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Luminescence of cation excitons in PbCl_2 and PbBr_2 crystals in a wide excitation VUV region

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Abstract. Host luminescence excitation spectra and reflection spectra of PbCl_2 and PbBr_2 crystals at low temperatures have been measured in the energy region of 4–30 eV using synchrotron radiation. High-efficiency host luminescence is connected to radiative decay of self-trapped cation excitons. It is shown that also in the region of excitation multiplication, e.g. if the excitation energy is larger than twice the band gap energy ($E > 2E_g$), and in the relaxation process of core excitons the radiative self-trapped cation excitons are formed. However, the recombination of hole and self-trapped electrons (band–band excitation) does not give rise to host luminescence.

1. Introduction

The interest of solid state physics in the crystals of lead halides (PbCl_2 and PbBr_2) stems first from their lowest electronic states corresponding to cation excitons [1] and second from the lately discovered electron self-trapping (STEL) at low temperatures in PbCl_2 crystals [2]. In the STEL centre the electron is trapped at a covalent σ_g bond of the $6p$ orbital of the $(\text{Pb}_2)^{3+}$ molecule oriented along the crystallographic a -axis. In terms of elementary excitations lead halide crystals are opposite to the thoroughly investigated alkali halide crystals, where the lowest electronic excitations are anion excitons and where at low temperatures holes autolocalize forming self-trapped holes (STH, V_k -centre). In these crystals the latter play an important role in the mechanism of host radiation, which is mainly caused by the relaxation of autolocalized excitons, STE, created in the recombination process $V_k + e^-$.

The aim of the present work was to investigate relaxation of electron excitations and migration of excitation energy, both of which can be connected to the cation excitons and the STEL centres. For this purpose the reflection and host luminescence spectra of PbCl_2 and PbBr_2 crystals were recorded in a wide VUV region at low temperatures, using synchrotron radiation.

Luminescence and the first excitonic states of these crystals have been thoroughly investigated in earlier reports [3–6] and therefore this spectral region (4–6 eV) is only briefly discussed in the present report. Furthermore, in PbBr_2 the exciton energy (≈ 4.0 eV) is close to the edge of transmission of our spectrometer where the accuracy of the obtained data decreases.

In a wide UV spectral region only reflection spectra have been previously recorded [7].

2. Experiment

Crystals of PbCl_2 and PbBr_2 were grown by the Stockbarger method from zone-refined and halogen-processed material. The crystals were cleaved along the plane perpendicular to the crystallographic c -axis before being inserted into a helium cryostat [8]. The unique construction of the cryostat enables us to record absorption, reflection, excitation and emission spectra of two different samples by shifting the sample holder along and rotating around a vertical axis. The crystals were kept at 8 K during the measurement.

The 550 MeV synchrotron at the MAX laboratory, University of Lund, was used as a VUV light source [8]. The spectra were recorded by a Hamamatsu R585 photomultiplier, operating in the photon counting mode. Simultaneously, the radiation from a sodium salicylate mesh, placed in front of the samples, was recorded to take into account the slow decrease and wavelength dependence of the synchrotron flux. The typical spectral resolution was 0.3 nm for excitation and reflection spectra and 5 nm for emission spectra. Reflection spectra were recorded using the sodium salicylate converter. More details about the experimental set-up can be found in [8].

3. Results

3.1. PbCl_2

The reflection spectra of the PbCl_2 monocrystal with a freshly cleaved surface are presented in figures 1 and 2. The cation exciton band at 4.7 eV, formed by 6s–6p transitions in the Pb^{2+} ion, is clearly separated from the band to band absorption edge at 4.9 eV [1]. In the high-energy region there are two strong bands (21.45 and 23.0 eV respectively). We assume that these might correspond to the cation core excitons.

The excitation of the crystal in the fundamental absorption region gives rise to the host luminescence. The recorded emission spectra (figure 3) are excited in three energy regions, characterizing different parts of the band structure: first in the lowest exciton band (figure 3(3)), next in the region of the multiplication of the electronic excitations

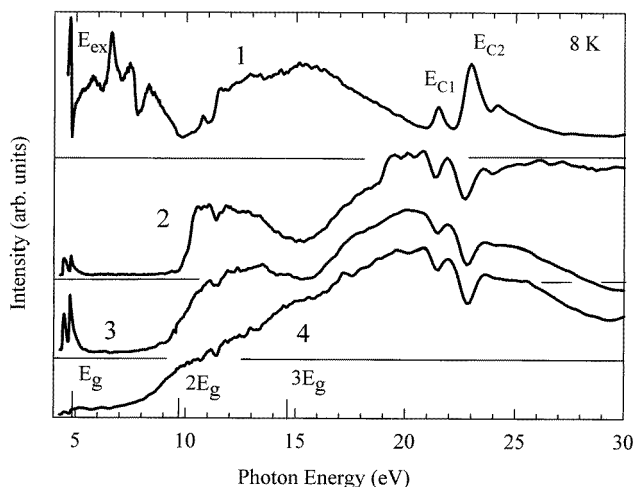


Figure 1. Reflection spectrum (1) and excitation spectra of 3.8 (2), 2.8 (3) and 2.55 eV (4) emission bands in PbCl_2 .

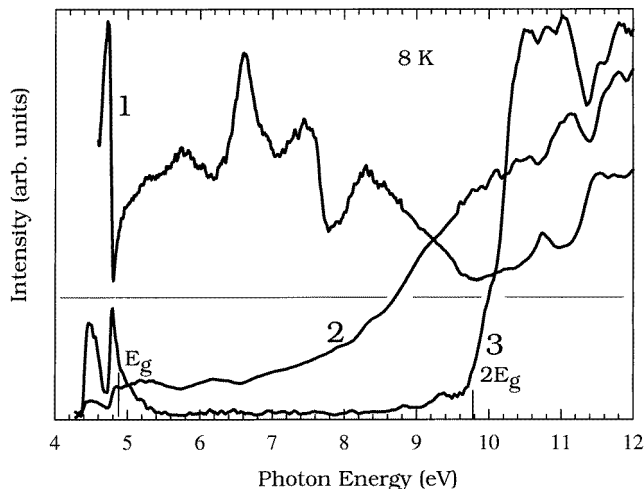


Figure 2. Reflection spectrum (1) and excitation spectra of 2.55 eV (2) and 3.8 eV (3) luminescence band in $PbCl_2$.

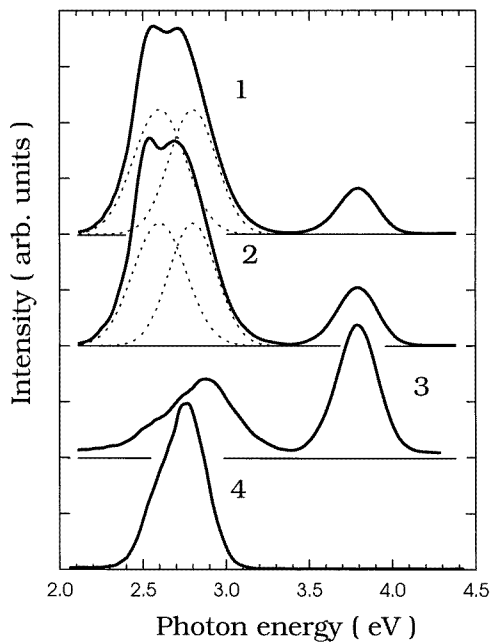


Figure 3. Emission spectra at excitation energy of 22 (1), 11 (2), 4.8 (3) ($PbCl_2$) and 22 eV (4) ($PbBr_2$) at 8 K.

(figure 3(2)) and finally (figure 3(1)) in the absorption band of the cation core excitons. The corresponding excitation spectra are presented in figures 1 and 2. By exciting the crystal with 4.8 eV radiation (the lowest exciton energy), the luminescence bands at 3.8 and 2.8 eV appear in the emission spectrum (figure 3(3)) and consequently these bands represent radiative decay of self-trapped excitons. The luminescence band at 2.6 eV, on the contrary,

cannot be excited with this energy (4.8 eV) and therefore it cannot be directly related to the exciton radiation.

The general behaviour of excitation spectra of 3.8 and 2.8 eV emission bands is similar. In both cases the emission efficiency from the exciton states is high by exciting in the lowest exciton band. The emission efficiency vanishes below the detection limit when the energy of excitation is increased into the band–band transition region until it reaches the threshold energy (E_t) of the multiplication of electronic excitations at $E_t = 9.8$ eV where the quantum yield increases abruptly again. In contrast, the intensity of the 2.6 eV radiation band is strong when exciting the crystal with radiation energy higher than 4.9 eV (band–band transitions), but this band is not present if the excitation energy corresponds to the transitions into the lowest excitonic zone. These differences clearly support the idea of 2.6 eV radiation being caused by the migration of the excitation energy to the crystal defects and not being related to the exciton luminescence of the crystal [4].

3.2. $PbBr_2$

The reflection spectrum of $PbBr_2$ is presented in figure 4. The whole spectrum is red-shifted because of the heavier anion. The energy shift of the spectral features at 21.2 and 22.7 eV is about 0.3 eV compared to the $PbCl_2$ spectrum. Also, the spectral features in the region 5–9 eV are clearly broader and less resolved than for $PbCl_2$. The maximum of the lowest excitonic band is at 3.99 eV and the beginning of band–band transitions is estimated to be 4.2 eV.

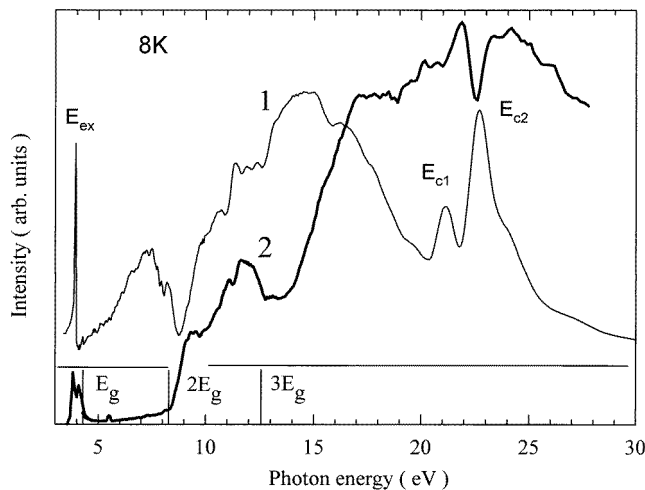


Figure 4. Reflection spectrum (1) and excitation spectrum of 2.8 eV luminescence band (2) in $PbBr_2$.

An excitation energy of 4 eV and higher than 8.4 eV gives rise to the main luminescence band of the crystal at 2.75 eV (figure 3(4)). However, the band is not symmetric and if the excitation energy corresponds to the band–band transition energy a weak radiation band appears at the long-wavelength (≈ 2.5 eV) side of the host luminescence band. Analogously to the $PbCl_2$ radiation, this band can be induced by the crystal defects, because it also appears in the spectrum if the excitation energy is slightly less than the maximum of the excitonic band.

The excitation spectrum of the host luminescence of the $PbBr_2$ crystal (figure 4) is very similar to the spectrum of $PbCl_2$. Note that both spectra are modulated with the reflection spectrum. The direct reflection losses and radiation losses because of surface defects are not taken into account. Nevertheless, the different parts of the band structure, excitonic, band-band and multiplication region, where the quantum efficiency of the host luminescence is significantly different, are clearly separated.

4. Discussion

4.1. Cation excitons in $PbCl_2$ and $PbBr_2$ crystals

It is well established that in all lead halide crystals the edge of fundamental absorption is dominated by cationic transitions of excitonic nature. These excitons originate from the electronic states of the Pb^{2+} ion. In addition to $PbCl_2$ and $PbBr_2$, the maxima of the reflection bands which correspond to the cationic excitons of the PbI_2 and PbF_2 crystals [9] are presented for comparison in table 1. The first excitonic band corresponds to the $6s^2\ ^1S_0-6s6p\ ^3P_1$ transition in Pb^{2+} [1]. However, this model is valid only in a first and rather crude approximation. A more detailed study of the formation of the excitonic states using the sequence of $PbCl_{2-x}Br_{2-2x}$ crystals [10] showed that a more exact excitonic model should also embrace a rather substantial influence of neighbouring anions. Such model calculations are not available at the moment. Also the lack of the band structure calculations makes the identification of most of the higher-energy reflection bands rather difficult and uncertain. However, it is almost certain that the intensive doublet structure in the spectral region of 20–24 eV (E_{c1} and E_{c2} , figures 1, 4) is related to the core cationic excitations. The energies of those transitions are practically independent of the anion and are close to the corresponding transitions $6s^2\ ^1S_0-5d^96s^26p\ ^3P_1$, 1P_1 , in the free Pb^{2+} ion (19.15, 22.85 eV) [11]. The origin of the band in the $PbCl_2$ spectrum with the highest transition energy, 24 eV, is not as clear as the origin of the above-mentioned ones. It may be analogous to the forbidden $^1S_0-^3D_1$ transition in free Pb^{2+} [9].

Table 1. Characteristic energies (eV) of lead halide crystals: first exciton band (E_{ex}), band gap energy (E_g), threshold of the multiplication of electronic excitations (E_t) and core excitons (E_{c1} , E_{c2}).

Crystal	E_{ex}	E_g	E_t	E_{c1}	E_{c2}	$E_{c2}-E_{c1}$
PbF_2 [9]	5.74			21.6	22.7	1.1
$PbCl_2$	4.69	4.9 [4]	9.8	21.5	23.0	1.5
$PbBr_2$	3.99	4.2 [4]	8.4	21.2	22.7	1.5
PbJ_2 [9]	2.5			20.7	22.2	1.5
Free Pb^{2+} ion [11]				19.15	22.85	3.7

4.2. Multiplication of electronic excitations

Depending on the energy of the photon, the different elementary excitations, excitons and e–h pairs, or high energetic excitations are created. The latter decay in the processes of energy relaxation finally into the same low-energy elementary excitations. By selectively creating different excitations it is possible, using luminescence centres, to investigate their relaxation

and role in the energy migration. In this respect excitation spectra of luminescence of both PbCl_2 and PbBr_2 crystals are very informative. The emission efficiency of the bands at 2.8 and 3.8 eV is high within the lowest-energy exciton band, but very low in the energy region that corresponds to the band–band transitions, where e–h pairs are created. The radiation intensity increases drastically in a very limited energy interval from the threshold energy $E_t = 2E_g$, exceeding two- to threefold the intensity of exciting in the excitonic region. Similar steep increases have not been observed in the well investigated alkali halide crystals. Presumably this is connected with the different mechanism of the multiplication of electronic excitation in the lead halide crystals. The excitation with the energy of $E \approx 2E_{ex} \approx 2E_g$ decays preferentially into two cation excitons whose radiative decay we can observe. The more than twofold increase of quantum efficiency can be explained with higher reflection losses and absorption at the surface defects if the excitation energy is close to the energy of the first excitonic band. The drastic increase of intensity at $E \approx 2E_g$ indicates that, according to the theory of multiplication of electronic excitations [12], preferably only one type of excitation, secondary excitons, is created in the process of multiplication of electronic excitations. The energy ratio $E_t \approx 2E_g$ indicates that the effective mass of one of the components of an electron–hole pair should be large and the width of the corresponding band should be small. This result perfectly agrees with EPR measurements for PbCl_2 crystal, which showed that the electron autolocalizes, $m_e \gg m_h$ [2], and also with hole conductivity measurements [13]. Therefore in this crystal the multiplication of the electronic excitations is primarily caused by the inelastic scattering of hot holes. EPR data for PbBr_2 crystals are not available, but considering the similar behaviour of the excitation spectra of both crystals we conclude that the electron autolocalizes also in PbBr_2 crystals.

The analysis of excitation spectra shows that by increasing the excitation energy the primary excitations finally decay into the cation excitons, which autolocalize and decay radiatively. Also a large fraction of core cation excitons decay into low-energy excitons. Therefore we may conclude that the luminescence of lead halide crystals is caused by the excitonic processes even if the exciting photon has high energy.

4.3. Models of host luminescence centres in PbCl_2 and PbBr_2 crystals

The luminescence of the pure crystals of PbCl_2 and PbBr_2 has been investigated in several earlier reports and also some models of radiation centres have been presented [1, 3–6, 14–16]. The main radiation bands at 3.8 and 2.8 eV in PbCl_2 and 2.8 eV in PbBr_2 crystals are connected to the cation excitations. The high quantum efficiency and the temperature dependence of the relative intensity of those bands indicate that this radiation is created by the decay of two different states of one radiation centre of the host crystal. According to the generally accepted model, the luminescence of the PbCl_2 crystal can be ascribed to the $^1\text{S}_0$ – $^3\text{P}_1$ transition in the Pb^{2+} ion where the excited state is split by the pseudo-Jahn–Teller effect ($^3\text{P}_1^{(1)}$, $^3\text{P}_1^{(2)}$). This model is supported by the long lifetime of those excited states at liquid helium temperature, 12 μs and 400 μs respectively [15, 16]. However, one cannot exclude the possibility that the electron of the cation exciton is localized on the dimer of $(\text{Pb}_2)^{3+}$, analogously to the structure of STEL [2]. In that case the host luminescence of lead halide crystals would be connected to the radiation of the quasi-molecule that is formed in the process of autolocalization of the cation exciton. This mechanism is analogous to the model of STE in alkali halide crystals, interchanging only the charge carriers. Analogous to the alkali halide crystals, the UV band at 3.8 eV energy is the σ -radiation of the quasi-molecule, because of the shorter lifetime compared to the other band at 2.8 eV and the damping of the radiation at temperatures above 10 K. The blue band at 2.8 eV is induced

by similar excitation and therefore it could be the π -component of the radiation of the quasi-molecule. Similarly in a $PbBr_2$ crystal the band at 2.8 eV is the π -component. The σ -component of this radiation could not be recorded.

The model of the dimer self-trapped exciton is supported also by the following lifetime analysis. If the radiation at 3.8 eV is caused by the transitions $^1S_0-^3P_1$ in the Pb^{2+} , then its decay time should be similar to the decay time of the radiation of Pb^{2+} centre in a KCl-Pb crystal. However, at 4.2 K they differ by more than an order of magnitude [15, 17]. Also the spin-orbit splitting energy of the radiating centre in the $PbCl_2$ crystal is approximately 60 times smaller than in the KCl-Pb crystal (10^{-3} and 6×10^{-2} eV, respectively). This large discrepancy can be explained by the autolocalizing of the electron at quasi-molecular structure. From the discussion above we can conclude that the relaxed excited state structure and parameters of the self-trapped exciton in lead halide crystals must be similar to the dimer lead centres in the corresponding alkali halide and not to the single Pb^{2+} centre.

The radiation at 2.6 eV differs substantially from the radiation discussed above. In contrast to the exciton bands, this radiation is induced by band-band excitations. Therefore the origin of this radiation must be different. Kitaura and Nakagawa [14] have proposed that this band is formed by tunnelling recombination of an STEL and a hole, trapped at the defect. This model is supported by the long decay time of the radiation.

The investigation of lead halide crystals enables us to determine whether the host luminescence of a crystal depends on autolocalizing of either a hole or an electron by comparing for example $PbCl_2$ -KCl and $PbBr_2$ -KBr crystals. It is well known that in the alkali halide crystals at low temperatures the holes autolocalize at the anions and V_k -centres are formed. The process $V_k + e^-$ gives rise to STE radiation. In contrast to the lead halide crystals, in alkali halide crystals the intensity of the host luminescence is substantial even when exciting band-band transitions [18]. Therefore we may conclude that the recombination of the free hole with the STEL at $(Pb_2)^{3+}$ does not produce STE radiation in the lead halide crystals. However, if the excitation energy is higher than the threshold for formation of secondary excitons ($E > 2E_g$) then the quantum efficiency of the STE is substantial. Now we may conclude that the STE model, well established for alkali halide and rare gas crystals, is not applicable for lead halide crystals just by change of the polarity of the charged carrier. In order to create an appropriate model, more precise theoretical calculations are necessary.

5. Conclusion

The analysis of luminescence and reflection spectra of $PbCl_2$ and $PbBr_2$ crystals at low temperatures in a wide VUV region shows that:

- (1) The excited states with large oscillator strength at 21–23 eV are cation core excitons.
- (2) The high-quantum-efficiency host luminescence (emission bands at 2.8 and 3.8 eV in $PbCl_2$ and at 2.8 eV in $PbBr_2$) is produced by radiative decay of self-trapped cation excitons. This process has high efficiency also in the energy region of multiplication of electronic excitations. Presumably the electron of the STE is localized at $(Pb_2)^{3+}$.
- (3) During the recombination of a free hole with a self-trapped electron (band-band transition) the radiating cation excitons are not produced and therefore the corresponding excitonic model of alkali halide crystals needs to be specified for the lead halide crystals.

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