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Institute of Physics, Academy of Sciences of the Ukrainian SSR, Kiev[1]

Optical Properties of GaSe Crystals Containing Mn Impurity Atoms

II. Excitonic and Impurity Emission[2]

By

Yu. P. Gnatenko, Yu. I. Zhirko, and Z. D. Kovalyuk

The impurity band ($E_{\max} = 1.842$ eV) observed in photoluminescence (PL) spectra of GaSe : Mn crystals is demonstrated to be due to intracentre transitions of the Mn^{2+} ion. The energy of a zero-phonon transition ($E_{ZPL} = 1.928$ eV) and of optical phonons participating in the formation of the PL of the electronic-vibrational band is determined. Emission of excitonic polarons — ferronic states, resulting from a spin polarization of the electron and hole, included in the exciton, and of local antiferromagnetic-ordered magnetic moments of Mn^{2+} ions is observed at $T < 20$ K.

Показано, что наблюдаемая в спектрах фотолюминесценции (ФЛ) кристаллов GaSe:Mn примесная полоса ($E_{\max} = 1{,}842$ eV) обусловлена внутрицентровыми переходами иона Mn^{2+}. пределена энергия бесфононного перехода ($E_{БФЛ} = 1{,}928$ eV) и оптических фононов участвующих в формировании ФЛ электронно-колебательной полосы. При $T < 20$ K в спектрах ФЛ наблюдается излучение экситонных магнитных поляронов — ферронных состояний, обусловленных спиновой поляризацией электрона и дырки входящих в экситон и локальных антиферромагнитоупорядоченных магнитных моментов ионов Mn^{2+}.

1. Introduction

Intra-centre transitions for layered crystals were first observed in the absorption spectra of Ni-doped GaSe crystals [1]. Based on an analysis of the impurity absorption structure, the type of optical transitions was determined and data on the nature of the electronic-vibrational interaction for optical transitions of the Ni^{2+} ion were obtained.

Introduction of manganese ions into GaSe crystals gives rise to additional, to those of undoped crystals, broad emission bands in the region from 2.0 to 0.62 eV [2 to 4]. However, the nature of the bands, including the manifestation of intra-centre transitions of Mn ions in the emission spectra, remains unclear.

The EPR studies of Mn-doped GaSe crystals determined [5 to 7] that manganese, in the Mn^{2+} state, substitutes Ga^{2+} in lattice sites. At Mn concentrations from 0.1 to 0.5 wt% the behaviour of the EPR spectra with increasing temperature [7] is typical for a resonance absorption in antiferromagnets and associated with antiferromagnetic Mn inclusion in GaSe. A complex EPR spectrum of exchange-bound Mn^{2+} pairs located in adjacent Ga sites within a layer is observed at 20 K. Clusters for which the formation of excitonic magnetic polarons detected earlier in PL spectra of semimagnetic semiconductors of the

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[1] Prospekt Nauki 46, SU-252650 Kiev 28, USSR,

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$Cd_{1-x}Mn_xTe$ type [8, 9] is possible, emerge at the above-mentioned Mn concentrations in GaSe crystals.

The present study involves the investigation of low-temperature PL spectra of GaSe crystals doped (GaSe:Mn) and intercalated (GaSe⟨Mn⟩) with manganese with the aim of obtaining data

(i) on intra-centre transitions of Mn^{2+} ions,
(ii) on the nature of the electronic-vibrational interaction,
(iii) on the effect of the Mn impurity on the excitonic PL spectra.

2. Experimental

The GaSe crystals under study were grown by the Bridgman technique. The concentration of the impurity introduced by doping or by intercalation was within 1 wt%. For studying the PL spectra, samples were placed into a helium cryostat where the temperature was stabilized accurately to 0.1 K. The spectrum was recorded by a СДЛ-I spectrometer operating in the synchronous detection mode. Excitation sources were Ar^+ (2.41 eV), Kr^+ (1.92 eV) and HeNe (1.96 eV) lasers, reflection geometry making and angle of 30° to the crystal *c*-axis.

3. Experimental Results

Fig. 1 shows PL spectra (E_{excit} = 2.41 eV) of GaSe:Mn (0.5 wt%) at $T = 4.5$ K. The emission in the short-wavelength region of the spectrum (2.11 to 2.05 eV) is due to the radiative recombination of direct and indirect free and bound excitons, and the broad band with a maximum at 2.0 eV due to the presence of structural defects in the crystal [10]. An intensive broad band with a maximum at 1.842 eV in the case of undoped crystals containing impurities of iron group elements (Co, Ni, Cr, Fe) was not observed earlier in PL spectra [10].

A distinctive feature of these spectra, as against the PL spectrum of a pure GaSe, is the dependence of the energy of the direct free exciton emission line of the place of excitation on the crystal plane. Thus, regions of the GaSe:Mn crystals are observed where the energetic position of this line (I_{FES} line)³), $E = 2.1095$ eV (curve 3), coincides with the free exciton emission line for a good-quality pure GaSe crystal [11]. For some other crystal regions the excitonic PL line position is shifted to the long-wavelength side (curves 1 and 2). The maximum shift corresponds to $E = 2.1081$ eV (I_{LES}-line). A similar shift shows up also for PL lines of direct bound excitons.

At Mn concentration below 0.1 wt% the energy of PL lines of free and bound excitons corresponds to undoped crystals and is independent of the place of excitation. In this case the PL intensities of the "defect" band at $E = 2.0$ eV and of the impurity band at $E = 1.842$ eV are weak as against the emission in the excitonic region of the spectrum.

The energetic shift of the I_{LES}-line to the long-wave side is accompanied by growing intensity of the "defect" band with $E = 2.0$ eV and the impurity band with $E = 1.842$ eV. This indicates that the Mn impurity at concentrations ≥ 0.5 wt% is inhomogeneously introduced into the GaSe crystal with formation of impurity clusters and structural defects. For establishing the nature of the impurity band with $E = 1.842$ eV it is essential to note

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³) The following designations are used in this paper: I_{FES} — direct free exciton emission line; I_{LES} — localized direct exciton emission line.

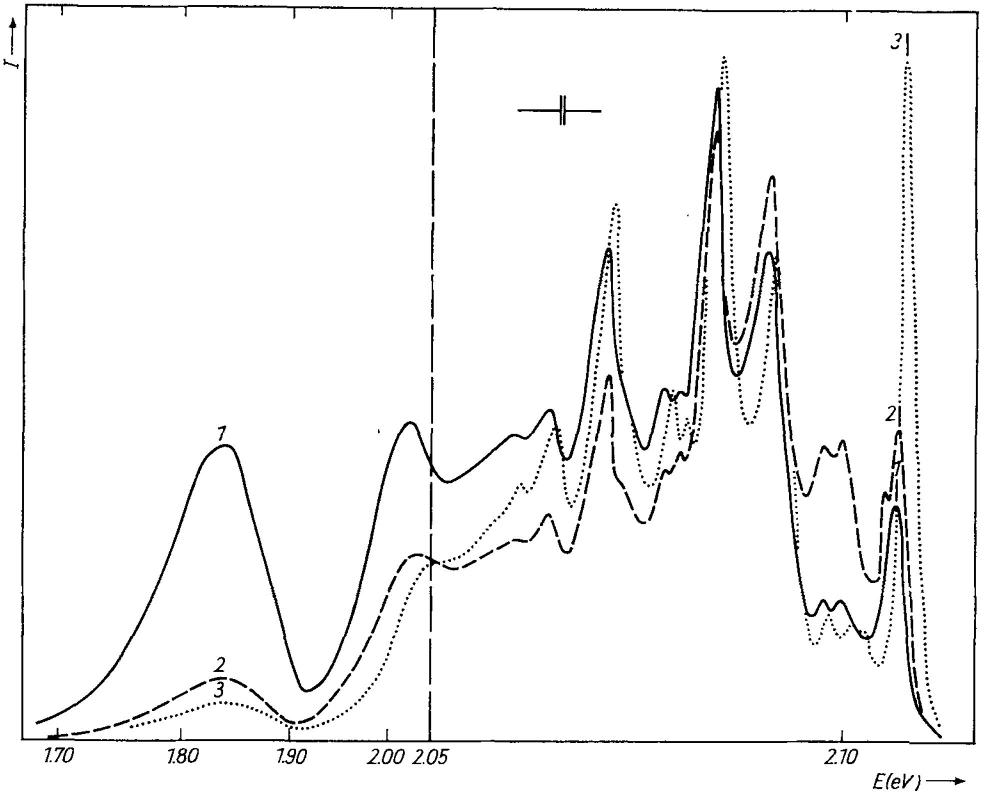

Fig. 1. PL spectrum of GaSe:Mn (0.5 wt%) crystals at $T = 4.5$ K from different crystal regions

that this band is observed in the PL spectrum at excitation with a HeNe laser ($E_{\text{excit}} = 1.96$ eV). For excitation with a Kr^+ laser ($E_{\text{excit}} = 1.92$ eV) no impurity band shows up in the PL spectrum. The investigation of the luminescence excitation spectra of the impurity as well as absorption spectra reveals on the background of band-to-band transitions a weak structurless band with maximum located in the region of 2.0 eV.

3.1 Impurity emission in GaSe : Mn crystals

The experimental results evidenced that the formation of the impurity band is directly associated with the introduction of the Mn impurity into GaSe. Mn doping of A^2B^6 semiconductor compounds (e.g. ZnTe [12], CdTe [13]) gives rise to an intensive band stemming from intra-centre transitions of Mn^{2+} in the 2.0 eV region, in the PL spectra. The energy of the PL impurity band in GaSe:Mn crystals ($E = 1.842$ eV) allows to infer that it results from a radiative recombination between the excited ${}^4T_1({}^4G)$ and the ground ${}^6A_1({}^6S)$ states of the Mn^{2+} ion [14].

Fig. 2 demonstrates the PL spectrum of the impurity band at $T = 4.5$ K, excited by a light from the transparency region of GaSe crystal ($E_{\text{excit}} = 1.96$ eV). On the high-energy side of the band one can see an equidistant phonon structure spaced at 8.0 ± 0.3 meV. The half-width of the impurity band shown in Fig. 2 is $H = 98$ meV, whereas for the case shown in Fig. 1, $H = 106$ meV. This indicates different degrees of inhomogeneous

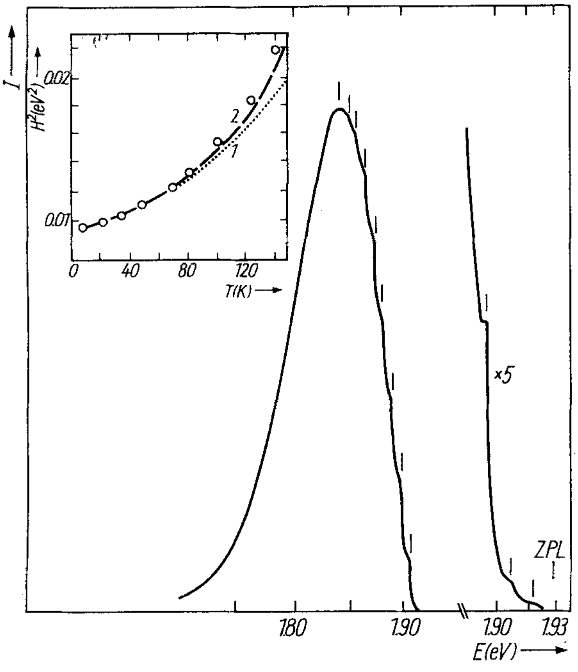

Fig. 2. PL spectrum of the impurity band of GaSe : Mn (0.5 wt%) crystal at $T = 4.5$ K. Insert: temperature dependence $H^2(T)$; open circles experimental data, (1) according to (1), (2) according to (2).

broadening of the impurity band in different crystal regions. Open circles in the insert of Fig. 2 represent the temperature dependence of $H^2(T)$. The thermal broadening of the electronic-vibrational band half-width is given by the semi-classical expression [13]

$$H^2(T) = H^2(0)\,\mathrm{cth}\,\frac{h\nu}{2kT} + H_{\mathrm{in}}^2\,, \tag{1}$$

where the ground and excited vibrational frequencies are equal $\nu_g = \nu_e = \nu$, and H_{in} is the inhomogeneous broadening. In the insert of Fig. 2 curve 1 gives the fit to the PL data in terms of (1). In the temperature range below 70 K curve 1 with the following parameters: $h\nu = 7.69 \pm 0.5$ meV, $H_{\mathrm{in}} = 74$ meV, $H(0) = 64$ meV, agrees fairly well with experimental values of $H^2(T)$. Note that the 7.69 meV vibration practically coincides with the half-layer optical 7.44 meV mode of pure GaSe crystal [15] and with the maximum at 9.3 meV in the low-frequency region of the one-phonon density of states in this material [16]. The large values of H_{in} and the Huang-Rhys coupling constant $S = 11$ ($H(0) = 2h\nu(2S\ln 2)^{1/2}$ [17]) made it impossible to observe the zero-phonon line (ZPL). In this case the energy of ZPL may be estimated as $E_{\mathrm{ZPL}} = E_{\mathrm{em}} + Sh\nu = 1.928 \pm 0.005$ eV, where E_{em} is the energy of the impurity band PL maximum and $Sh\nu$ is the energy shift of the impurity band in absorption and PL spectra with respect to E_{ZPL}[18]. The observed discrepancy between curve 1 and PL data for temperatures above 70 K (Fig. 2) may be attributed to the participation of one more phonon as it happened in real crystals.

To describe the electronic-vibrational band broadening processes with participation of more than one phonon, the above relation (1) can be presented in the following form:

$$H^2(T) = H_0^2(0)\prod_{j=1}^{n}\mathrm{cth}\,\frac{h\nu_j}{2kT} + H_{\mathrm{in}}^2\,. \tag{2}$$

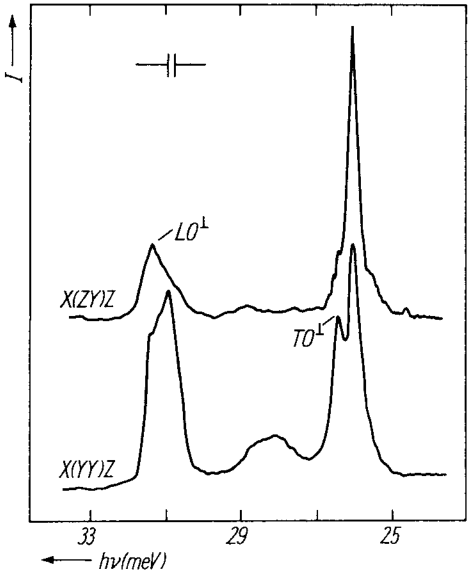

Fig. 3. Polarized Raman scattering spectra of GaSe : Mn(0.5 wt%) crystal at $T = 300$ K in right-angle geometry ($z \parallel c$-axis), $E_i = 1.92$ eV

The most adequate agreement between values calculated with (2) and experimental values of $H^2(T)$ was obtained for phonons with energy $h\nu_1 = 7.69$ meV and $h\nu_2 = 28.5$ meV. The broadening of the electronic-vibrational PL band versus temperature with the participation of the two above-specified phonons, calculated with (2), is shown in the insert of Fig. 2 (curve 2). As seen, curve 2 much better than curve 1 coincides with experimental values in the region of $T > 70$ K. In order to obtain additional data on the nature of the electronic-vibrational interaction in GaSe : Mn crystals, the study included an analysis of the vibrational spectrum of this crystal.

Substitution of Ga^{2+} ions by Mn^{2+} ions will result in a change both of the volume and reduced mass of the unit cell, i.e. in the emergence of local modes as in $GaS_{1-x}Se_x$ crystals [15, 19]. The frequency of the local mode for a one-dimensional binary (AB) chain containing light substitutional impurities C at $x = 0$; 1 [20] is $h\nu_{loc}^2 = h\nu^2(\mu_{AB}/\mu_{AC})$, where μ_{AB}, μ_{AC} are reduced masses of the host and impurity unit cells and ν is the frequency of the TO-phonon of the host. An additional confinement imposed on local modes in layered crystals [21] is that these vibrations should be polarized in the plane of the crystal layers, i.e. for GaSe should have E symmetry. Thus, interlayer vibrations of E symmetry, $E^{\parallel 2} = 7.44$ meV and $E^{|3}(TO_\perp) = 26.4$ meV, for which at isovalent substitution $Mn^{2+} \rightarrow Ga^{2+}$, in accordance with the requirements of [20, 21], local modes $h\nu_{loc} = 8$ meV and $h\nu_{loc} = 28.3$ meV, respectively, emerge, should be separated from the vibrational spectrum of the ξ-GaSe crystals.

Polarization studies of Raman scattering spectra of GaSe crystals containing various defects as well as iron group (Ni, Cr, Co, Mn) impurities (Fig. 3) allow to conclude that the observed additional structures in the regions of 28.5 and 30.75 meV are associated with defects of crystal layers. We note that these vibrations are polarized only in the plane of the crystal layers. The vibration with frequency 28.3 meV is also observed for γ-GaSe crystals with a high content of defects [22] in the same $Y(XX)\,Z$ geometry.

3.2 Excitonic emission in GaSe : Mn crystals

It should be believed that the observed long-wavelength shift of the emission line of a direct free exciton at $T = 4.5$ K (Fig. 1) for GaSe crystal regions with higher Mn content is associated with a radiative recombination from localized excitonic states (LES).

The long-wavelength shift of excitonic PL lines for GaSe crystal regions with ordering of Mn^{2+} ions may also be due to the existence of an exchange interaction between spins of electron and hole bound in the exciton and localized magnetic moments of Mn^{2+}, i.e. to the magnetic polaron effects for the LES. These effects were earlier detected for excitons bound to point defects in semimagnetic semiconductors of the $Cd_{1-x}Mn_xTe$ type [8] (in this case the exchange interaction with the participation of electron and hole coupled with a point defect, is also taken into account). Since formation of regions with antiferromagnetic ordering of Mn^{2+} ions is characteristic of GaSe:Mn (0.5 wt%) crystals [7], the polaronic effects should in this case be regardered as formation of ferrons, first proposed for antiferromagnetic semiconductors [23]. The exchange interactions between spins of carriers and localized magnetic moments of Mn^{2+} ions results in ferromagnetic ordering in antiferromagnetic regions of the GaSe:Mn crystal within a crystal sphere determined by the Bohr radius of the exciton localized on defects.

Fig. 4 shows temperature dependences of energy and half-width of I_{FES}-lines (curves 1 and 1′) and I_{LES}-line (curves 2 and 2′) for GaSe:Mn (0.5 wt%) crystals. As is seen, the temperature dependences exhibit a qualitatively different behaviour. For the I_{FES}-line the shape of the temperature dependence is the same as for a pure GaSe crystals. For the I_{LES}-line in the range of $T = 4.5$ to 20 K a shift to the short-wavelength region is observed, and at further temperature increase the shift occurs in the same manner as for the I_{FES}-line, but the slope is somewhat smaller. The temperature dependences of a half-width $H(T)$ of these lines differ as well. The $H(T)$ dependence for the I_{FES}-line at $T > 30$ K saturates, whereas for the I_{LES}-line a broadening first occurs up to 15 K and at 15 to 25 K the $H(T)$ dependence has a plateau, a further temperature increases is accompanied by a large broadening.

The degree of magnetic ordering due to spin correlations of carriers and Mn^{2+} ions, and hence also the change in the energy of excitonic states, are strongly temperature dependent. This gives rise to a high-energy shift of excitonic PL lines with increasing temperature. For crystal regions with smaller impurity concentrations no high-energy shift of the I_{FES}-line at $T < 20$ K is observed. The LES energy with respect to free exciton states is determined by the relative shift of the I_{LES} and I_{FES} PL lines. The temperature dependence of such a shift, Δ_{LES}, (insert of Fig. 4), is a nonmonotonous function. The decrease of the Δ_{LES} value in the $T < 20$ K range, as noted above, is associated

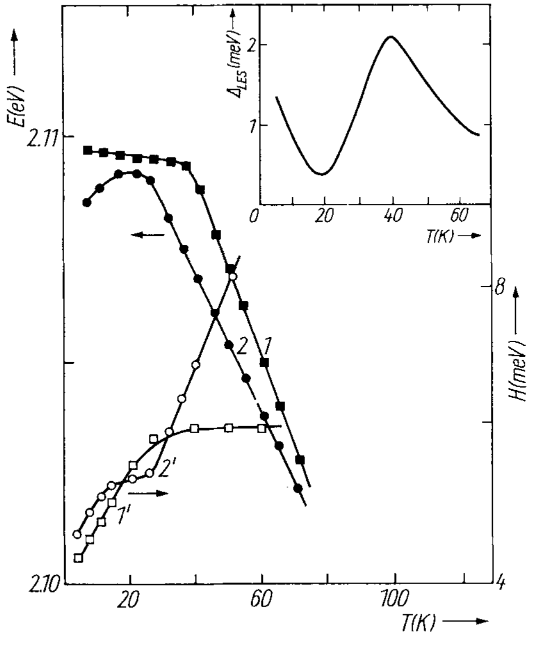

Fig. 4. Energy shift (curves 1 and 2) and broadening (curves 1′ and 2′) with increasing temperature of PL lines corresponding to (1), (1′) emission of a free exciton (I_{FES}-line) in pure GaSe and (2), (2′) of a localized exciton (I_{LES}-line) in GaSe:Mn crystals. Insert: temperature dependence of Δ_{LES}

with a ferronic state for the LES. The behaviour of the $\Delta_{\mathrm{LES}}(T)$ dependence in the $T > 20$ K range calls for an analysis of the specific features of migration of LES excitations, conducted in [24] for the case of semiconductor solid solutions.

According to [24] the probability of excitation transfer between LES exceeds that of their radiative recombination, and therefore, the emission occurs from the long-wavelength wing of the LES density tail. The efficiency of migration of the excitation between LES depends on the density of states, the temperature, and the level of excitation. At $T = 4.2$ K the LES thermalization, as demonstrated for semimagnetic semiconductors $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ [25], is not complete, and localization of excitons proceeds at a higher rate than for nonmagnetic solid solutions which is associated with the influence of the magnetopolaronic effect on the localization process. Because of this, an additional localization of LES for GaSe : Mn crystals, which is due to the formation of ferronic states in them, occurs mainly for LES with a low localization energy, exhibiting a high density of states.

At temperature increase above 25 K the ferronic state for LES is destroyed, which promotes the increase of the spectral diffusion speed. The increase of the Δ_{LES} value, observed in the temperature range 20 to 40 K, is therefore caused by an increase in the LES excitation migration speed and their full thermalization sets in with the emission of interlayer – flexural and optical – vibrations. A smooth decrease of Δ_{LES} (similarly to that in solid solutions $\mathrm{Zn}_{1-x}\mathrm{Cd}_x\mathrm{S}$ [24]) at higher temperatures is associated with the fact that processes with absorption of low-frequency interlayer vibrations become active in processes of migration of the LES excitations, i.e. the excitations are transferred from deep to more shallow LES.

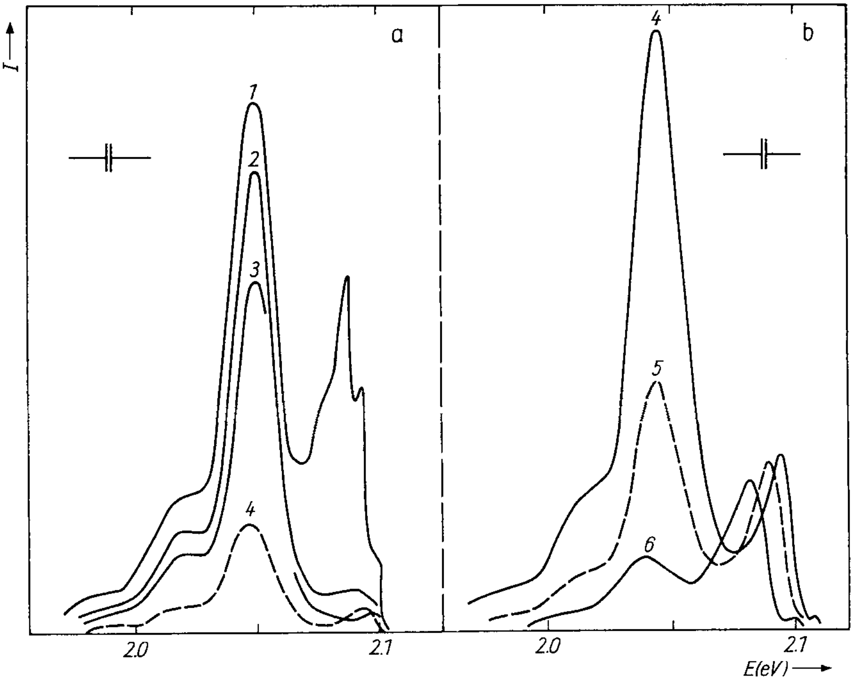

Fig. 5. PL spectra of GaSe⟨Mn⟩ crystal at (1) T = 4.5 K, (2) 20, (3) 30, (4) 45, (5) 60, and (6) 80 K. Curves 4 to 6 in b) ar shown with fivefold magnification

3.3 Emission of localized excitons in GaSe⟨Mn⟩ crystals

Introduction of impurity atoms by intercalation results in a severe distortion of the crystal lattice, which is evidenced by the absence of the emission line of direct free excitons in the PL spectrum at $T = 4.5$ K as well as by a large broadening of the emission lines of bound excitons (Fig. 5). Intense PL bands in the region of 2.066 to 2.0 eV are due to a radiative recombination of indirect localized excitons. Formation of such LES was earlier observed for rare-earth ion-doped GaSe crystals [26]. The PL band of indirect LES for GaSe⟨Mn⟩ occurs at longer wavelengths and is markedly broadened, which evidences a strong distortion of energy bands and an inhomogeneous broadening. The additional structure at the long-wavelength wing of indirect LES is its TO- and 2 TO-phonon replica. Possible structural defects arising at the distortion of GaSe crystals are dislocations.

At temperature increase above 30 K (Fig. 5) the PL intensity of indirect localized excitons declines drastically and at $T \geqq 60$ K a direct free exciton and its phonon replica start manifesting themselves. The energetic position of the maximum of the PL line of a direct free exciton at $T = 60$ K indicates that this line is due to the LES emission. The observed temperature redistribution of PL intensities between direct and indirect LES stems from the resonant between the direct excitonic state and the indirect conduction band [27].

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