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Emission bands of CsCdBr₃

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Abstract. Optical properties of CsCdBr₃ crystals have been investigated. Three emission bands peaking at 3.3, 2 and 1.8 eV are induced by ultraviolet excitation. Correlation with intrinsic luminescence properties of alkali halides leads to the assignment of the bands to emission from Br₂^{•-} centres.

1. Introduction

CsCdBr₃ belongs to the large family of AMX₃ crystals which adopt the CsNiCl₃ structure (Visser *et al* 1980). In this hexagonal structure, (MX₆)⁴⁻ octahedra sharing opposite faces form infinite linear chains, which are parallel to the C₃ axis and have the stoichiometry ((MX₃)⁻)_n. Cs⁺ ions, compensating this negative charge, occupy positions between the chains. The one-dimensional character of this structure arises because distance between two divalent ions adjacent in a chain is much shorter than the inter-chain distance (3.361 Å and 7.675 Å, respectively).

Optical and magnetic properties of trivalent and divalent ions introduced as impurities into ((MX₃)⁻)_n chains of AMX₃ crystals have been studied in particular (Barthem *et al* 1985, Henling and McPherson 1977, McPherson and Henling 1977, McPherson and McPherson 1981, McPherson *et al* 1970, 1977, 1978, Wolfert and Blasse 1984). As the trivalent ions tend to enter these materials as pairs, the optical and magnetic properties have been related to the chain structure. However, until now only a few studies have been carried out on the optical properties of the pure materials (Andraud *et al* 1985, 1987, Vishnevski *et al* 1984, Wolfert and Blasse 1984).

In this paper the optical properties of CsCdBr₃ are reported and are interpreted by analogy with the intrinsic luminescence of alkali halides.

2. Experimental procedure

Crystals of CsCdBr₃ were synthesised by the Bridgman method under a bromine atmosphere. The hexagonal structure of crystals and the impurity concentration (less than 10 ppm) have been checked by crystallographic and analytical methods. The crystals

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are colourless and transparent. Furthermore they can be easily oriented with respect to the C_3 axis, since they cleave along it. The crystals were mounted on the cold finger of a variable-temperature cryostat (Lake Shore Cryotronics type LTS 21). The luminescence was excited with an XBO 150 xenon lamp and a Jobin-Yvon (type HD10) double monochromator. The luminescence was dispersed through a Jobin-Yvon (type HR 1000) monochromator and detected by a Hamamatsu (type 649) photomultiplier coupled to an amplifier. The excitation and emission spectra were corrected for the system response.

Two procedures were used for lifetime measurements. For excitation in the 4 eV range, the experimental set-up consisted of an AVCO nitrogen laser, pumping a tunable dye laser (Molelectron DL 200) with wavelengths ranging from 593 to 644 nm. The dye laser output was amplified (Walleinstein and Hansch 1975) and doubled by means of a potassium dihydrogen phosphate crystal to produce an ultraviolet beam at 4 eV. The emission was analysed with a Jobin-Yvon (HR 1000) monochromator and detected with a photomultiplier (RTC XP 1020). For excitation in the 5 eV range, decay time measurements were performed using a TRW deuterium flash lamp (Pulse duration, 5 ns). The excitation and emission wavelengths were selected with interferential and cut-off filters; the luminescence was detected with a photomultiplier (RTC 56TVP). In both cases, a box-car averager (PAR 162) was used to record the emission decay curves.

3. Results

3.1. Fluorescence spectra

Three main emission bands were observed for all crystals studied. When excited in the band gap at 3.9–4 eV (the absorption edge peaking at least at 5 eV), $CsCdBr_3$ crystals (Andraud *et al* 1985, 1987) show an intense luminescence (emission band A) peaking at about 3.29 eV at 10 K (figure 1). This band disappears at 100 K but, with increasing temperature, another emission band (B) is detected at 1.9 eV at 80 K; this shifts with

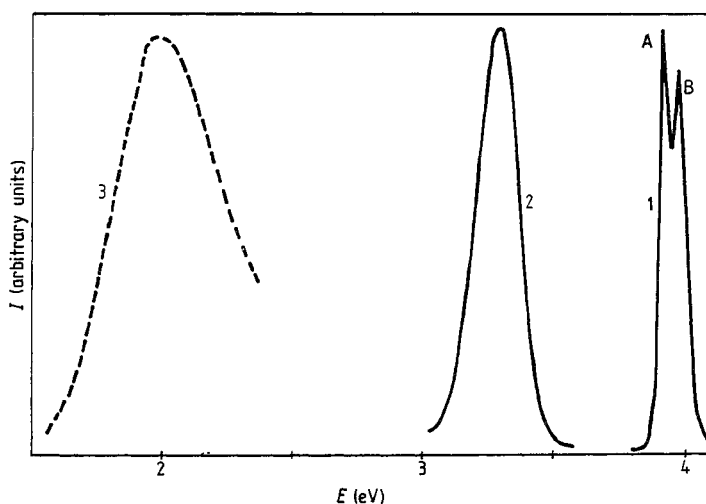


Figure 1. Emission bands A and B and their excitation spectrum in $CsCdBr_3$ at $T = 10$ K (—) and $T = 170$ K (---): spectrum 1, excitation spectrum; spectrum 2, emission spectrum $I \times 1$; spectrum 3, emission spectrum, $I \times 15$.

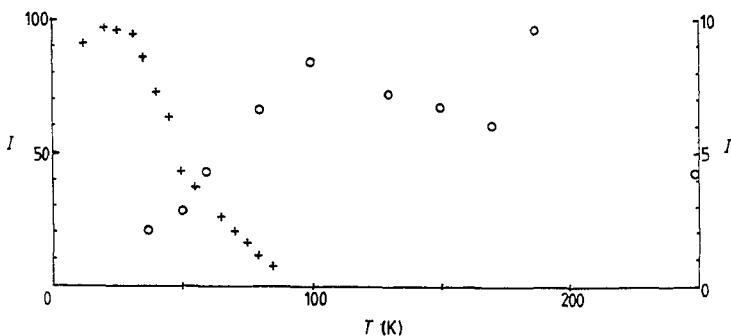


Figure 2. Intensity variations of emission bands A and B with temperature in CsCdBr₃: +, $E = 3.3$ eV, left-hand intensity scale; O, $E = 1.9$ eV, right-hand intensity scale.

increasing temperature towards higher energies (2.1 eV at 300 K). The variations in the intensity I of these bands with temperature are reported in figure 2, where the much higher intensity of emission band A with respect to the emission band B should be noted. The efficiency of emission band A was found to decrease with an activation energy of about 25 meV. The thermal behaviour of the widths of the two bands is given in figure 3. These two curves were fitted using the well known law:

$$\delta(T) = \delta(0) \coth(\hbar\omega/2T)$$

where T is the absolute temperature and $\hbar\omega$ the average energy of the phonons.

$\hbar\omega$ can be estimated for both bands to be 50 cm^{-1} ; this value seems to be reasonable in the light of the Raman data (Pilla *et al* 1987a, b, Orinchai *et al* 1982).

Both emission band A and emission band B have the same excitation spectra, which consists of a well defined doublet. The two components, whose half-width is 50 meV, peak at 3.91 and 3.97 eV and are almost completely polarised parallel and perpendicular to the C_3 axis respectively (figure 4). It should be noted, however, that, as regards the luminescence spectrum, no polarisation of emission bands has been detected; moreover,

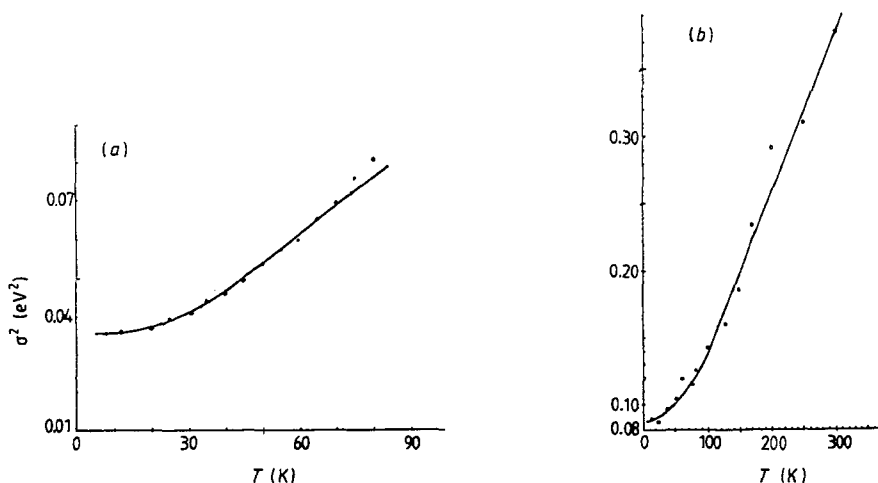


Figure 3. Thermal variations in the half-widths of emission bands in CsCdBr₃: (a) emission band A; (b) emission band B.

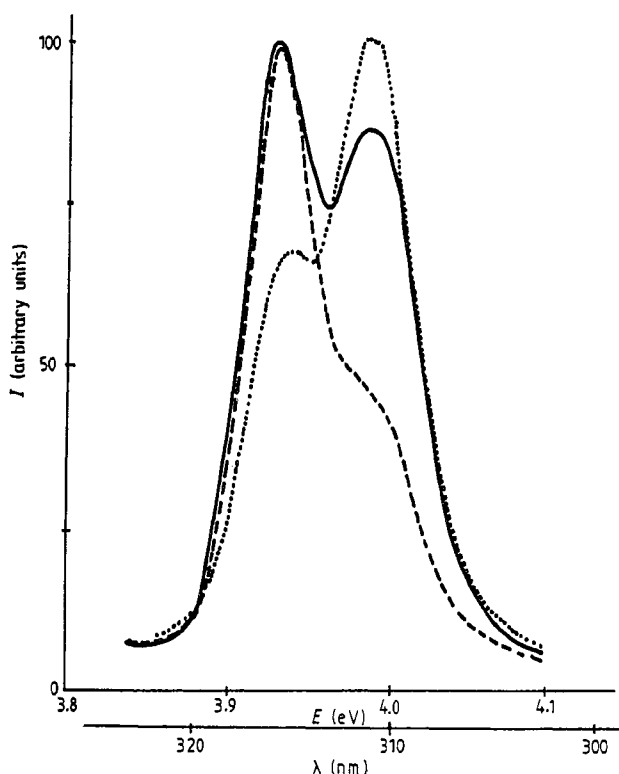


Figure 4. Excitation spectra of emission bands A and B ($T = 10$ K): —, unpolarised excitation; ····, E perpendicular to the C axis; ---, E parallel to the C axis.

no difference in either emission has been detected even by means of high-resolution selective excitation in the two components.

Under 5 eV excitation, a structured emission (C) with maxima at 1.6 and 1.8 eV was detected (figure 5(a)). The intensity of this luminescence is very weak with respect to emission band A. The excitation spectrum of this emission consists of a wider band peaking at 5.1 eV (figure 5(b)). No study of the intensity variation of emission band C with temperature was attempted owing to the poor signal and to the strong overlap of the two components. In addition to the emission bands A, B and C, a weak band at 2.9 eV is observed in the temperature range 50–150 K (figure 6); its excitation spectrum consists of a band centred at 4.1 eV. This emission is more intense in crystals grown from starting materials containing iodides instead of bromides; moreover, in the former crystals, an additional absorption band at 4.2 eV, which nearly corresponds to the excitation energy of the 2.9 eV emission had been observed. Since similar emission and excitation bands have already been observed in $\text{CsCdCl}_3: \text{I}^-$ crystals (Pidzyrilo and Khapko 1985), we also assign these features to I^- -related impurities and we shall not consider them in the following.

3.2. Decay time

Decay time measurements were performed on emission bands A, B and C. The results obtained in the temperature range 10–300 K are shown in figures 7 and 8 for emission A and C, respectively.

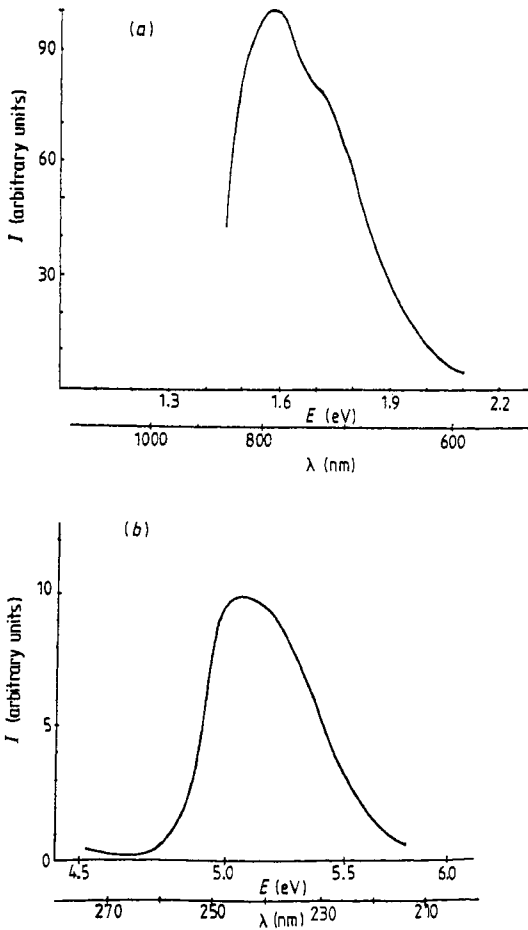


Figure 5. (a) Spectrum of emission band C under 5 eV excitation; (b) excitation spectrum of emission band C.

The decay of emission band A consists of a single exponential over the whole temperature range studied; with increasing temperature the lifetime remains constant up to 30 K (20 ns) and then decreases (for $T \geq 70$ K, the decay rate is faster than the 4 ns exciting pulse).

Emission band C has a double-exponential decay, which has been fitted with two lifetimes (150 and 50 μs at 10 K). These times greatly decrease above 60 K and 70 K, respectively. These two decay times have been unambiguously ascribed to the 1.6 eV and 1.8 eV emission, respectively by means of selective excitations. The lifetime of emission band B was measured and gave a value of 3 μs at 70 K and 1.5 μs at 150 K.

4. Discussion

Assignment of bands A, B and C to impurity emission can be definitively discarded owing to the low level of impurities (less than 10 ppm) in the crystals investigated and to the existence of these bands whatever the starting materials and growth method.

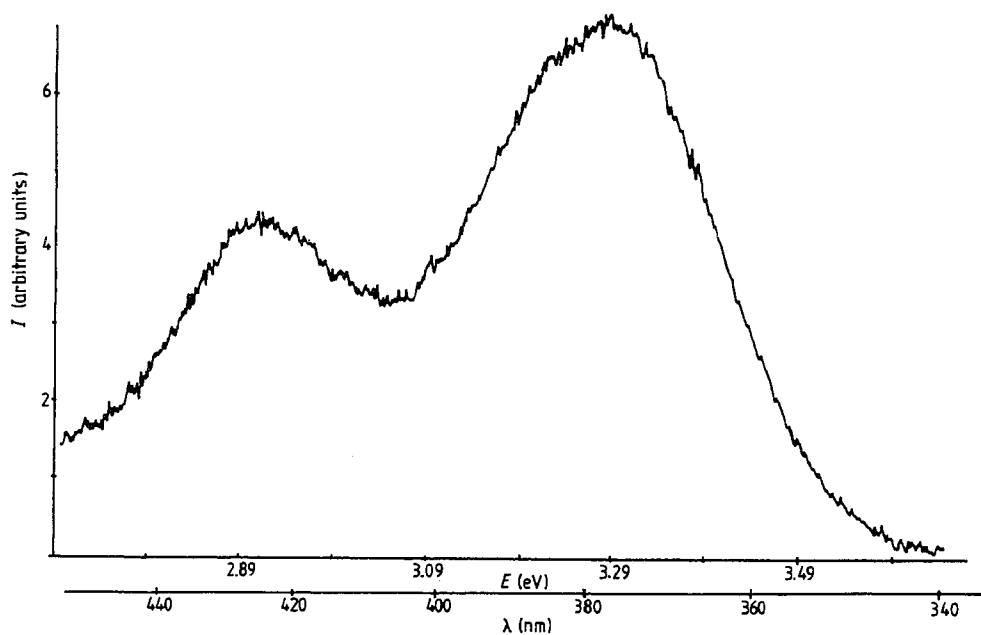


Figure 6. I^- impurity emission in CsCdBr_3 .

In order to explain the origin of these observed features, a comparison with the intrinsic luminescence of alkali halides could be helpful. In the latter systems, the luminescence is obtained either by means of ultraviolet excitation in the excitonic region or using ionising radiations. The luminescence spectra consists of three bands (σ , π and E_x emissions in order of decreasing energy) originating from excited states of X_2^{2-} centres, where X represents a halogen atom. Holes induced by irradiation are immediately self-trapped to form the well known $V_K (X_2^-)$ centres, while electrons are trapped at a shallow excited state of the X_2^- centre, forming a self-trapped exciton (X_2^{2-} centre). Both the short-lived emission and the long-lived emissions are ascribed to transitions of the types $^1\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ and $^3\Sigma_u^+ \rightarrow ^1\Sigma_g^+$, respectively. For the latter the multiplicity forbiddenness is partially removed by the spin-orbit mixing of the $^1\Pi_u$ and $^3\Sigma_u^+$ states.

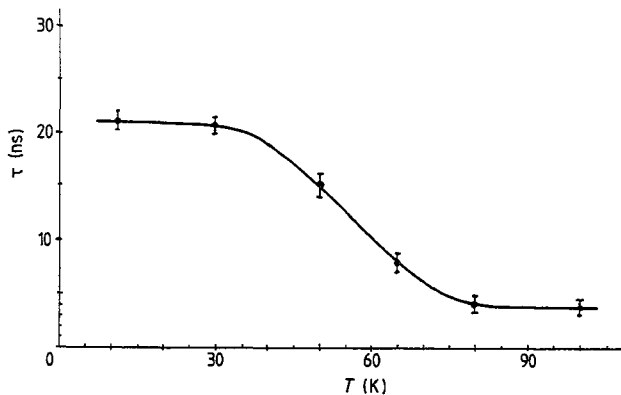


Figure 7. Variation in the lifetime of emission band A with temperature.

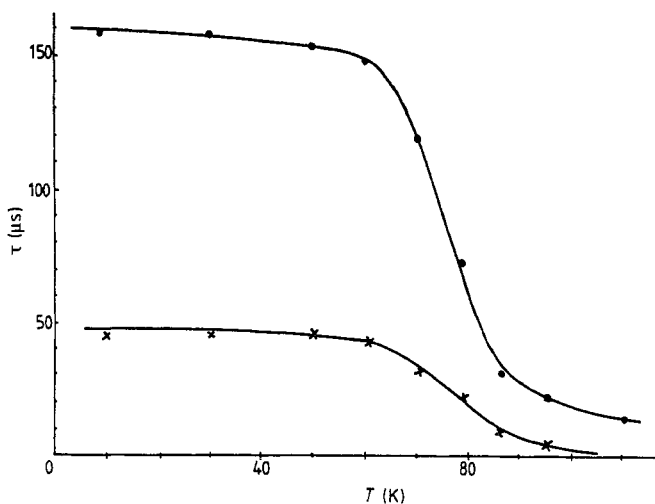


Figure 8. Variation in the lifetimes of emission band C with temperature: ●, 1.6 eV emission; ×, 1.8 eV emission.

Two models have been proposed to explain the origin of these three emissions. The discussion concerns the orbital states involved in these three transitions. The first model is based on studies of the electronic structure of NaCl self-trapped excitons by a Hartree-Fock method (Stoneham 1974). From these calculations the σ and π emissions are assumed to originate from different orbital states, since their difference in energy is larger than the separation between singlet and triplet states deriving from a same orbital configuration. In this hypothesis, both σ and π bands are ascribed to the decay of the higher singlet and lowest triplet self-trapped exciton states, respectively, while the E_x emission has an extrinsic origin arising from perturbed self-trapped exciton (Itoh 1984).

A second model has been developed in order to explain the characteristics of the excitation and emission bands in alkali iodides (Nishimura *et al* 1979). In this case, both

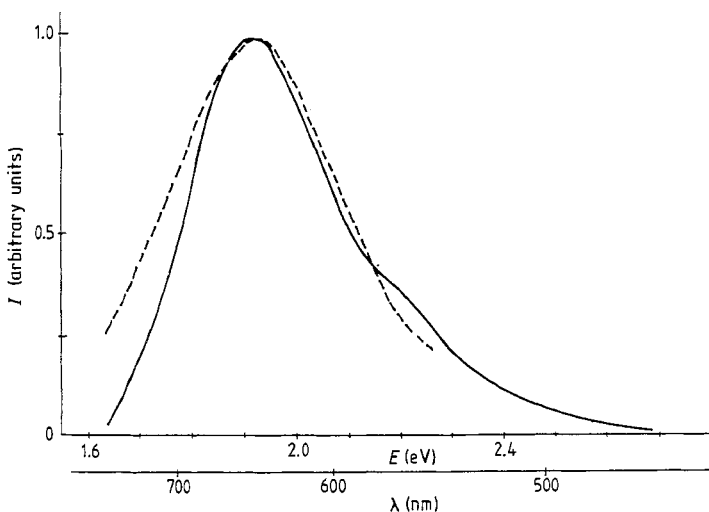


Figure 9. Emission spectrum of CsCdBr_3 pure crystals ($T = 75 \text{ K}$): —, excited by x-rays; ---, excited at 4 eV.

σ and π emissions have been related to the $n = 2$ exciton state and ascribed to $A\sigma_g 2s : {}^1\Sigma_u^+$ and $A\sigma_g 2s : {}^3\Sigma_u^+$ self-trapped exciton state luminescence, respectively; the E_x emission which has the same excitation spectrum as the $n = 1$ resonance luminescence, is assigned to the radiative decay of the self-trapped $1s$ exciton in the triplet state:

$$A\sigma_g 1s : {}^3\Sigma_u^+$$

where A stands for the outermost electronic configuration of the halogen molecule X_2^- , i.e. $(\sigma_g np)^2(\pi_u np)^4(\pi_g np)^4(\sigma_u np)$ and $\sigma_g 1s, \sigma_g 2s$ for the hydrogen-like states where the electron is trapped to form X_2^{2-* centres.

It is tempting to relate emission bands A, B and C emissions observed in $CsCdBr_3$ crystals to the σ, π and E_x bands in alkali halides. In fact, the number of observed emissions, their energy, their lifetimes and their relative intensity qualitatively agree with the assignment of these bands to Br_2^{2-} -like centres.

In this hypothesis, emission band A, which is very intense with respect to the other emission bands and whose lifetime is short, could be ascribed to the totally allowed transition ${}^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$; in the same way, because emission bands B and C have weaker intensities and longer lifetimes, they are assigned to the partially allowed transition ${}^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$.

From their relative positions, emission bands A, B and C could correspond to the σ, π and E_x emissions of alkali halides, respectively. Since bands A and B have the same excitation spectrum, they could involve the same electron orbital and should be ascribed to the transitions

$$A\sigma_g 2s : {}^1\Sigma_u^+ \rightarrow A\sigma_u 4p : {}^1\Sigma_g^+$$

$$A\sigma_g 2s : {}^3\Sigma_u^+ \rightarrow A\sigma_u 4p : {}^1\Sigma_g^+$$

in the framework of the previously discussed second model, while emission band C originates from the $A\sigma_g 1s : {}^3\Sigma_u^+$ state.

This assignment would be supported by the study of the luminescence excited by x-rays, which corresponds to direct electron-hole recombination and consists of two bands at 2.2 and 1.9 eV (figure 9(a)). Because of the following observations, these two bands cannot be assigned to the (σ, π) transitions.

(i) Their relative intensities do not correspond to a totally allowed and a multiplicity-forbidden transition.

(ii) Their energy separation is small compared with the σ - π separation of a few electronvolts in alkali halides (Kabler and Patterson 1967).

Consequently, because of its higher efficiency, the 1.9 eV band is assigned to intrinsic luminescence, while the weaker emission at 2.2 eV may arise from ionising-radiation-stabilised centres such as Cd^+ . It is indeed well known that ions having a $(ns)^1$ valence electron, such as $Cu^0, Ag^0, Tl^{2+}, Cd^+$ and Pb^{3+} are created as a result of a reduction by the irradiation (Beaumont *et al* 1971). The existence of a single band in the intrinsic luminescence of $CsCdBr_3$ could lead us to ascribe the 1.9 eV band to a π -type transition because of observations on alkali halides in which the π -emission is always present while the σ -emission is not.

The exact coincidence of the 1.9 eV band and the 4 eV excited band B (figure 9(b)) supports the assignment of the latter to a π -type transition.

The proposed assignment of the optical transitions of $CsCdBr_3$ crystals to Br_2^{2-} centres needs further justification, however. In the alkali halide case, the V_k centres are

created only by excitation in the conduction band at low temperatures and are not stable above 100 K. In the system under investigation, these centres are present in as-grown crystals and are stable at room temperature; this can be ascribed to the low dimensionality of these compounds, where the Br₂⁻ pseudomolecule is much more 'isolated' than in a cubic crystal, if we assume that it is located on a stacking fault as the behaviour of some doped crystals seems to suggest. The increase in the luminescence of order of magnitude in crystals doped with divalent M²⁺ (M²⁺ ≡ Pb²⁺ or Sn²⁺) ions where the CsMBr₃ compounds have the corner-sharing perovskite structure suggests that these centres are related to stacking faults in which two broken chains are connected through a halide ion (Andraud *et al* 1985). To our knowledge, it is the first time that the presence of such a centre has been proposed. A study is in progress which will give a model for the energy levels of these centres, taking into account all the observed effects.

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