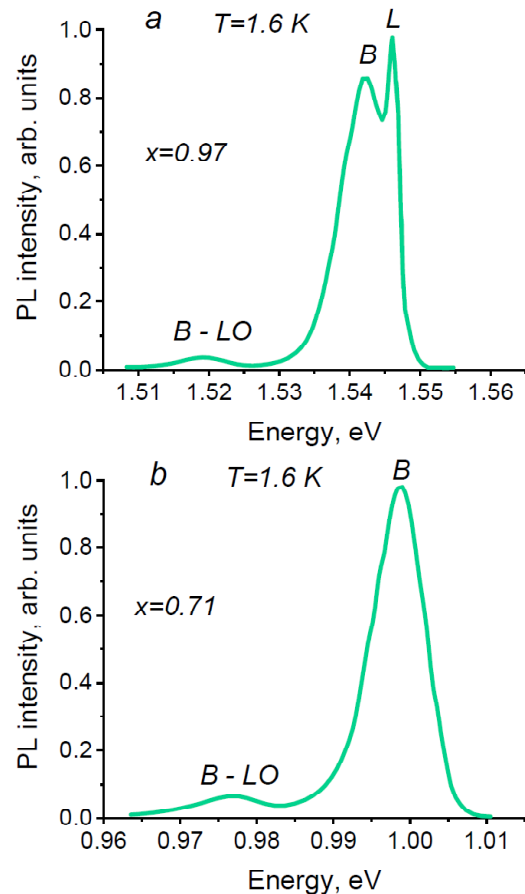
Fig. 2. PL spectra of MCT sample with $x = 0.97$ (*a*) and $x = 0.71$ (*b*) (replotted using the data from [19]).
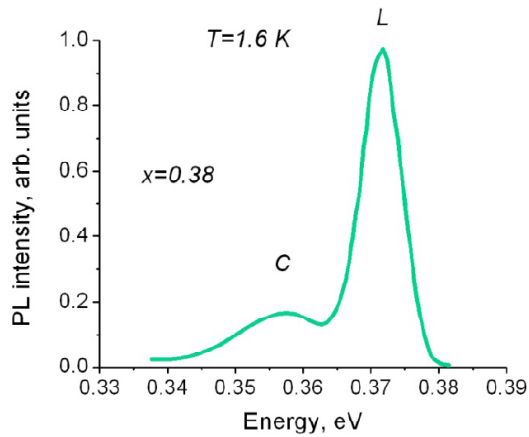
Fig. 3. PL spectrum of MCT sample with $x = 0.38$ (replotted using the data from [19]).
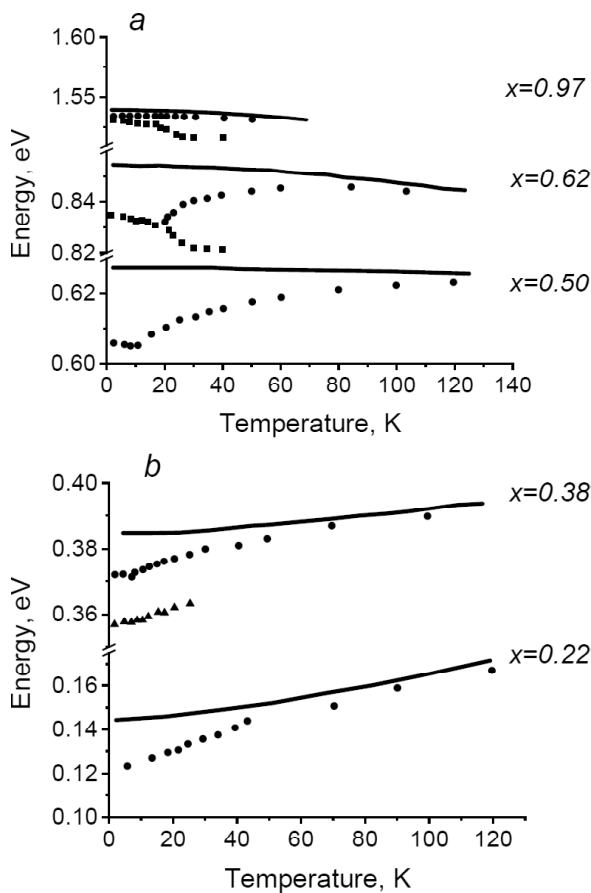
Fig. 4. Temperature variation of PL peak energy along with the calculated temperature $E_g(T)$ dependence (solid lines) for MCT samples with larger (*a*) and smaller (*b*) *x* (replotted using the data from [19]): line *L*, circles; line *B*, squares; line *C*, triangles.

PL spectra of samples with large *x* (high Cd content, Fig. 2) contained two dominant lines *B* (positioned at 1.542 eV (FWHM=7 meV) for sample with *x*=0.97 and at 0.998 eV for sample with *x*=0.71 (FWHM=6 meV)) and *L* (positioned at 1.546 eV with FWHM=4 meV for sample with *x*=0.97), as well as LO phonon replicas of peak *B*.
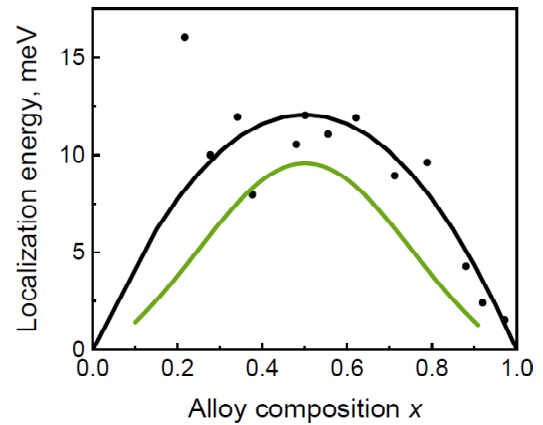
Fig. 5. Dependence of the exciton localization energy on the composition. Dots show experimental values obtained by Lusson et al. [19], upper curve shows $x(1-x)$ alloy disorder function, lower curve, a calculated dependence of amplitude of compositional fluctuations on *x* obtained for MCT by Shilyaev et al. [20].

Peak *L*, on the basis of the data available at the time in the literature, was attributed to the recombination of a bound exciton (BE). At the same time, the appearance of peak *L* was explained by the recombination of an exciton localized in potential fluctuations caused by alloy disorder. The peak *L* was found to shift towards higher energies with temperature increasing. Such a shift was understood as thermal delocalization of the exciton, up to the energy of a free exciton. Peak *C* corresponded to electron-acceptor (*c–A*) recombination and was observed in samples with *x* < 0.5. In particular, in sample with *x*=0.38 (Fig. 3) this peak was distanced from the high energy peak (peak *L*, positioned at 0.371 eV with FWHM=7 meV) by 14 meV.

The relative intensity of the line *C* vs the main line appeared to be dependent on the laser spot position on the sample, and the intensity of line *C* saturated with excitation power increasing. These effects suggested that this *c-A* line was related to impurities in small concentration, which were non-homogeneously distributed in the sample. The FWHM of this line in sample with *x*=0.38 equaled 16 meV, i.e., this line was much broader than excitonic lines.

Fig. 4 shows temperature variation of PL peak energy along with the calculated temperature dependence of the bandgap in MCT for five samples studied in [19]. As can be seen, in all cases the energies of the PL peaks at low temperatures are much smaller than the calculated bandgap energies. At $T > 100$ K the energy of the PL peak starts to approach the calculated E_g. For sample with *x*=0.97, temperature dependence of the free exciton ground state energy was measured with reflectivity (not shown), and the energy of peak *L* appeared to be close to that energy.

The general conclusion by Lusson et al. [19] was that the observed PL was caused by two types of exciton recombination: recombination of a bound exciton (BE) and recombination of an exciton localized on fluctuations of the composition (LE). The dependence of the localization energies deduced from the measurements on the alloy composition is plotted in Fig. 5, where dots show experimental data (blue shift of PL peak in respect to calculated E_g value at 50 K). As can be seen, this energy can exceed 10 meV and follows a parabolic dependence on the composition $x(1-x)$ (upper solid curve). For comparison, Fig. 5 also shows a calculated dependence of amplitude of compositional fluctuations on x obtained for MCT by Shilyaev et al. [20] within the frames of the model by Baranovsky and Efros developed in 1978 [21] (lower curve), which has a similar, though not exactly the same, shape, and gives slightly smaller energy values.

On the basis of the results of the experiments by Lusson et al. [19] and by combining these data with the PL data obtained on a ZnHgTe bulk crystal [22], Oudjaout et al. [23] developed a model of the density of states for composition fluctuations ('tail-state distribution'). The model covered the cases of one- or two-particle localization and gave the following expression for the energy ε dependence of the luminescence intensity I_L:

$$I_L \sim \frac{n(\varepsilon)}{\tau_R} = \beta n_0 (\tau_R)^{-1} g(\varepsilon) \tau(\varepsilon) \exp[A(\varepsilon)],$$

where $A(\varepsilon)$ is the integral $\int_0^\varepsilon w(\varepsilon') g(\varepsilon') \tau(\varepsilon') \, d\varepsilon'$. Here, β is the capture coefficient, n_0 is a free exciton concentration, $g(\varepsilon)$ is the density of localized states, $w(\varepsilon)$ is the coefficient of transfer from higher energy states, and $\tau(\varepsilon)$ is the effective lifetime determined by the radiative recombination (time constant τ_R) and transfer to lower energy states:

$$\tau(\varepsilon) = \frac{\tau_R}{1 + \exp[\delta(\varepsilon_M - \varepsilon)]},$$

with ε_M and δ being adjustable parameters.

The paper by Fuchs et al. [24] described the study of PL in MCT performed using the Fourier transform infrared spectroscopy (FTIR) in conjunction with the technique of double modulation. This method, due to its significant sensitivity, made it possible, for the first time, to study PL of narrow-bandgap MCT, where, as was mentioned above, under standard conditions two major factors interfere with PL observation: a decrease in the luminescence intensity due to non-radiative Auger recombination and background thermal radiation.

The PL spectra of samples with $x = 0.22$, that is, in the spectral region of the order of 10 µm, were obtained.

The authors found the broadening of the spectral line with increasing excitation power in 15-400 mW range. In addition, the dependence of the PL intensity on the temperature was investigated, and it was found that the intensity was increasing up to a temperature of $T = 27$ K, where it had a maximum, and then decreased again. Calculations showed that it was a relaxation of the wavevector conservation rule that was responsible for this effect.

Fuchs et al. [25] later performed more systematic study of carrier localization in narrow-bandgap ($x = 0.23$) p–type MCT grown by THM. The dependence of low-temperature PL on the excitation power was investigated once again. With pumping energy increasing, the spectral shape of the PL peak (which at low excitation represented a double-peak structure with an energy separation of 6 meV) more and more resembled one broad peak. This was explained by the fact that the effective mass of electrons in the material was small and the density of states in the conduction band was also small, so the phenomenon of band filling was observed even at a moderate excitation power.

An increase in the intensity of the PL was obtained with increasing temperature in the $T = 10$–30 K range. At higher temperatures the intensity decreased. The authors of [25] proposed a model describing recombination in MCT, which assumed radiative recombination of an electron-hole plasma without conservation of the wavevector. They underlined the importance of consideration of alloy disorder with its influence on the valence band density of states and minority carrier lifetime, especially at low temperatures. In their opinion, due to an energetic re-distribution of the heavy holes with varying temperature among the different parts of the density of states, the minority carrier lifetime becomes a function of temperature, assuming different non-radiative *e-h* (electron-hole plasma) recombination efficiencies for localized or extended hole states. They also believed that their results indicated the necessity of a better understanding of non-radiative recombination with full inclusion of the effects of alloy disorder, something, that to the best of the knowledge of the authors of this review has still not been done.

References [17-25] represented a body of works on PL in MCT published by the researchers at CNRS (France) and Fraunhofer Institute (Germany), independently or in co-operation. It can be said that they significantly contributed to the understanding of the origin of optical transitions in MCT, introducing and developing the idea of the strong effect of the alloy disorder on the PL spectra.

Kurtz from Sandia National Laboratories (USA) et al. [26] made an attempt to study PL from narrow-bandgap MCT more systematically. They studied quite

a few (in fact, twenty two) 'one of a kind' MCT samples grown by MOCVD and LPE on II-VI (CdTe, CdZnTe), GaAs, Si/GaAs and sapphire substrates. The intensities and FWHMs of the observed PL peaks varied vary broadly (in some samples, no PL signal could be observed at all). A low PL intensity (or its absence) was noted in un-annealed samples, relative to samples annealed in saturated Hg vapor to reduce mercury vacancy concentration. This was explained by the fact that mercury vacancies decrease the lifetime of charge carriers and increase the rate of non-radiative recombination. The PL peak observed in the spectra was interpreted by the authors as that due to interband transitions, in view of the matching of the values of the peak energy with the bandgap value obtained using optical transmission. The authors of [26] also compared the PL spectra of samples grown by MOCVD and LPE before and after annealing in Hg vapor. Before annealing, the dominating PL peak was broadened and shifted towards lower energies in respect to E_g, which indicated the dominance of recombination via a shallow acceptor associated with mercury vacancies. This made it possible to estimate the level of the acceptor E_A, which equaled 12 meV (above the valence band) for $x = 0.216$ and 19 meV for $x = 0.234$, consistent with other observations [10-13].

A large body of works on optical properties of MCT was published by the researches from Humboldt University in Berlin. One of their first works was published by Werner and Tomm in 1987 and represented an attempt to test PL as a tool for monitoring the lateral composition homogeneity of MCT samples [27]. The p-type samples with hole concentration ~10^{16} cm^{-3} were studied. They had $x \sim 0.33$ and were grown by THM from a Te-rich solution zone and by the Bridgman method from a near-stoichiometric melt. It was concluded that the registered PL spectra was due to interband transitions with k-conservation additionally broadened due to E_g inhomogeneity, where conservation of the wavevector was described by the well-known formula:

$$I(h\omega) \sim (h\omega - E_g)^{1/2} \exp\left(-\frac{h\omega}{k_B T}\right),$$

where $I(h\omega)$ is the luminescence intensity at the photon energy $h\omega$, and k_B is Boltzman's constant, while for relaxed k-conservation rule the square root is replaced by the power of 2.

A year later the same authors [28] discussed the nature of the PL peaks in MCT using the example of samples with larger composition, $x = 0.58$. Two lines were observed in the PL spectrum, separated by about 25 meV. The high-energy line corresponded to interband recombination. The low-energy peak, in view of its dependence on the energy and the nature of the excitation (cw or pulse), was attributed to the DAP transitions.

Gille et al. [29] carried out investigations of the PL of MCT samples with the composition $0.35 < x < 0.7$ grown by THM. The aim of the experiments was to find a relation between the chemical composition of the material as determined by electron microprobe, and the PL spectrum. As a result, the authors of [29] proposed an expression that related the photon energy from PL data and the composition, which they determined using an electron microprobe. This relation lead to the following $E_g(x)$ dependence at $T = 30$ K:

$$E_x(x) = -0.780 - 0.5909x + 1.9483x^2$$
$$+0.1087x^3 - 2.364x^4 + 1.212x^5.$$

It was argued that the derived dependence made it possible to determine the composition from PL measurements with high accuracy. In relation to PL spectra, the authors of [29] mostly observed a main high-energy peak, whose energy was close in value to E_g, as well as a low-energy peak, which arose at low temperatures. They were unsure of the exact nature of the high-energy peak, but believed that interband transitions without wavevector k conservation were promising candidates.

Werner et al. in their conference paper [30] reported on the results of PL studies of MCT samples with various x grown by THM. The PL spectra of samples with average composition $x = 0.58$ recorded at different excitation power values are shown in Figs. 6 and 7.

The authors believed that the high-energy peak A with energy ~720 meV (Figs. 6a and 6b) in these spectra corresponded to an interband transition, since its intensity strongly decreased with temperature decreasing, up to the point that it was invisible against the background of peak $B1$ (peak energy 707 meV, PL spectrum not shown) at low temperatures. The nature of low-energy peaks was not fully understood. Peak B (Fig. 6b) was attributed to the recombination of the bound exciton (BE), while peak $B2$ (Fig. 6a), to the c-A transition. Concerning peak $B1$ (not shown) it could be a donor-valence band (D-v) transition. Peak C (FWHM $\approx$ 30 meV) was attributed to the DAP transition, peak D (FWHM $\approx$ 90 meV), to the transition involving deep levels (Figs. 6c and 6d). These peaks were observed only in samples with high degree of electrical compensation.

In samples with a larger composition, $0.58 \leq x \leq 0.74$, peak $B1$ and its phonon replicas dominated at low temperatures. With temperature increasing, this peak gave way to peak A (interband transitions). Peak $B1$ in these samples was attributed to the emission of a bound exciton (BE). Samples with $0.22 \leq x \leq 0.58$ showed only a $B1$ peak at very low temperatures. It was found that the distance between peaks $B1$ and A, as well as the temperature, at which one peak transformed into another,
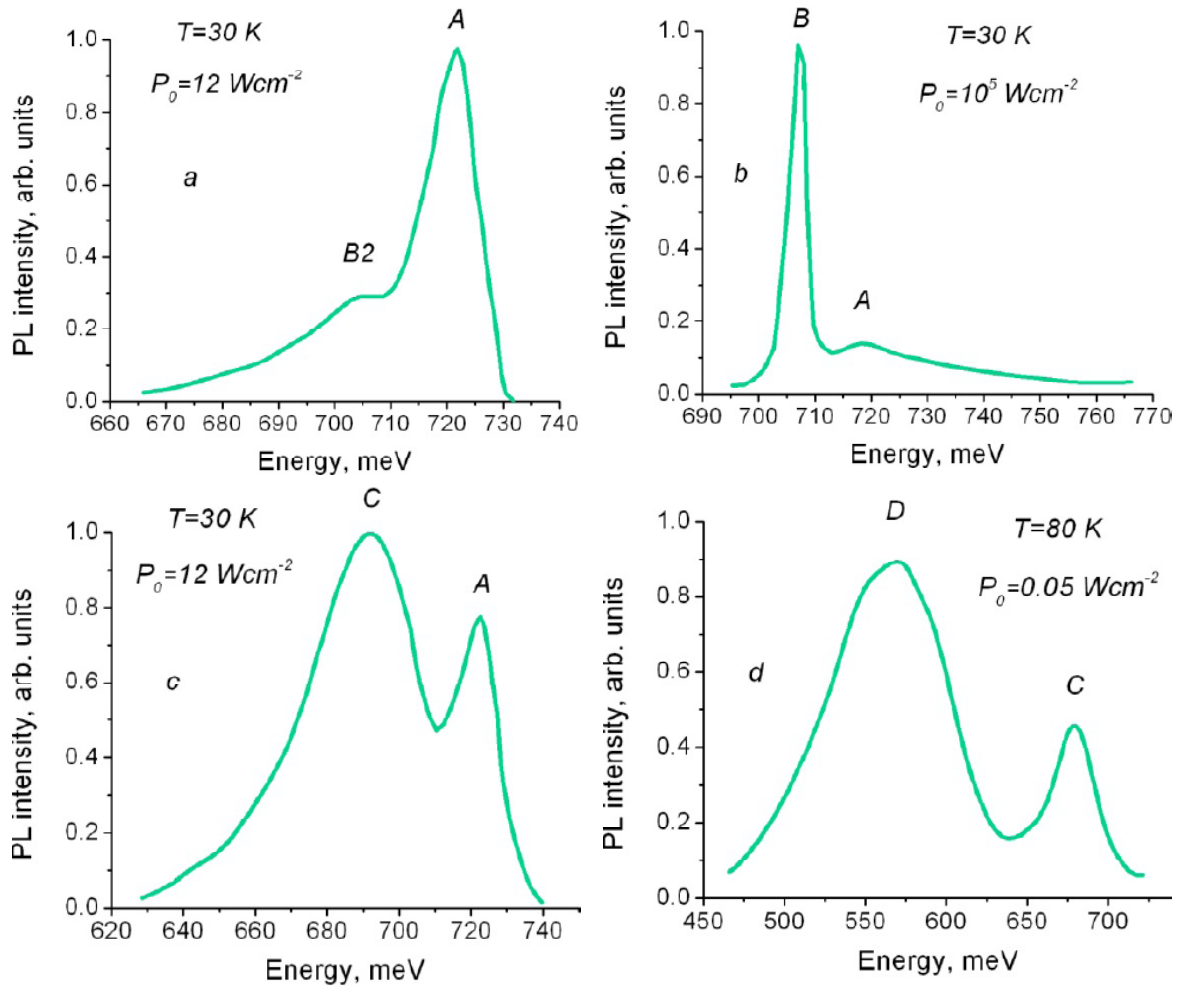
Fig. 6. PL spectra of MCT samples with $x = 0.58$ recorded at various temperatures and excitation power values (replotted using the data from [30,31]). Details of line designations are given in the text.
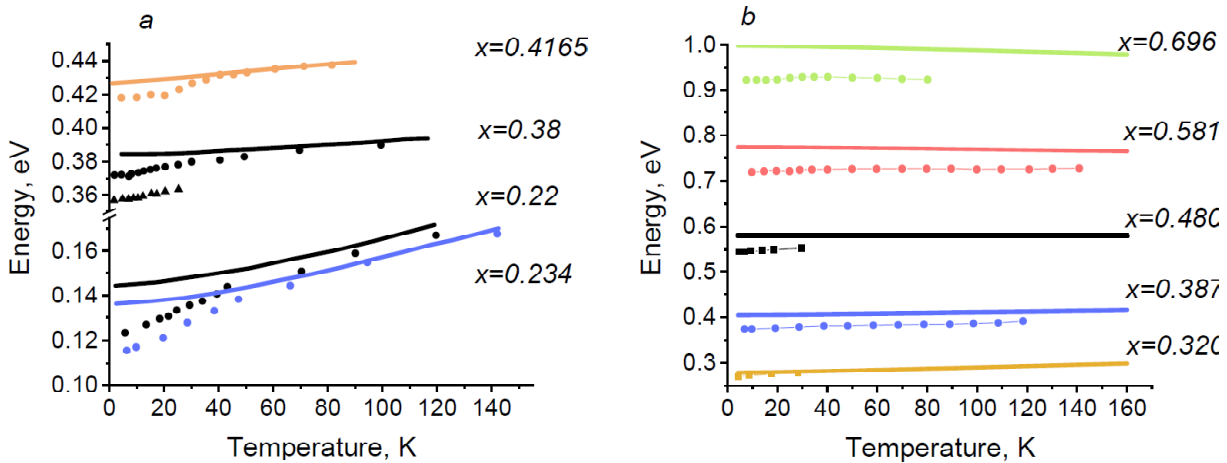
Fig. 7. Temperature dependences of PL peak energy for MCT with 'small' (*a*) and 'large' (*b*) CdTe content (composition *x*) (symbols) and calculated $E_g(T)$ dependences for corresponding *x* values (solid lines). The data for $x = 0.22$ and $x = 0.38$ is taken from [19]; $x = 0.234$, from [25]; $x = 0.4165$, from [37]; $x = 0.320$ and $x = 0.480$, from [10]; $x = 0.387$, $x = 0.581$ and $x = 0.696$, from [29].

linearly decreased with E_g decreasing. In a material with $x < 0.3$, these lines were not distinguishable.

The more detailed interpretation of these results was given by Werner et al. in a journal article devoted exclusively to the material with $x = 0.58$ [31]. In addition to PL

studies, the authors of [31] investigated the homogeneity of the alloy using transmission and reflection measurements. The phenomenon of emission re-absorption was established, and it was found that this reabsorption shifted peaks *A* and *B1* towards lower energies

by 2±1 meV and 3±1 meV, respectively. At high excitation energies, the authors found a wide tail of peak *A* on the high-energy side, which confirmed their assumptions about the interband nature of this peak. The interpretation for other peaks (*B*, *B1*, *C,* and *D*) also remained unchanged: peak *B1*, which replaced the interband peak A at low temperatures, was presumably related to a bound exciton or deep donors (acceptors); peak *B* appeared near peak *A* at $T > 30$ K and was attributed to the conduction band-acceptor (*c-A*) transition; peak *C* was attributed to DAP transitions, since it shifted towards lower energies with the decrease in excitation power or increase in time between the excitation and detection. Peak *D* appeared only at low excitation powers and referred to deep levels in the bandgap. Thus, a wide variety of radiative recombination channels were observed and clearly identified, the only exception being the high-energy peak whose character was not completely understood.

The idea of using PL as a tool for analyzing the value of the bandgap, the carrier lifetime, and the quality of heterointerfaces, as well as to monitor defects like inclusions in MCT was further developed by Tomm et al., when they investigated the optical properties of bulk MCT (grown by THM) and LPE-grown films [32]. The spatial distribution of the quantities mentioned above was investigated by applying the mapping technique that was well-known for III-V semiconductors. For epitaxial films, the influence of the interface between the substrate and the film on the optical properties of the samples was revealed, since these samples contained wide layers with variable composition associated with the diffusion of mercury. Also, stimulated emission from MCT with *x*=0.25 with FWHM below 1.5 meV was reported.

Schmidt et al. [33] described PL mapping of semiconductor MCT wafers, which was introduced by Tomm et al. [32], in a few more details. The maps of integral luminescence were studied at different powers of the exciting laser. It was found that at high excitation levels PL described the recombination in the material quite well, since the rate of radiative recombination did not depend on the degree of doping and on other external factors.

Herrmann et al. [34] discussed mechanisms of broadening of the transmission and PL spectra for MCT. In the transmission spectrum, broadening is understood as an exponential tail located below the absorption coefficient that corresponds to the interband transition. This broadening is called the Urbach tail, and is associated with the exciton-phonon interaction. The authors noted that broadening of the PL spectrum is usually attributed to the alloy disorder, regardless of what the high-energy peak of the

spectrum is associated with: an interband transition for smaller compositions or a transition associated with a free exciton for larger compositions. As a result of their own experiments, the authors of [34] concluded that broadening in MCT with small *x* occurs mainly due to temperature. For larger compositions, broadening became independent of temperature and was associated with the alloy disorder.

The same year (1990) Tomm et al. [35] published the first and the only one, to the best of our knowledge, detailed dedicated review on PL in MCT (a number of other materials, including HgMnTe and lead chalcogenides was also considered; some works on PL in MCT were also, as mentioned previously, briefly reviewed later in [5]). Tomm et al. concluded, once again, that for narrow-gap MCT the luminescence was dominated by direct interband transitions. Bound excitons were observed in wider-gap MCT and disappeared with composition decreasing. At low temperatures, bound exciton transitions took place and their phonon replicas were observed. Under these conditions, one could observe both external excitons associated with impurities and internal excitons localized on fluctuations of the composition.

The important factors were noted down in [35], that are still, at least in our opinion, hindering the systematic study of PL in MCT. The first one relates to the fact that investigated samples often very much differ with respect to parameters like type of conductivity, carrier concentration, and mobility. The excitonic lines are known to very sensitively react to these parameters due to screening. The other major problem with PL studies in MCT is the insufficient knowledge of the bandgap value for a given composition. The term "insufficient", when it relates to an uncertainty of 'just' about 10 meV, has to be compared with typical energies like the binding energy of a free exciton (electron plus heavy hole) of about 0.3 to 10 meV for $0.25 \leq x \leq 1$ (0.1 eV $< E_g < 1.6$ eV) or the ionization energies of hydrogen-like impurities which are of the same order of magnitude (possibly, with the exception of acceptors in wider-gap material). These small energies can be further reduced by screening due to larger carrier concentrations.

In relation to impurity luminescence in MCT, the data available at that time were very limited. In brief, optical transitions to very deep levels (130 meV) [14,36] and from a deep donor (110 meV) to valence band [16] were observed, as well as numerous transitions from conduction band to an acceptor state with E_A varying from 12 to 30 meV. As mentioned above, in a number of cases DAP transitions were observed. The review by Tomm et al. [35] also mentioned some early works on PL of MCT, including superlattices, grown by MBE, but since the material in question was grown in the course of the very first experiments on synthesizing MCT by this technique, the results obtained, in our opinion, currently do not bear much meaning. We shall consider the PL of MBE-grown MCT in

the second part of the review, which will be published later.

Herrmann et al. [37] described the results of the studies of MCT with $x = 0.4$. This composition, in the opinion of the authors of [37], was of special interest as it represented a point where optical properties that were dominated by exciton effects (in 'wide-gap' MCT) changed for those governed by interband transitions typical of narrow-gap material. Having measured the transmission spectrum, the authors of [37] obtained a small Urbach tail, so the effect of composition inhomogeneity was excluded from consideration. The PL spectra were recorded at $T = 5$ K. Spectra that were obtained from freshly etched samples contained typical exciton (BE) peaks with phonon replicas. At high excitation energies, delocalization effects took place, which manifested itself in a shift of the peak towards higher energies. Exciton localization energy was obtained as 8 ± 2 meV, and this number agreed with that determined by thermal delocalization and with the data obtained by Lusson et al. [19] and mentioned above (see Fig. 5).

When the same sample was examined after 5 months of storage, a decrease in the PL signal amplitude by an order of magnitude was obtained, and the position of the peak was independent of the excitation energy (which is typical of interband transitions). Also, low-energy peaks appeared in the spectrum. One of them was assigned to the hydrogen-like acceptor level, and the other, to the trap-to-band transition. In total, three acceptor levels were found and identified, first being the hydrogen-like acceptor with the energy level deduced from the three methods as 15 ± 2 meV, 16 ± 2 meV and 17 ± 1 meV, respectively. These values were supported by the transmittance spectra, whereas the acceptor character of this defect was proven with transport studies. The second acceptor energy was estimated from splitting of the main luminescence line and was seen from a transport data analysis. Its depth was about just 1.5 meV. Also, a 40 meV deep level was detected in PL, absorption and photoconductivity studies. It was also noted that in the temperature dependence of luminescence, there was a mixing of contributions from phonon replicas and various acceptors.

Herrmann and others [38] analyzed the nature of optical transitions in MCT in more detail. They noticed that in narrow-gap MCT ($x \sim 0.3$) both the excitonic binding energy and the excitonic oscillator strength scaled down with decreasing energy gap. As a consequence, free exciton became instable, excitons bound to different defects or impurities or localized in potential fluctuations became undistinguishable, and in the 'extreme' narrow-gap situation ($x \sim 0.2$), only a single broad line was present in the PL spectrum, which was usually attributed to k-conserving interband ('electron-hole

plasma') transitions. At the same time, in p-type samples with $x \sim 0.3$, the nature of the optical transitions appeared to depend on the doping (carrier concentration): at low carrier concentrations ($p \leq 10^{15}$ cm^{-3}) excitonic emission was the dominating process, whereas at high carrier concentrations ($p > 10^{15}$ cm^{-3}) interband transitions were dominating. In wider-gap MCT ($0.4 < x < 0.8$), the near-to-edge emission was due to localized intrinsic excitons trapped in potential wells due to alloy disorder.

Two years after they first addressed the problem of the PL line Urbach tail broadening mechanisms in MCT with $0.2 < x < 0.6$ [34], Herrmann et al. re-considered their results [39]. The two types of broadening remained in place: the one that depended on temperature and was related to the exciton-phonon interaction, and the other one that did not depend on temperature, and was associated with alloy disorder. The authors of [39] found that the constant broadening associated with the alloy disorder decreased with the decrease in the bandgap. At the same time, temperature-dependent broadening was characteristic of narrow-gap materials due to the predominance of interband transitions and a decrease in the probability of excitonic transitions. For $x > 0.35$, the temperature-independent broadening corresponded to the dominance of an exciton line in luminescence, where excitons were localized due to the presence of the Urbach tail, as was shown in absorption experiments.

Herrmann et al. also proposed a new model for the absorption coefficient in narrow-bandgap MCT, which considered both the band tails and the band filling [40]. Investigating the PL of MCT samples grown by THM and MBE methods, they obtained very similar spectral intensities; however, the FWHM of the PL spectrum for MBE-grown was significantly larger than that for THM-grown sample. Thus, the tail energy was higher for the epitaxial film (14 meV *vs* 2 mev in THM-grown sample as estimated by the authors of [40]). From this it followed that transitions with the participation of tail states dominated in PL of MBE samples. Still, the fact that PL intensities of the two types of samples did not differ appreciably, was indicative of the fact that the tail states (band-like as well as localized) did not contribute significantly to non-radiative recombination processes.

Tomm et al. [41] performed the study in an attempt to reveal the exact nature of exciton luminescence in narrow-gap ($x = 0.3$) MCT. Interestingly, in that study samples with comparable thermal delocalization energies of the localized intrinsic excitons trapped in disorder-induced potential wells exhibited very different magnetic-field-dependent localization. The reasons for this remained unexplained.

Fig. 7 summarizes some data on the temperature dependence of the PL peak energy obtained by various

authors (composition values are given according to original data, also note that different $E_g(T)$ relations were used in different works, in Fig. 7b the same $E_g(T)$ relation was used as in Fig. 1). As can be seen, in all cases the temperature range for the PL studies was limited to ~140 K. In all cases of narrow-gap MCT (Fig. 7a), as mentioned above, at very low temperatures the energy of the peaks E_{PL}, irrespective of their origin, was lower than calculated E_g values. The difference between E_{PL} of the highest-energy lines and calculated E_g was larger for samples with smaller x and reached ~20 meV at ~5 K for samples with $x \approx 0.23$.

Finally, in 1995 Tomm et al. published a paper, which summarized the achievements of the Humboldt University optics research group in the field of the study of excitonic effects and luminescence properties of MCT [42]. They presented the E_g dependence of the screening of the Coulomb interaction for a number of narrow-gap semiconducting materials, including MCT and lead salts, where the critical carrier concentration (Mott density) for the screening was roughly estimated by taking the ratio of the Debye length and exciton radius to be about 1.2 for a temperature of 10 K. The curve for MCT is given in Fig. 8, where the area below the curves is the excitonic range with respect to the screening criterion. The curves for the lead salts (not shown) appeared to be much lower than that for MCT with the same E_g value because their mirror-like band structure in fact results from the absence of a heavy hole band ('rock salt' structure) and consequently, from the absence of heavy hole excitons. For MCT, the heavy hole excitonic binding energy scales from the well-known value of 10 meV for CdTe to about 1 meV for MCT with $x=0.33$. Conversely, the exciton radius increases with the bandgap narrowing and reaches 27 nm for $x=0.5$ and 200 nm for $x=0.2$.
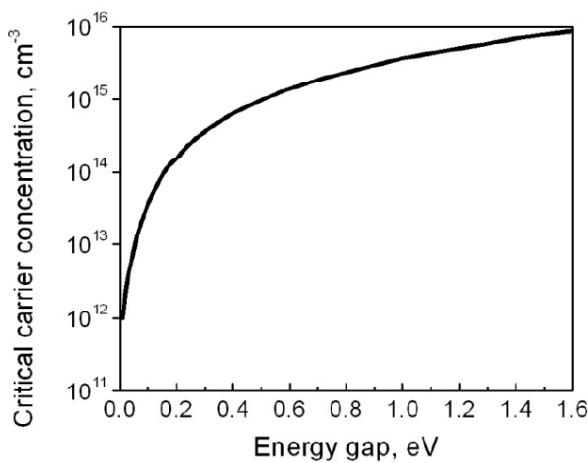
Fig. 8. Critical carrier concentration for exciton shielding as a function of the energy gap of MCT (replotted using the data from [42]).

The authors of [42] studied excitonic effects in MCT in a very wide composition range. Interestingly, they found that for a wide-bandgap material ($x=0.965$), which has an energy gap of only 5% less than that of CdTe, the PL spectrum looked very different from the well-known CdTe spectra. The MCT PL spectrum was dominated by localized intrinsic excitons, bound excitons (including acceptor-bound excitons) and LO phonon replica of the free exciton ground state as well as phonon replicas of the BE emission.

For medium-bandgap material ($0.4 < x < 0.7$) only one excitonic line followed by a number of LO phonon replica was observed. For CdTe mole fractions below 0.4 the LO phonon replica of the excitonic emission vanished. The excitonic character of the PL in this case was firmly established using FTIR PL-excitation spectroscopy and magnetophotoluminescence (MPL).

For narrow-gap MCT ($x < 0.30$) the authors of [42] analyzed in detail samples with the narrowest PL FWHMs (~ 5 meV) in high-quality bulk MCT with CdTe fractions below 0.3. For these narrow-gap samples they performed MPL measurements and gain spectroscopy study. It was noted that an excitonic contribution observed on the low-energy side of the PL lines was well described by exciton-phonon interaction.

The PL works by optics group at Humboldt University listed above were mostly performed using the material grown 'in-house'. Later in the 1990s, this group also performed a number of experiments on the material grown by metalorganic molecular beam epitaxy (MOMBE) at Georgia Tech Research Institute [43]. For a sample with $x=0.28$, at 6 K the FWHM of the single PL line constituted just 7.9 meV. The spectral shape was fitted with the Anderson model assuming a tailing energy parameter, E_{op}. The Urbach parameter, E_0, extrapolated to 0 K, was ~2.1 meV, which value was much smaller than the value of 4-6 meV typically found at the time for 'standard' MBE-grown films. The authors of [43] also analyzed the dependence of PL on the excitation power. An increase in the intensity and a shift of the PL peak toward shorter wavelengths with an increase in the excitation power indicated the band filling. As soon as the electrons filled the band, the exciton became screened due to the large number of electrons and holes, and the exciton binding energy became zero, so luminescence became associated with interband transitions.

Tran et al. [44] continued these studies and obtained a temperature dependence of the PL peak in 15-30 K temperature range. The position of the peak was found to correspond to the results of $E_g(x,T)$ calculations performed according to the Hansen model [45]. Investigation of the PL as a function of the excitation power suggested that at low temperatures and low excitation

powers, the emission had an excitonic nature. With excitation power increasing, interband transitions became dominating.

Summers et al. [46] performed a study of the optical and electrical properties of MCT grown by MOMBE and doped with iodine. For all investigated samples, the PL intensity of the doped samples exceeded that from un-doped reference samples with the same x value. At room temperature, an average increase of about 30% in intensity and a reduction of the FWHM of the PL spectra by about 10% compared to reference samples were observed. The authors of [46] believed that the reduction in the FWHM was mostly due to the absence of a shoulder on the low energy tail of the spectra, which shoulder in the unintentionally doped samples was assigned to contributions by screened hydrogen-like acceptor states.

Ravid et al. [47] studied PL of MCT film with $x=0.38$ grown by MOCVD. One of the studied samples was covered with a CdTe cap layer. The spectrum of the as-grown film at $T = 12$ K and an illumination power of 0.2 mW showed FWHM=31 meV, which, as the authors of [47] thought, was most probably caused by compositional non-uniformities and by band tail states. This FWHM value appeared to be much larger than the value of 17 meV reported for an as-grown MCT film with similar composition grown by LPE, indicating a much better uniformity and quality of the LPE-grown material. Using the temperature dependence of the peak energy of the PL line E_{PL} and the empirical expression for the energy gap given by Hansen et al. [45], a composition $x=0.387$ was obtained. Next, the authors of [47] used the well-known expression that relates E_{PL} with E_g and was mentioned above, which can be given in derivatives as $dE_{PL}/dT = dE_g/dT + \alpha k_B$, where $\alpha = 1/2$ and 2 for carrier recombination with and without wavevector conservation, respectively. From Hansen's expression it followed that $dE_g/dT = 0.12 \cdot 10^{-3}$ eV/deg, which yielded $\alpha = 2.9$. This implied that the transitions took place without wavevector conservation, indicating the presence of a high density of defect states near the band edges.

Kraus et al. [48] performed one of the first truly systematic studies of the PL of MCT samples grown by MBE. GaAs was used as a substrate. The authors of [48] presented the results of studying epitaxial films with $0.25 \leq x \leq 0.93$. In their studies, they observed only one peak in the PL spectra of all samples at $T = 4.2$ K. From a systematic comparison of PL and transmission properties Kraus et al. concluded that the PL properties over a wide range of temperature could be described by a model that took into account exponential band tails. Since the low-temperature PL peaks were below the absorption edge, the radiation was not related to the interband transition, so the authors believed that at low temperatures

PL originated in optical transitions from states in an exponential tail, i.e. in the fundamental bandgap. Significant contributions from states within the conventional conduction or valence bands were observed only at higher temperatures. When comparing the results of the PL investigation with those of the transmission studies, it was found that the PL peak shifted closer to the absorption edge with increasing temperature. This, and the increase in the peak FWHM with x increasing were associated with the effects of alloy disorder. Since the effective electron mass decreases with decreasing band gap, the maximum contribution to disordering shifts from the composition $x = 0.5$ to a higher value of x.

Starting from the early 1990s, Chinese researches begun to publish papers on growth and characterization of MCT, and PL studies were also performed. Since in this part of the review we limited ourselves to 1966-1996 timespan, we shall mention here only two very early works. Guo et al. [49] provided information on the PL of MCT grown by MBE on a CdTe/GaAs substrate; this was one of the first reports on good-optical-quality MCT samples grown by this technique on foreign substrates. The PL spectrum of MCT sample with $x = 0.284$ at 10 K demonstrated a strong emission peak at 227 meV with a FWHM=14.5 meV. This peak was attributed to interband transitions.

Variable-temperature (in the 4.2-115 K range) and excitation-intensity-dependent PL measurements have been performed on Sb-doped MCT with the emphasis on the impurity behavior of Sb by Chang et al. [50]. In addition to the observation of the localized exciton, acceptor-bound exciton, interband and bound-to-free transition-related PL lines, the Sb-doping-related acceptor level of about 30 meV above the bottom of the valence band at 4.2 K was obtained. Also, Guo et al. studied PL of a series of arsenic-implanted CdTe and MCT films with $x\sim0.4$ annealed at different temperatures [51]. They found that more arsenic ions could occupy the Te sublattice after the annealing at 450 °C compared to the annealing at 400 °C, and the acceptor level of As$^+$ in the Te sublattice for MCT with $x \approx 0.39$ was found to equal 31.5 meV.

Finally, we should consider results of PL studies in MCT obtained at Ioffe Institute. Unfortunately, some of the English translations of the original Russian papers published by the authors from this Institute can now be found only in libraries, since the early (up to 1997) issues of Soviet journals such as Soviet Physics – Semiconductors, Soviet Physics – Solid State, etc., are unavailable online (let us note that papers by Chinese authors published in Chinese in Infrared and Millimeter Waves journal and only abstracted in English are not reviewed here either).

One of the first works authored by the researches from Ioffe Institute on PL and cathodoluminescence in MCT (x=0.3) was published in 1978. In that work, Ivanov-Omskii et al. [52] observed that in the temperature range 17 to 77 K the luminescence spectra were independent of the method of excitation and consisted of two bands. The energy separation of the bands did not depend on the type of conductivity of the sample.

Later, the same group studied the MCT sample with similar composition but with a strong degree of electrical compensation [53,54]. The PL spectrum of this n-type sample was found to consist of three bands. An investigation was made of the behavior of the spectrum as a function of temperature, magnetic field, excitation rate, and a time between the end of excitation and detection. The DAP nature of the long-wavelength band in the spectrum was demonstrated. An analysis of the behavior of this band made it possible to determine the total ionization energy of a donor and an acceptor, where $E_A + E_D$ equaled 18-20 meV. The other two bands were suggested to arise from the annihilation of the exciton bound to a neutral acceptor.

When investigating the spectra and kinetics of the PL and photoconductivity of a similar sample at temperatures 4.2 and 15 K [55], the photoconductivity spectra were found to have singularities corresponding to radiative BE recombination lines. It was found that at 4.2 K the main photoconductivity relaxation mechanism involved formation of an exciton bound to a neutral acceptor with its subsequent radiative recombination.

It should be noted that at that time many researches were quite skeptical on the possibility of observing exciton luminescence in narrow-gap MCT. However, independent observations such as those by the group headed by Ivanov-Omskii and discussed here (see also [56]) for MCT with $x = 0.30$ and those by Tran et al. for MCT with $x = 0.28$ [44] confirmed the excitonic nature of the PL signal coming from narrow-gap MCT.

In 1984, the group headed by Ivanov-Omskii reported on observing low-temperature stimulated emission from n-type MCT crystals with $x \sim 0.3$ and electron concentration at 77 K of 10^{14} cm^{-3} subjected to optical pumping. The emitted radiation was due to BE radiative recombination [57]. The threshold of the stimulated emission appeared to be much lower than expected [58].

The presence of the acceptor level with energy ~30 meV, mentioned in some papers by other research groups [35,50], was confirmed for epitaxial MCT films grown from stoichiometric melts on CdTe substrate [59]. Also, a deeper level with energy of ~70 meV was found for this type of samples in PL experiments [60] (see also [56]). In the latter work, room-temperature PL from MCT samples was also detected.

Later, Ivanov-Omskii et al. [61] studied IR PL in MCT ($0.232 < x < 0.622$) in magnetic fields up to 6T. They found that for narrow-bandgap material ($x < 0.35$) the Zeeman effect (including spin-splitting) was pronounced quite well, and the PL line shift followed that expected for free-to-free transitions. For the wider-bandgap MCT ($x > 0.35$) BE PL dominated and only weak PL line shifts in magnetic field were observed. This again confirmed domination of excitonic luminescence in wider-bandgap MCT and interband character of the PL in the narrow-gap material. Note that MPL of the sample with x=0.23 was later studied by some of the authors of [61] in more detail [62], and it was concluded that for p–type samples (hole concentration $7 \cdot 10^{15}$ cm^{-3}) in magnetic field CHCC Auger process dominated, and not CHHL, typical of p–type material in zero magnetic field. The second finding in [62] was that higher sub-bands did not affect electronic spectra of the conduction band in narrow-gap MCT.

Bazhenov et al. [63] studied PL of p-type MCT bulk crystals with $x \approx 0.4$. The low-temperature PL spectra of these samples contained two lines, the low-energy line disappeared at $T > 63$ K. This line was interpreted as originating in band-to-acceptor transition with $E_A \sim 18$ meV. The high-energy line was identified as being due to interband transitions. The temperature-driven shift of this line agreed well with $E_g(x,T)$ expression by Schmit and Stelzer [64], which for this sample yielded $x = 0.46$. At $T = 300$ K, the value of the external quantum efficiency was estimated from the experiment as being equal to 0.12%, internal quantum efficiency, 13%.

Later, Bazhenov et al. [65] investigated quantum efficiency of the PL emitted from MCT in a composition range $0.4 \leq x \leq 0.74$. Only interband recombination was considered in the calculations. Calculated quantum efficiency showed a maximum at $x = 0.65$. The values of quantum efficiency determined from the experiment were much lower than those predicted by the calculations, which was indicative of the presence of the Shockley-Reed-Hall recombination centers in the material.

Georgitse et al. from the same group in their PL experiments performed on Bridgman-grown bulk MCT samples with $x = 0.61$ and $x = 0.69$ [66] observed two lines separated by ~21 meV. Later in the PL spectra of these samples they also found the third line, also separated by ~21 meV from the second, low-energy, line [67]. In sample with $x = 0.57$ only two lines were found. For a wider-bandgap sample, the high-energy PL line had a fine structure, containing in fact five narrow PL peaks. This line was interpreted as originating in recombination of an exciton bound to a deep acceptor, and the energy of the acceptor was estimated to equal ~70 meV. The other lines in the spectra were attributed to LO (CdTe sublattice) phonon replica of the exciton line.

Finally, Belotelov et al. [68] studied PL of boron-implanted MCT with x=0.38 and electroluminescence of *p-n* junctions fabricated with the implantation. Bulk material was used for the fabrication of *p-n* junctions. First, the authors of [68] studied the PL of the initial *p*-type material, for which purpose the implanted layer was chemically etched from the surface of the part of the structure. The hole concentration in this material equaled ~10^{16} cm^{-3}. At T=15 K, the PL spectrum of the material contained three lines. The high-energy line was identified as formed by interband transitions. Low-energy line was interpreted as originating in band-to-acceptor transition with E_A~18 meV. At high excitation level, a kink was clearly seen on the low-energy side of the band-to-band line, and this was explained by the presence of a shallow acceptor with E_A~5 meV. As to the implanted *n*-type layer (which had electron concentration ~10^{18} cm^{-3}), the authors of [68] were unable to detect PL signal from this material.

Before concluding this part of the review, we should once again emphasize that drawing some conclusions on the basis of all the works cited here presents a serious challenge not only because of different attitudes of different authors towards interpretation of their results, but also because of the strong inconsistencies of the properties of the material investigated in different studies. Obviously, the samples studied by different authors were grown by different methods, had different thermal histories (and, correspondingly, differed in conductivity type and/or carrier concentration), and were given different treatments before measurement. This could result in very different results obtained for nominally very similar samples, at least in application to electrical properties [8,69]; in optical studies, in addition to that, the presence of oxides and residues on the surface can be quite misleading [5,37,68]. Also, as mentioned above, there is also the uncertainty in determining the exact energy gap of MCT (see, e.g., [45,64,70,71]); this uncertainty is of the order of a few meV, which is larger than the exciton binding energy in MCT. Yet another factor is the uncertainty in the broadening of the luminescence lines, partly considered in some of the papers reviewed. As discussed, charge carriers and excitons can experience a randomly varying microscopic potential due to the stochastic distribution of Cd and Hg atoms on the cationic site, so a PL peak could be less or more broadened or shifted depending on the nature of the transition involved as well as the random nature of the MCT alloy at that composition [5]. This effect seems to be more pronounced in MBE-grown MCT as the material fabricated by an inherently non-equilibrium method [12].

The strong effect of alloy disorder on the PL spectra of MBE-grown MCT and the fact that modern MCT-based structures for IR detectors are typically based on complex multi-layer epitaxial structures grown by non-equilibrium methods such as MBE or MOCVD mean that by 2000 the era of the PL studies of 'pure' MCT was basically over. We can briefly summarize these results as follows:

1) High-quality MCT sample with a 'wide bandgap', which means CdTe molar fraction of at least 0.4, demonstrated at low temperatures PL spectra with localized exciton transitions, bound excitons, and phonon replicas of excitonic emission.

2) The data on samples with 'narrow-bandgap' ($x \leq 0.4$) are a bit divisive, some authors insisted on observing in these samples pure 'free-to-free' transitions, but in some experiments excitonic emission was clearly observed.

3) Optical transitions to acceptor levels were observed in numerous studies with the energy of the levels varying from 12 to 30 meV ('shallow acceptor'), equaling ~70 meV ('deep acceptor'), and, on some occasions, reaching 110-130 meV ('very deep level').

4) Donor-acceptor pair recombination was also observed on numerous occasions.

5) The spectra broadening due to alloy disorder was postulated and several models were developed, but in general no consensus was reached among the authors on how to process the spectra and extract corresponding parameters.

Still, in general the PL studies performed in the early years laid a very good foundation for the future studies of the properties of MCT, when the material would be grown by MBE or by MOCVD with interdiffused multilayer process (IMP). The PL results obtained on bulk crystals and LPE-grown films served as a solid reference point, when the quality of the newly synthesized material was for some reason questionable.

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