Enhanced photoluminescence from sub-wavelength crystallites attached to the fractured surface of cleaved host crystals, and the transfer of emitted light to the dark side of macroscopically thick absorbing samples of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ with $x = 0.2$ is reported. The conventional model based on Kirchhoff’s law of radiation is found to fail to describe the experimental photoluminescence line and its red shift relative to the optical absorption, and a more adequate novel theoretical model implying population inversion is proposed.

Keywords: $\text{CdMnTe}$, photoluminescence, optical absorption, electron microscopy, nanoparticles

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1. Introduction

$\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ solid solutions have been primarily synthesised for experimental verification of the concept of exchange interaction of Mn magnetic moments with electron and hole spins [1–7]. The discovery of giant Faraday rotation in these crystals invoked magneto-optical device engineering [8–12]. It triggered research in low-dimensional structures with magnetic ions [13–15] for nanophotonics and spintronics [16]. Besides magnetic interaction, cadmium substitution just by smaller-size Mn atoms brings about the crystal lattice contraction allowing for graded band-gap structure engineering for photoelectronic devices. Mn-related bands of high-energy photon absorption in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ also find applications in X- and $\gamma$-ray detectors [17].

One of the basic crystal parameters determining the spectral range of applications is the energy gap $E_g$ between the valence band top and conduction band bottom. As the lattice constant decreases nearly linearly, $a/\text{nm} = 0.647 - 0.0133x$ [18], $E_g$ is nearly linearly increasing with the Mn molar contents $x$. Attempts to deduce $E_g(x)$ from the optical absorption (OA) or photoluminescence (PL) spectral measurements indeed reveal nearly linear behaviour for $x < 0.4$. Above this value, PL line branch appears at 2 eV, independent of $x$, which is related to transitions between the excited and ground states of Mn ions [5, 19–23]. OA measurements also show $E_g(x)$ tending to saturate for $x > 0.4$, but at somewhat higher level of 2.15–2.25 eV, depending on lattice temperature [12]. At any value of $x$, the values of $E_g(x)$ deduced from OA and PL turn out to be different, and the origin of this difference is not clear.

OA coefficient $a(h\nu)$ measured as a function of photon energy $h\nu$ at the low-energy tail of the fundamental absorption edge is analysed conventionally using Urbach’s rule and Varshni formula [24], and $E_g$ is extracted as one of the five adjustable parameters depending on the Mn contents. Some of the adjustable parameters are formal, e. g. the “phonon energy”, which needs to be about twice as high as the highest-energy phonon mode in these
materials: LO phonon energy is about 24 meV in CdTe, and it does not change much with the rise of Mn contents [25].

Energy gap determination seems to be more reliable when the exciton-related peak of the absorption coefficient is resolved [26]. Nevertheless, the “true” energy gap value remains questionable as the OA tail and OA peak measurements give different $E_g$ values and the PL peak is red-shifted relative to that of OA.

The shift of the PL peak has been explained recently by the inverted population of states in a matter spatially confined to the sub-wavelength scale [27–29]. The self-organised confinement of light emitters to nanometre-scale clusters in the Cd$_{1-x}$Mn$_x$Te bulk was deduced earlier from the analysis of composition disorder and magnetic fluctuations [30].

This article reports on experimental observation of new effects in light interaction with Cd$_{1-x}$Mn$_x$Te crystals: PL enhancement by sub-wavelength crystallites attached to the fractured surface of cleaved host crystals, and the transfer of emitted light to the dark side of macroscopically thick absorbing samples of Cd$_{1-x}$Mn$_x$Te with $x = 0.2$. Theoretical PL line models and conclusions are presented below.

2. Experiment

Cd$_{1-x}$Mn$_x$Te crystals grown by the Bridgeman method with $x = 0.2$ were selected in order to have band-gap PL below the Mn atomic-level luminescence line (being at 2 eV). Samples were prepared for PL measurements by cleaving in order to get optically perfect surface area. However, at the cleaving instant, numerous different-size crystallites are produced attaching to the surface by electrostatic and magnetic forces (Fig. 1).

The smallest resolvable crystallite size is about 10 nm, and the largest crystallites observed are up to 1 µm size. At this piloting stage of the experiment, we have omitted the specification of a particular crystallite responsible for emission. We observed bright light outbursts when scanning manually the samples by the Ar laser beam. Focusing the beam allowed to select visually a single star-like emitter and to record its spectrum (Fig. 2).

3. Theory

The modelling of PL spectral distribution is conventionally addressed to van Roosbroeck and Shockley who published their theory of recombination radiation balanced in details with the light absorption in crystals [32]. In this model, radiation intensity is
\[ I(E) = D n^3 \kappa \frac{E^5}{\exp[E/(k_B T_{ef})] - 1}. \] (1)

Here \( E \) is the photon energy, \( D \) is the apparatus-related constant, \( n \) is the refraction index, \( \kappa \) is the absorption index, \( k_B \) is the Boltzmann constant, and \( T_{ef} \) is the effective temperature that not necessarily equals that of the crystal lattice. In other recipes (named after Stepanov or Kennard-Stepanov [33], or Kubo-Martin-Schwinger [34, 35]) the Plank's factor \( 1/\{\exp[E/(k_B T_{ef})] - 1\} \) in Eq. (1) is replaced by the Boltzmann or other universal function \( f(E, T) \). All the approaches rely basically on Kirchhoff’s law of thermal-equilibrium radiation, except for the explicit form of the universal function \( f(E, T) \).

Figure 3 illustrates the result of intensity calculation using Eq. (1) with the values of \( n(E) \) and \( \kappa(E) \) for \( \text{Cd}_{0.8}\text{Mn}_{0.2}\text{Te} \) as given by the complex dielectric function \( \varepsilon(E) \) deduced from reflectivity measurements in Ref. [31], supposing the effective temperature to be \( T_{ef} = 400 \text{ K} \). The adjustable effective temperature is conventionally attributed to the light-emitting ensemble (excitons, electron-hole gas, etc.); therefore, it is set high compared to the crystal lattice temperature. The choice of \( T_{ef} \), which enters the Planck’s factor only, affects the intensity spectrum slope and magnitude, and the peak position is determined by the dispersion of the refraction and absorption coefficients. As is seen in Fig. 3, this theory does not model the experimental PL line shape: the theoretical intensity maximum is practically at the position of maximum absorption, whereas the experimental PL peak is significantly red-shifted.

Further we will turn to an alternative concept [27–29]. Suppose that the particles interacting with light can be in two allowed states only: the ground one with the energy \( E_l \) and zero dipole moment, and the excited one with the energy \( E_m \) and a finite dipole moment. For the light energy absorption, the light-induced change of dipole moment needs to be in phase with the light electric field, whereas the acts of energy emission need the dipole moment change to be in opposite phase to the light electric field. The Schrödinger equation solution for perturbation by time-dependent electric field results in the oscillator-like contributions to the dielectric function,

\[ \varepsilon(E) = \varepsilon_\infty(E) + \frac{\beta_{lm}^2 N_l}{[(E_m - E_l)^2 - (E_l)^2] + i\varepsilon \Gamma_{lm}} - \frac{\beta_{ml}^2 N_m}{[(E_m - E_l)^2 - (E_l)^2] + i\varepsilon \Gamma_{ml}}, \] (2)

where \( \varepsilon_\infty(E) \) is the background dielectric function, \( \Gamma_{lm} \) is the joint level broadening parameter, and \( \beta_{lm}^2 \) is the coefficient controlled by the square matrix element of the dipole moment operator for the l-m transition. The values of \( \Gamma_{ml} \) and \( \beta_{ml}^2 \) for m-l transitions are here supposed to be the same as for l-m transitions, and \( N_l \) and \( N_m \) are the occupation numbers of the ground and excited levels.

Let the light absorbing/emitting matter be bounded in a sub-wavelength-size spheroid surrounded by a dielectric medium. A quasi-static approximation can be then used for finding the spheroid electric and magnetic moments [36]. The power absorbed or emitted by the spheroid electric dipole perturbation is [37]
\[ P = \frac{1}{2} \frac{E}{\hbar} \varepsilon_0 \varepsilon_M V \left( \frac{1}{L} \right)^2 \]
\[ \times \frac{\text{Im} \varepsilon(E)}{[\text{Re} \varepsilon(E) + \varepsilon_\infty \gamma_L]^2 + [\text{Im} \varepsilon(E)]^2} |E_0|^2. \] (3)

Here \( \varepsilon_\infty \) is the dielectric constant of matrix surrounding the spheroid, \( V \) is the spheroid volume, \( L \) is its depolarisation factor (e.g. \( L = 1/3 \) for the sphere), \( \gamma_L = (1/L) - 1 \), \( E_0 \) is the light wave electric field amplitude in the matrix. The matrix dielectric constant \( \varepsilon_M \) is not well defined for crystallites being at the air/crystal interface. The crystallite depolarisation factor is generally tensor [38] and its values can be influenced by the crystallite image in the host crystal. A similar complexity of factors has been considered by Berreman in his theory [39] of infrared radiation scattering on the rough surface of ionic crystals. The pits and bumps at the surface in that model have been concluded to act as sub-wavelength spheroids with the fractional values of \( \gamma_L \) giving rise to resonant distortions in the Reststrahl band.

By adapting these concepts for the visible light interaction with electronic oscillators, we compare here two simple cases of a spheroid being in air and that embedded in the host matrix. We take again the complex dielectric function \( \varepsilon(E) \) of \( \text{Cd}_{0.8} \text{Mn}_{0.2} \text{Te} \) as deduced from reflectivity measurements in Ref. [31] keeping the background component independent of whether the crystal is in normal or in excited state and inverting sign (when modelling emission) of the component of inter-band transitions. This model gives the PL line shape and peak position in good agreement with the experiment (Fig. 4).

Although Fig. 4 presents calculations for the particular (50 nm) size spheroid, the peak position according to Eq. (3) should remain insensitive to the size change as far as the spheroid remains essentially smaller than the light wavelength. Some variation of the peak positions can arise depending on the crystallite shape due to shape-dependent depolarisation factors. The crystallite size, i.e. the amount of light-emitting matter, controls the peak height. The calculated PL spectra have smaller widths compared to the experimentally obtained spectrum, and this question remains for future analysis including both the homogeneous and inhomogeneous broadening contributions.

As is seen in Eq. (3), for sufficiently small level broadening \( \Gamma_{\text{lm}} \to 0 \) and transparent matrix \( (\varepsilon_M > 0) \), the power absorption/emission is peaked at the condition of \( \text{Re} \varepsilon(E) = -\varepsilon_\infty \gamma_L \) that requires the value of \( \text{Re} \varepsilon(E) \) to be negative. For the normal population \( (N_l > N_m) \) the resonance (peak absorption) takes place at the photon energy higher than the inter-level distance: \( E_{\text{OA}} > E_m - E_l \). For the inverse population, the resonance (peak emission) takes the place at a lower energy side: \( E_{\text{PL}} < E_m - E_l \), i.e. The PL peak is red-shifted relative to that of absorption. Taking for absorption the population numbers of \( N_l = 1, N_m = 0 \), and for emission the values of \( N_l = 0, N_m = 1 \), respectively, and tending \( \Gamma_{\text{lm}} \to 0 \), one gets from Eq. (2) the value of \( \text{Re} \varepsilon(E) = \varepsilon_\infty \gamma_L \) this gives

\[ E_m - E_l = \sqrt{(E_{\text{OA}}^2 + E_{\text{PL}}^2)/2}, \] (4)

and the red shift, which is-

\[ \Delta = E_{\text{OA}} - E_{\text{PL}} = \beta \sqrt{\left( E_{\infty} + \varepsilon_M \gamma_L \right) \sqrt{(E_{\text{OA}}^2 + E_{\text{PL}}^2)/2}}. \] (5)
Although the band-gap $E_g = E_m - E_l$ and the red shift $\Delta$ evaluation require complementary experiments on absorption in crystallites instead of absorption spectrum of the bulk crystal$^1$, it is interesting to make at this stage tentative estimations based on Eqs. (4) and (5). Experimental OA and PL peak positions give the red shift, which is $\Delta = 31$ meV, and the oscillator strength measure for the conduction-valence-band transitions; it is $\beta_{cv}^2 = (0.88 \pm 0.34)$ eV$^2$, with the large error bar due to the uncertainty of $\varepsilon M_L$ values. The band-gap value for CdMnTe with Mn mole contents $x = 0.2$ is then $E_g \approx (E_{OA}^2 + E_{PL}^2) / 2 \approx 1.89$ eV.

4. Dark side lighting

Unexpected bright photoluminescence appeared also on the dark side of approximately 1-mm thick crystal. The absorption coefficient at the position of the PL peak is of the order of $1 \times 10^4$ cm$^{-1}$ (Fig. 4) ruling out the conventional transmission of light from the illuminated one to the dark side. It is likely that energy transfer to the dark side is mediated by magnetically interacting Mn$^{2+}$ ions.

5. Conclusion

The scanning electron microscopy of the cleaved Cd$_{0.8}$Mn$_{0.2}$Te crystals revealed multiple crystallites created at the crystal cleaving instant. The crystallites are quite tightly bound to the surface by electrostatic and magnetic forces. The SEM-resolvable crystallite size ranged to 10 nm. The scanning of the fractured surface with the Ar laser beam revealed the crystallites giving bright photoluminescence. The theory by van Roosbroeck and Shockley [32] based on Kirchhoff’s law of radiation, which is conventionally used in the PL line analysis, does not describe the red shift of PL relative to OA. The red shift, which is the most common feature in experimental PL observations, is in reasonable agreement with calculations based on the model suggested by Brazis [27–29] taking into account normal/inverted states of the sub-wavelength emitters/absorbers. The enhanced light emission and absorption by the fractured surface and particularly unexpected bright photoluminescence observed on the dark side of Cd$_{0.8}$Mn$_{0.2}$Te crystals are encouraging features for experimental research continuation aiming at a more controllable technology. The dark-side lighting relation to Mn$^{2+}$ challenges for experimental research in the whole range of Mn molar contents. In the more Mn-reach structures, the theoretical model will also need to take into account internal optical transitions in Mn$^{2+}$ competing with the transitions between the valence and conduction bands.

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References


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$^1$ OA peak position for Cd$_{0.8}$Mn$_{0.2}$Te, as shown in Fig. 4, has been determined in earlier experiments [31].
SKELTO PAVIRŠIAUS SĄLYGOTA CdMnTe KRISTALŲ FOTOLIUMINESCENCIJA

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Santrauka

Eksperimentiškai tiriant skelto Cd1-xMnxTe (x = 0,2) monokristalo paviršiaus fotoliuminescenciją nustatyta, kad švytėjimas sustipriša kiekvieną kartą, kai žadinantis Ar lazerio spindulys nutaikomas į kurį nors iš aibės kristalų, kuriais paviršius pasidengia skaldymo metu. Ryškus švytėjimas aptiktas ir tamsioje (nesužadinėtoje) pusėje, šviesai praėjus per storą neskaidrą kristalą. Elektroniniu mikroskopu paviršiuje buvo pastebėti kristalai didesni už dešimtį nanometrų. Parodyta, kad įprastinis fotoliuminescencijos modelis, pagrįstas Kirchhoff'o spinduliavimo dėsniu, neaprašo eksperimentinio spektro smailės raudonojo poslinkio nuo sugerties smailės. Eksperimentą paaškināna naujas modelis, grindžiamas dviejų lygmenų normalios ir atgrąžos užpildos teorija.