PECULIARITIES OF EXCITON AND EPR SPECTRA OF 2H-PbI_2 LAYERED CRYSTALS WITH HIGH CONCENTRATION OF Mn IMPURITY

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Recent results on the study of exciton and EPR spectra of PbI_2 layered crystals of the 2H polytype doped with a high concentration of the Mn impurity are discussed. The anomalous temperature shift of the exciton band $n = 1$ is found and explained by means of anharmonic vibrations of the layered lattice at T<40 K and low-frequency optical phonons at T>40 K. It is shown that single Mn^{2+} ions cause six weak lines, while exchange-bound Mn^{2+} ions cause the intense broad line in EPR spectra.

1. Introduction

Semiconductors with ferro-group transition ions are of particular interest. They can reveal spin effects and thus are promising materials for the application in spintronics [1, 2]. However, contrary to the case of diluted magnetic semiconductors on the basis of traditional II—VI and III—V compounds, a much less attention has been paid to highly anisotropic layered crystals.

The effect of the Mn and Cr impurities with a concentration of $\sim 10^{18}$ cm^{-3} on the exciton and impurity spectra of BiI_3 layered crystals was considered in [3—6]. It was found that Mn and Cr atoms are incorporated into the crystal lattice as Mn^{2+} and Cr^{3+} ions that replace Bi^{3+} ions at their sites. They cause the broadening of three-dimensional (3D) and quasi-surface exciton bands and lead to the appearance of two new photoluminescence bands (1.1 and 1.83 μm). The EPR spectra of CdI_2 and PbI_2 single crystals with low concentrations of the divalent V, Mn, and Cr impurities were measured comprehensively as functions of temperature in [7]. It was found, in particular, that the ligand hyperfine interaction is different for Mn impurities in two above lattices. This may be attributed to different covalent bonds due to a local distortion of MnI_6 octahedra. The low-temperature spectral studies of exciton and phonon states in $Pb_{1-x}Mn_xI_2$ layered crystals were presented in [8]. It was shown that the samples under study belonged to the 4H-polytype. In these crystals, the giant amplification of the interband Faraday effect was also detected [9] and explained in the framework of the model of exchange interaction between optically excited charge carriers and the spin subsystem of Mn^{2+} ions.

Among about 30 polytypes of lead iodides, the simplest and most commonly encountered one is the hexagonal 2H-polytype (a= 4.557 Å; c= 6.979 Å). It may serve as a very good model object, because its unit cell contains only one sandwich consisting of three-layer packets I—Pb—I. Unfortunately, 2H-PbI_2 layered crystals doped with Mn have not been investigated so far. Such investigations are intriguing to a certain extent. On the one hand, these crystals belong to the same D_{3d}^3 space group as MnI_2 [10]; on the other hand, the Mn^{2+} ion radius (0.91 Å) is smaller than that of Pb^{2+} (1.26 Å). Therefore, manganese can easily replace lead at its sites in the host matrix.

This paper is devoted to the investigation of excitons and EPR-centers in 2H-PbI_2 layered crystals with a high concentration of Mn impurities.

2. Results and Discussion

PbI_2 crystals (2H-polytype), undoped or containing of about 10 wt. % Mn, were Bridgman-grown. The samples with mirror surface and optical $\boldsymbol{C}$ axis perpendicular to the cleavage plane were cut off from a bulk crystal in air with a blade. The special precautions have been taken to avoid any deformation. The exciton reflection spectra (at light polarization $\boldsymbol{E} \perp \boldsymbol{C}$) were recorder with an automated setup [11] in a temperature range from 5 to 200 K. The energy resolution was better than 0.5 meV. The relative error of the measurements of reflection spectra did not exceed 3%. Temperature was stabilized

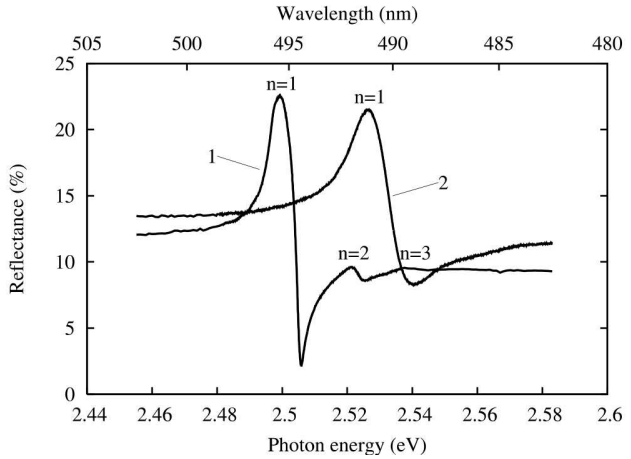

Fig. 1. Exciton reflection spectra of pure (curve *1*) and Mn-doped (curve *2*) PbI_2 single crystals; $T = 5$ K, $\boldsymbol{E}\perp\boldsymbol{C}$

with accuracy of ±0.1 K. The EPR spectra were measured with a radio spectrometer "Radiopan" at a frequency of 9.0818 GHz. The error of the g-factor determination did not exceed 10^{-4}.

The typical exciton reflection spectra of 2H-PbI_2 and 2H-PbI_2(Mn) layered crystals (at T= 5 K and $\boldsymbol{E}\perp\boldsymbol{C}$) are shown in Fig. 1. One can see that the introduction of the Mn impurity into the crystal lattice causes a considerable high-energy shift of the exciton oscillation $n = 1$, its broadening, and the disappearance of the $n = 2$ and $n = 3$ exciton excited states. Since the base exciton oscillation of the doped sample is located between the exciton bands of undoped 2H-PbI_2 and MnI_2 crystals [12], we can conclude that the reason for this shift is the formation of a $Pb_{1-x}Mn_xI_2$ ($x \approx 0.1$) solid solution.

The influence of temperature on the energy position E_{ex} and the half-width H of the exciton band $n = 1$ of both crystals is presented in Fig. 2. One can see that the anomalous temperature dependence $E_{ex}(T)$ takes place for both undoped and doped crystals. It increases at $T<$ 40 K and decreases at $T>$ 40 K with approximately the same coefficient dE_{ex}/dT (given for the above temperature regions in Table 1). This temperature behaviour of $E_{ex}(T)$ can be explained on the basis of the essential influence of both anharmonic vibrations of the layered lattice (starting at a low temperature) and low-frequency optical phonons (starting at higher temperatures) [4].

The half-width of the exciton band demonstrates also the unusual temperature broadening. It practically does not change at $T<$40 K and increases nonlinearly at $T>$40 K. When determining the phonon energy, we made efforts to describe the temperature behaviour of

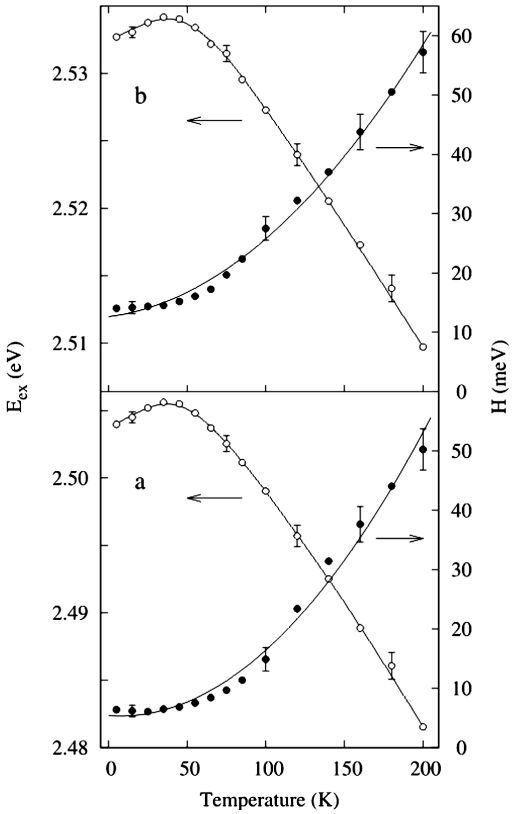

Fig. 2. Temperature dependence of the energy position of the ground-state exciton absorption band (open points) and its half-width (solid points) of 2H-PbI_2 (*a*) and PbI_2(Mn) (*b*) layered single crystals. Fitted curves $H(T)$ are calculated from Eq. (1)

the half-width on the basis of the known theoretical expressions for $H(T)$ in the cases of the strong and weak exciton-phonon interactions [13]. But such expressions fail to describe the experimental data obtained. Using some extrapolations, we found the empirical formula

$$H(T) = AT^2 + BT + C \qquad (1)$$

that describes the half-widths of exciton bands sufficiently well (the continuous curves). Here, A, B and C are some parameters given in Table 2. The analysis of Table 2 shows that the corresponding parameters A are

T a b l e 1. Temperature coefficients of the exciton energy shift for pure and Mn-doped samples

Crystals	T (K)	dE_{ex}/dT (eV/K)
2H-PbI_2	< 40	$(+5.6 \pm 0.5)\times10^{-5}$
	> 40	$(-1.6 \pm 0.1)\times10^{-4}$
PbI_2(Mn)	< 40	$(+5.1 \pm 0.5)\times10^{-5}$
	> 40	$(-1.7 \pm 0.1)\times10^{-4}$

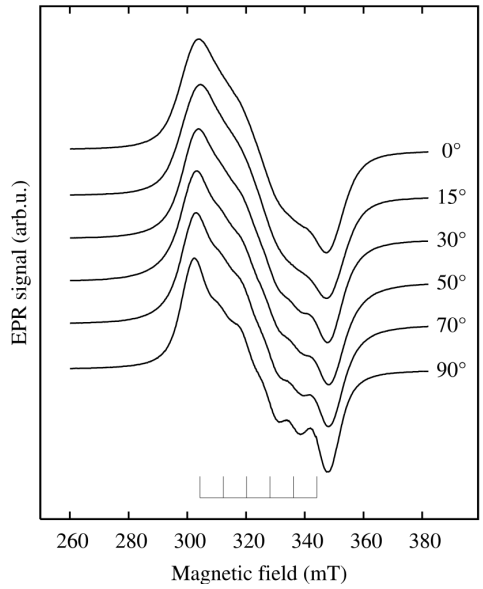

Fig. 3. EPR spectra of PbI_2(Mn) single crystals. The angle θ between the magnetic field $\boldsymbol{B}$ and the optical axis $\boldsymbol{C}$ of a crystal is indicated for each curve (to its right). $T = 77$ K, $\nu = 9081.8$ MHz

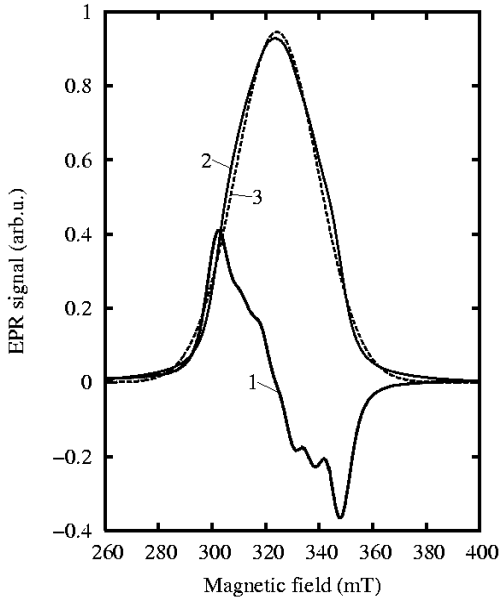

Fig. 4. EPR spectrum of PbI_2(Mn) single crystals at $\theta = 90°$ ($T = 77$ K, $\nu = 9081.8$ MHz) (curve *1*), the result of the integration of the experimental curve (curve *2*), and the fitting by a Gaussian (curve *3*)

approximately equal in both cases, while B and C are higher for the Mn-doped samples. According to the numerical simulation of the exciton absorption lineshape under lattice vibrations at high temperatures made in [14], the temperature dependence of the exciton linewidth can be described as $T^{3/2}$, T^1, and T^2 in 1D, 2D, and 3D crystals, respectively. Thus, the dependence $H(T) \sim T^2$ reflects the bulk property of the lattice and therefore supports the well-known fact that excitons in layered substances are three-dimensional.

The EPR signal was registered for the Mn-doped samples only. The EPR spectra (taken at $T = 77$ K) are presented in Fig. 3 for different angles θ between the magnetic field $\boldsymbol{B}$ and the optical axis $\boldsymbol{C}$. One can see from Fig. 3 and Fig. 4 that every EPR spectrum consists of an intense broad line with a linewidth ≈ 45.3 mT and several weak narrow lines. The number of the weak lines is six; they are pronounced most clearly when $\theta = 90°$. They are located at the same interval $(72 \pm 1) \times 10^{-4}$ cm^{-1} from one another; this value coincides with the known hyperfine splitting of Mn^{2+} in PbI_2 [7]. This fact shows that the considered lines belong to the

T a b l e 2. Fitting parameters of Eq. (1) for pure and Mn-doped samples

Crystals	A (eV/K^2)	B (eV/K)	C (eV)
2H-PbI_2	$+1.2836\times10^{-6}$	-1.7935×10^{-5}	$+0.5376\times10^{-2}$
PbI_2(Mn)	$+1.0\times10^{-6}$	$+3.3089\times10^{-5}$	$+1.2649\times10^{-2}$

$|-1/2\rangle \leftrightarrow |1/2\rangle$ electron transition of a single Mn^{2+} ion in the 2H-PbI_2 crystal lattice. Their $g_\perp$-value (2.0015 ± 0.001) coincides practically with that of the broad line (2.001 ± 0.001). This coincidence is not accidental and indicates that the broad line is caused by the Mn^{2+} ions. Indeed, the Mn^{2+} ions replace the Pb^{2+} ions at sites of the PbI_2 crystal lattice, because both ions have the same charge states and the local symmetry (D_{3d}) and are the stable paramagnetic centers in a wide temperature range. Using the obtained EPR data and the standard sample, we estimated the concentration of paramagnetic centers; it was about 10^{21} cm^{-3}. Such high concentration of paramagnetic centers gives rise to the formation of a $Pb_{1-x}Mn_xI_2$ ($x \approx 0.1$) solid solution with Mn^{2+} ions bound by the exchange interaction. Due to the exchange and magnetic dipole-dipole interactions between Mn^{2+} ions, the hyperfine spectrum of individual Mn^{2+} ions is transformed into a single intense broad line [15]. Since the integral intensity of the lines of individual Mn^{2+} ions is essentially lower than the intensity of the broad line, we can conclude that the investigated samples are basically the $Pb_{1-x}Mn_xI_2$ ($x \approx 0.1$) solid solution. They retain the highly anisotropic properties of layered crystals, because the angle dependence of EPR spectra holds, and $g_\perp$-value (2.001 ± 0.001) of the broad line is higher than its $g_\parallel$-value (1.9955 ± 0.001).

Thus, single Mn^{2+} ions (presented in a small amount) and exchange-bound Mn^{2+} ions (with high concentration) were registered in 2H-PbI_2(Mn) layered crystals by the EPR technique. The former ions cause six weak lines, while the latter ones cause an intense broad line.

3. Conclusions

It is shown that PbI_2 layered crystals with about 10 wt. % Mn impurity are a $Pb_{1-x}Mn_xI_2$ solid solution (2H-polytype). It is shown that the temperature shift of the energy position $E_{ex}(T)$ and a broadening of the half-width $H(T)$ of the exciton band $n = 1$ are close to those in undoped samples. We proposed the explanation for the value of $E_{ex}(T)$ on the basis of anharmonic vibrations of the layered lattice at low temperatures ($T < 40$ K) and low-frequency optical phonons at higher temperatures ($T > 40$ K). It is shown that $H(T)$ is proportional to T^2 and reflects the 3D character of excitons in layered substances. It was found that the EPR spectra of 2H-PbI_2(Mn) are basically caused by the exchange-bound Mn^{2+} ions.

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ОСОБЛИВОСТІ ЕКСИТОННИХ І ЕПР-СПЕКТРІВ ШАРУВАТИХ КРИСТАЛІВ 2H-PbI_2 З ВИСОКОЮ КОНЦЕНТРАЦІЄЮ ДОМІШОК МАРГАНЦЮ

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Р е з ю м е

Наведено результати експериментальних досліджень екситонних і ЕПР-спектрів шаруватих кристалів PbI_2 політипу 2H, легованих марганцем високої концентрації. Виявлено аномальний температурний зсув екситонної смуги поглинання $n = 1$, що пояснюється впливом ангармонічних коливань шаруватої ґратки при $T < 40$ K і низькочастотних оптичних при $T > 40$ K. Показано, що поодинокі іони Mn^{2+} зумовлюють появу шести слабких ліній в спектрі ЕПР, в той час як обмінно-зв'язані іони Mn^{2+} — інтенсивну широку смугу.