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# Luminescence of $s^2$ Ions in $CsCdBr_3$ and $CsMgCl_3$

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The luminescence properties of $Bi^{3+}$ in $CsMgCl_3$, of $Bi^{3+}$ and $Pb^{2+}$ in $CsCdBr_3$, and of undoped $CsCdBr_3$ are reported. For $CsMgCl_3$–$Bi^{3+}$ two luminescent centers are observed. One is ascribed to isolated $Bi^{3+}$ ions and the other to a $Bi^{3+}$–vacancy–$Bi^{3+}$ complex. For $CsCdBr_3$ only one luminescent center is observed. The Stokes shift amounts 2.1 eV and the quenching temperature is low (~40 K). Undoped $CsCdBr_3$ shows also luminescence which seems to be related to structural disorder. Finally, the luminescence properties of $CsCdBr_3$–$Pb^{2+}$ are discussed. Below 80 K luminescence of intrinsic $Pb^{2+}$ ions is observed. This luminescence is in the green spectral region. The luminescence above 100 K is ascribed to $Pb^{2+}$ ions in a layer of slightly disordered bromine ions: excitation occurs in these bromine ions and is transferred to $Pb^{2+}$ ions. © 1984 Academic Press, Inc.

## Introduction

The compounds $CsCdBr_3$ and $CsMgCl_3$ belong to an extensive series of $AMX_3$ halides which adopt the hexagonal $CsNiCl_3$ structure (*1*). This structure can be described as an array of infinite parallel chains of $MX_6^{4-}$ octahedra sharing opposite faces. The chains are negatively charged and have the stoichiometry $(MX_3^-)_n$. The $Cs^+$ ions occupy positions between the chains. Since the distance between adjacent divalent ions in the chains is much shorter than the distance between the chains, these materials have a one-dimensional character (*2*). The octahedral coordination of the $M^{2+}$ ion is trigonally distorted, because the $MX_6^{4-}$ octahedron is elongated along the threefold axis of the $(MX_3^-)_n$ chain. These $CsMX_3$ salts are "accommodating" host materials (*3–5*).

A wide variety of divalent transition metal ions like $V^{2+}$, $Mn^{2+}$, $Fe^{2+}$, and $Co^{2+}$ can be introduced as impurities into the $(MX_3^-)_n$ chain. Recently it was shown that trivalent ions can also be incorporated into the $(MX_3^-)_n$ chain (*5*). Since the $M^{2+}$ ion is replaced by a trivalent ion, charge compensation is required. For charge compensation several possibilities exist. One possibility is that the trivalent ion enters the chain in conjunction with small monovalent ions like $Na^+$ or $Li^+$. Another possibility is that the trivalent ions enter the chain in pairs. Two trivalent ions replace three divalent ions. The trivalent ions are situated at each side of the vacancy, resulting in a $M^{3+}$–vacancy–$M^{3+}$ complex. This possibility was demonstrated by McPherson for the case of $CsCdBr_3$ doped with trivalent rare earth ions (*6*). In $Ce^{3+}$-doped $CsCdBr_3$ several $Ce^{3+}$ centers were observed by luminescence measurements (*7*). This illustrates the several charge-compensating possibilities. In $CsCdBr_3$ doped with $Ce^{3+}$ and $Tm^{3+}$ efficient energy transfer from

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$Ce^{3+}$ to $Tm^{3+}$, in the $Ce^{3+}$–vacancy–$Tm^{3+}$ complex, was observed, even at very low activator concentration (one part in $10^3$ or less).

With this view we decided to study the luminescence of $CsCdBr_3$ doped with $Bi^{3+}$ and eventually $CsCdBr_3$ doped with $Bi^{3+}$ and trivalent rare earth ions. It appeared that the $Bi^{3+}$ emission in $CsCdBr_3$ is at relatively low energy, so that efficient energy transfer to trivalent rare earth ions is improbable. Because of the interesting properties of $CsCdBr_3$ as a host lattice the luminescence of several activator ions in this lattice was studied. The luminescence properties appeared to be complicated. The major part of this paper deals with the luminescence of the $Bi^{3+}$ ion and the $Pb^{2+}$ ion in $CsCdBr_3$. The luminescence properties of the $Bi^{3+}$ ion in $CsMgCl_3$, a compound with the same crystal structure as $CsCdBr_3$, are also reported. The luminescence of $CsCdBr_3$–$Ce^{3+}$ will be published elsewhere (*7*).

## Experimental

### *Sample Preparation*

The compound $CsCdBr_3$ was prepared by dissolving Cd metal (Light & Co., 99.999%) and CsBr (Merck, Suprapur) in HBr (Baker, analyzed, 48%) and evaporated to dryness. The powder obtained in this way was brought into an ampule and dried under vacuum at a temperature of 200°C for 12–16 hr. After the material was dry it was molten under a bromine atmosphere and filtered through a quartz filter (G3) into a crystallization ampule. This material was crystallized also under a bromine atmosphere by the Bridgmann method.

The dopant ions were added by dissolving the corresponding bromides or oxides in the initial HBr solution. The crystals containing $Bi^{3+}$ or $Pb^{2+}$ were also prepared in a slightly different way. First, crystals of pure $CsCdBr_3$ were prepared. To this material $Cs_3Bi_2Br_9$ crystals (*8*) were added. This mixture was again molten and crystallized under a bromine atmosphere. The samples of $CsCdBr_3$–$Pb^{2+}$ were prepared by adding $PbBr_2$ crystals (*9*) and CsBr (1 to 1) to $CsCdBr_3$ crystals. Further the same method as for $CsCdBr_3$–$Bi^{3+}$ was followed. The optical properties of samples prepared in this way and samples prepared by dissolving Cd metal, CsBr, and dopant material together were the same.

The crystals were checked by X-ray diffraction using Cu$K\alpha$ radiation. Undoped $CsCdBr_3$ crystals were analyzed by X-ray fluorescence and atomic absorption measurements. This analysis did not show large amounts of impurities. The major impurities found were K(~50 ppm), Cl(~30 ppm), I(<5 ppm), and Pb (<3 ppm). In the case of the doped $CsCdBr_3$ crystals we observed a concentration gradient of the dopant ions along the direction of growth. The concentrations of $Bi^{3+}$ and $Pb^{2+}$ in $CsCdBr_3$ were determined by atomic absorption spectrometry. The samples of $CsCdBr_3$–$Bi^{3+}$ used for the optical measurements contained about 100 ppm $Bi^{3+}$, that of $CsCdBr_3$–$Pb^{2+}$ 30 ppm $Pb^{2+}$.

The crystals of $CsMgCl_3$–$Bi^{3+}$ (1 at.%) were obtained from Professor G. L. McPherson. Because $CsMgCl_3$ is highly hygroscopic, all handlings were carried out under a dry nitrogen atmosphere.

### *Instrumentation*

The emission and excitation spectra were recorded on a Perkin–Elmer spectrofluorometer (MPF-3L) equipped with an Oxford Instruments CF100 helium-flow cryostat. Emission spectra were corrected for photomultiplier sensitivity. The photon flux per constant energy interval ($\Phi$) is obtained by multiplying the radiant power per constant wavelength interval by $\lambda^3$. The excitation

spectra were corrected for the transmittance of the monochromator and the lamp intensity with the use of Lumogen T-rot GG as a standard (*10*).

Decay-time measurements on undoped $CsCdBr_3$ and $CsCdBr_3$–$Bi^{3+}$ were performed using an EG&G 108 AU Xe flash lamp (pulse width ~1 μsec) and a TRW $D_2$ flash lamp (pulse width ~10 nsec). The detection apparatus has been described in detail elsewhere (*11*). Excitation and emission wavelengths were selected with the use of interference and cut-off filters. For the decay-time measurements on $CsMgCl_3$–$Bi^{3+}$ a photon-counting system (EG&G) was used. Details of this system have been described elsewhere (*12*). The emission wavelength was selected by a double monochromator (Jobin Yvon, HRD 1), equipped with a photomultiplier tube (RCA C31034). Measurements of the time-dependent behavior of the emission bands in $CsCdBr_3$–$Pb^{2+}$ were performed using a nitrogen laser (Molectron, Model UV 14). The emission was analyzed with a Spex 1704 X 1-m monochromator and detected by a photomultiplier tube (RCA C31034). A PAR Model 162/165 boxcar averager was used to record time-resolved spectra and decay curves.

## Results and Discussion

### *$CsMgCl_3$–$Bi^{3+}$*

For the crystals of $CsMgCl_3$–$Bi^{3+}$ two luminescent centers are observed (Fig. 1). One center has its excitation band at 4.37 eV and its emission band at 2.96 eV. The intensity and position of this emission and excitation band are independent of temperature, up to room temperature. At 4.2 K the decay time of the emission is about 80 μsec. The decay time decreases steadily to 20 μsec at 300 K.

The outer center has its excitation band at 4.04 eV and its emission band is situated around 2.48 eV. The intensity of this emission band is constant up to a temperature of about 80 K. Above this temperature the emission intensity decreases (Fig. 2). The decay time of this emission is short: at 4.2 K it amounts to about 500 nsec. From work by McPherson on $CsMgCl_3$–$Bi^{3+}$, $Tm^{3+}$ it was found that this $Bi^{3+}$-center shows energy transfer to $Tm^{3+}$ (*13*). So this center can be associated with the $Bi^{3+}$–vacancy–$Bi^{3+}$ complex for agreements similar to those given in Ref. (*5*).

The emission band at 2.96 eV is ascribed to a single $Bi^{3+}$ ion at a $Mg^{2+}$ site. However, the decay times of this $Bi^{3+}$ center are

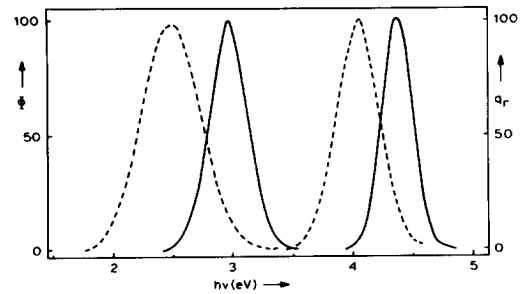


FIG. 1. Emission and excitation spectra of the luminescence of $CsMgCl_3$–$Bi^{3+}$ at 8 K. Broken lines relate to the 2.48-eV emission and drawn lines to the 2.96-eV emission. Φ gives the spectral radiant power per constant energy interval in arbitrary units. The $q_r$ gives the relative quantum output.

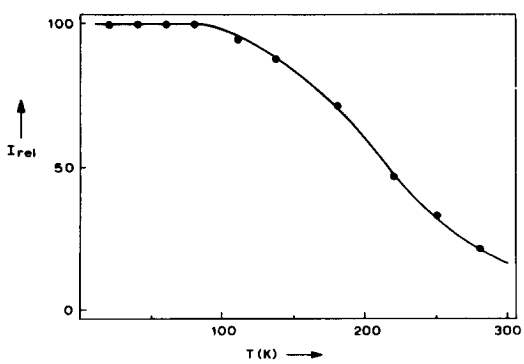


FIG. 2. Emission intensity of the 2.48-eV emission of $CsMgCl_3$–$Bi^{3+}$ as a function of temperature. The excitation energy was 4.04 eV.

anomalous for an isolated $s^2$ center, because the LHeT value is rather short and the RT value is too long. Moreover, a comparison with $Cs_2NaYCl_6$–$Bi^{3+}$ (*13*) shows also deviating behavior. In $Cs_2NaYCl_6$, which has cubic-ordered perovskite structure, the $Bi^{3+}$ ion occupies a regular octahedron. The luminescence spectra show vibrational structure. It has been shown (*14*) that the smaller the site, the more pronounced this fine structure. On this basis we expect for a center $Bi^{3+}_{Mg}$ in $CsMgCl_3$ a small Stokes shift. This is not observed, since the Stokes shift is about 1.4 eV. A large Stokes shift suggests off-center position for $Bi^{3+}$ (*12*). Therefore we assume that the $Bi^{3+}$ ion is associated with a $Mg^{2+}$-vacancy, so that the $Bi^{3+}$ ion shifts alongside the chain direction toward the vacancy. For such a center a large Stokes shift is not unexpected. In addition the energy level structure becomes very complicated which may account for the anomalous decay times.

*$CsCdBr_3$–$Bi^{3+}$*

For the crystals of $CsCdBr_3$ doped with $Bi^{3+}$ ions only one emission and excitation band is observed (Fig. 3). The emission band is situated around 2.12 eV and has its excitation band at 4.33 eV. The positions of the excitation and emission bands do not depend on temperature. The intensity of the emission band decreases in the temperature region from 10 up to 40 K. At 50 K the emission is completely quenched. The decay time of the emission is short, viz. 8 $\mu$sec at 1.5 K. Up to a temperature of 10 K the decay time remains constant. At temperatures above 10 K the decay time decreases steadily to 1 $\mu$sec at 40 K. The temperature dependence of the emission intensity and of the decay time are equal (see Fig. 4).

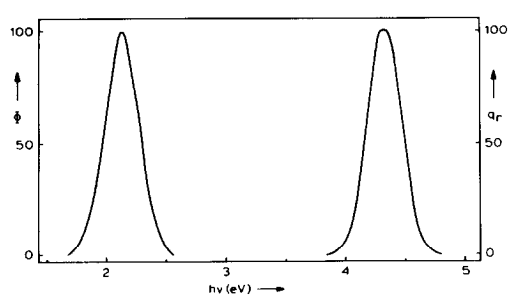


FIG. 3. Emission and excitation spectra of the luminescence of $CsCdBr_3$–$Bi^{3+}$ at 8 K.

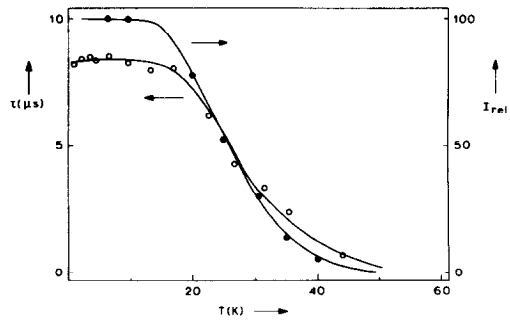


FIG. 4. Emission intensity (●) and decay time (○) of $CsCdBr_3$–$Bi^{3+}$ as a function of temperature. Excitation energy was 4.33 eV.

It seems probable that the $Bi^{3+}$ ion is incorporated in the lattice in the same way as the trivalent rare earth ions. The observed Stokes shift is extremely large, viz. about 2.1 eV. Also for some oxidic bismuth compounds such a large Stokes shift is observed: $Bi_2Ge_3O_9$ (Stokes shift: 2.5 eV), $Bi_4Ge_3O_{12}$ (2.25 eV), and $Bi_2Al_4O_9$ (2.2 eV) (*12*). Quenching of the emission of these compounds starts at 80, 170, and 200 K, respectively. This is at considerably higher temperatures than in the case of $CsCdBr_3$–$Bi^{3+}$. Another difference between the emission of $CsCdBr_3$–$Bi^{3+}$ and the oxidic bismuth compounds is the low-temperature value of the decay time. For $CsCdBr_3$–$Bi^{3+}$ this decay time is 8 $\mu$sec, but for the bismuth compounds it is between 70 and 200 $\mu$sec. It cannot be excluded, however, that the short decay time of $CsCdBr_3$–$Bi^{3+}$ is due to a considerable contribution of nonradiative processes, because the quenching temperature is so low.

In other bromides, e.g., $K_4Bi_2Br_{10} \cdot 4H_2O$ and $Rb_3BiBr_6$ (*15*) and in $LaOBr-Bi^{3+}$ [16] the $Bi^{3+}-Br^-$ charge-transfer state plays an important role in the luminescent processes on the $Bi^{3+}$ ion. This may also be the case for $CsCdBr_3-Bi^{3+}$ which complicates the situation even more.

We conclude that the $Bi^{3+}$ ion in $CsCdBr_3$ and $CsMgCl_3$ can be charge-compensated in a special way. As a consequence the resulting luminescent centers are rather complicated. It is impossible to specify the nature of the optical transitions involved in any detail, which stresses, once again, our lack of knowledge of the energy level scheme of the $Bi^{3+}$ ion in low-symmetry coordination. Since the introduction of $Pb^{2+}$ in $CsCdBr_3$ does not require charge compensation, we investigated also $CsCdBr_3-Pb^{2+}$. Here, however, we met other difficulties.

### *$CsCdBr_3$*

At 4.2 K undoped $CsCdBr_3$ shows a strong emission at 3.29 eV with an excitation at 3.91 and 3.97 eV (Fig. 5). The minimum in the excitation spectrum corresponds to the maximum in the absorption spectrum, which is a well-known phenomenon for crystals. The optical absorption edge of $CsCdBr_3$ is at about 4.90 eV at 77 K.

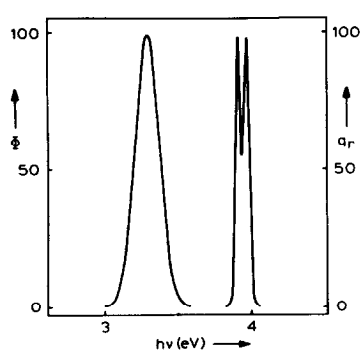


FIG. 5. Emission and excitation spectrum of the luminescence of $CsCdBr_3$ at 8 K.

Excitation in the absorption edge does not yield any luminescence at all, so that the emission must be related to a center with an energy level below the absorption edge. The luminescence is quenched at about 100 K. The decay time of the 3.29-eV emission is short: at 1.5 K ~ 100 nsec. This luminescence is also observed in some of the doped $CsCdBr_3$ crystals. It is not observed in the crystals doped with $Bi^{3+}$ or $Mn^{2+}$ and its intensity is weak in the case of $CsCdBr_3-Ce^{3+}$. On the other hand the intensity of this emission is high in the case of $CsCdBr_3$ doped with large divalent ions, e.g., $Pb^{2+}$ or $Eu^{2+}$.

Chemical analysis of the crystals of undoped $CsCdBr_3$ showed no large amounts of impurities, so that it seems unlikely that this emission originates from impurities. Another possibility to explain this emission would be the presence of $Cd^{\cdot}$ in the crystal. This type of center has $s^2$ configuration and can give rise to luminescence. Because the crystal was grown in a bromine atmosphere, formation of this type of center is unlikely. The luminescent centers are not formed under the influence of radiation. A crystal of $CsCdBr_3$ was exposed to ultraviolet radiation for several hours. After this treatment no changes in the luminescent properties were observed.

Experimental work on $KNiCl_3$ leads us to the hypothesis that the luminescent centers may be due to stacking faults. The compound $KNiCl_3$ adopts the same crystal structure as $CsCdBr_3$. Recent investigations on this compound by Visser *et al.* showed a large amount of disorder in the lattice (*1, 17*). In these hexagonal $ABX_3$ compounds the chains of face-sharing octahedra are shifted relative to each other. By using electron diffraction it was shown that these displacements are not very well ordered throughout the observed regions. In parts of the crystal the diffraction pattern could be indexed on the basis of two overlapping super structures. This is a local ef-

fect and cannot be detected by X-ray diffraction. The origin of these extra reflections lies in a different kind of stacking. It is possible that those phenomena occur also in $CsCdBr_3$. In that case the luminescence originates probably from a bromine ion in a part of the crystal where the stacking is slightly different. The excited state on these bromine ions can be considered as a bound exciton and is comparable to the excited state at $I^-$ in $CdBr_2$ (*18*). The $I^-$ ion in $CdBr_2$ has also an excited state below the optical absorption gap and gives rise to luminescence. It will be shown below that the exciton bound to stacking faults in $CsCdBr_3$ becomes mobile above some 80 K.

This hypothesis is enhanced by the fact that in $CsCdBr_3$–$Pb^{2+}$ and $CsCdBr_3$–$Eu^{2+}$ the intensity of the 3.29 eV emission is higher than in undoped $CsCdBr_3$. The compound $CsPbBr_3$ adopts the cubic perovskite structure (*22*), while $CsMnBr_3$ has a hexagonal structure (*23*). The radius of the $Cd^{2+}$ ion is in between the radii of $Mn^{2+}$ and $Pb^{2+}$ (*24*). The compound $CsCdBr_3$ has a hexagonal structure. The introduction of $Pb^{2+}$ or $Eu^{2+}$ ions in the lattice can cause distortions in the stacking of the bromine ions. In this way a single $Pb^{2+}$ or $Eu^{2+}$ ion is able to introduce many distorted bromine ions. On the other hand the 3.29 eV emission is not observed for crystals of $CsCdBr_3$–$Mn^{2+}$. Probably the hexagonal stacking is stabilized by smaller divalent ions like $Mn^{2+}$. The 3.29-eV emission is not observed for crystals of $CsCdBr_3$–$Bi^{3+}$ and it is weak for crystals of $CsCdBr_3$–$Ce^{3+}$. Obviously the hexagonal stacking can also be stabilized by the $M^{3+}$–vacancy–$M^{3+}$ complex (with $M^{3+}$ = $Bi^{3+}$ or $Ce^{3+}$).

In conclusion, the ultraviolet emission observed for $CsCdBr_3$ is tentatively related to bromine ions in a slightly distorted environment. The number of these distorted bromine ions is strongly influenced by the nature of dopant ions.

*$CsCdBr_3$–$Pb^{2+}$*

The luminescence properties of $CsCdBr_3$–$Pb^{2+}$ are complicated. Several emission and excitation bands with remarkable temperature dependencies are observed. At 8 K two emission and excitation bands are observed. One set of spectra is identical to those of the center observed in the case of undoped $CsCdBr_3$. The temperature dependence is also the same: the emission is quenched at a temperature of 100 K. There is also an emission band at 2.45 eV with excitation bands at 3.72 and at 3.81 eV (Fig. 6a). Quenching of this emission starts at temperatures above 40 K (Fig. 7). The decay time is short at 4.2 K (~50 nsec). This emission is ascribed to a $Pb^{2+}$ ion on a $Cd^{2+}$ site. In first approximation the $Pb^{2+}$ ion is octahedrally coordinated. Like the $Bi^{3+}$ ion, the $Pb^{2+}$ ion has $6s^2$ configuration. The ground state is $^1A_{1g}$ (in Mulliken notation in case of $O_h$ symmetry; $^1S_0$ in the case of the free ion). The excited state consists of $^3A_{1u}(^3P_0)$, $3T_{1u}(^3P_1)$, and $^3E_u$ + $^3T_{2u}(^3P_2)$ in sequence of increasing energy. The transition $^1A_{1g} \rightarrow {}^3T_{1u}$ is allowed

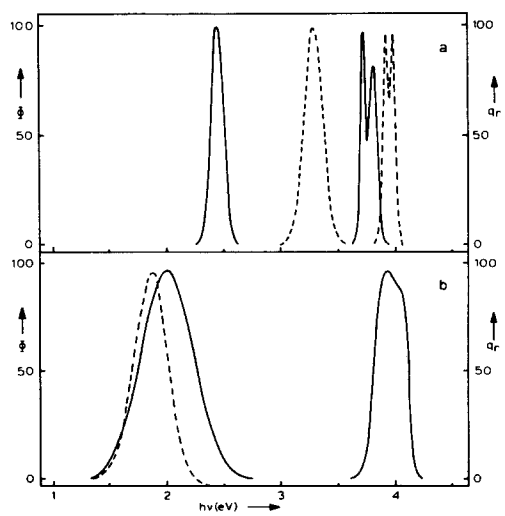


FIG. 6. Emission and excitation spectra of the luminescence of $CsCdBr_3$–$Pb^{2+}$ at 8 K (a) and at 300 K (b). Dashed line in (b) is the emission spectrum at 120 K.

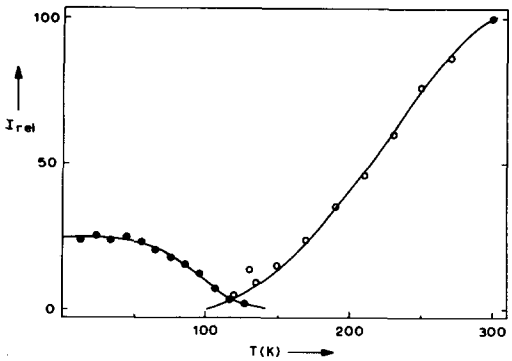


FIG. 7. Temperature dependence of the relative intensity of the two emission bands in $CsCdBr_3$–$Pb^{2+}$. The (●) refers to the 2.45-eV emission. Excitation energy was 3.75 eV. The (○) refers to the 1.85-eV (2.00-eV) emission, excitation was at 3.80 eV.

by spin–orbity interaction. The transitions from $^1A_{1g}$ to $^3A_{1u}$ and $^3E_u$ + $^3T_{2u}$ are forbidden. Usually emission at low temperature is from the $^3A_{1u}$ level (forbidden) and at higher temperatures from the $^3T_{1u}$ level. The actual site symmetry of the $Pb^{2+}$ ion is trigonal. This lowering leads to a splitting of the $^3T_{1u}$ level. This is the splitting observed in the excitation spectrum. It amounts to 0.1 eV.

There are two possibilities to explain the short decay time of the emission at low temperature. The first is that, due to the trigonal site symmetry of the $Pb^{2+}$ ion, one of the $^3T_{1u}$ components is lower in energy than the $^3A_{1u}$ level, so that even at low temperature no emission is observed from the $^3A_{1u}$ level. The second and more probable possibility is that the $^3A_{1u}$ level is still lower in energy than the $^3T_{1u}$ level (or components from this level) but that even at low temperature part of the emission originates from the $^3T_{1u}$ level. Recently Kang *et al.* pointed out that in that case only the short decay time is observed, if conventional detection techniques are used (*19*). From our experimental results we are not able to decide which explanation is the correct one.

At temperatures above 100 K another emission band appears. The intensity of this emission band increases steadily with increasing temperature. At 300 K the intensity of this emission band is about four times the intensity of the 2.45-eV emission at 8 K. The position of the emission band shifts from 1.85 eV at 120 K to 2.00 eV at 300 K (Fig. 6b). The decay curves of this emission are exponential. The decay time is constant in the temperature region of 120 K up to 300 K, viz. 1.6 $\mu$sec. The position of the excitation band is independent of temperature. The excitation band is almost identical to the excitation band of the 3.29-eV emission observed for undoped $CsCdBr_3$. The excitation band belonging to the 1.85-eV emission of $CsCdBr_3$–$Pb^{2+}$ is thermally broadened. Because of the agreement of the excitation bands it is assumed that the 1.85-eV emission belongs to $Pb^{2+}$ ions in the vicinity of distorted bromine ions as pointed out above. At temperatures below 100 K, the 3.29-eV emission is observed just like for undoped $CsCdBr_3$. At higher temperatures the exciton state on the bromine ions becomes mobile and the 3.29-eV emission is quenched. In the case of $CsCdBr_3$–$Pb^{2+}$, the $Pb^{2+}$ ions in the stacking fault area trap the migrating exciton which recombines radiatively at the $Pb^{2+}$ ions.

This model is confirmed by time-resolved measurements shown in Fig. 8. At first sight it was surprising that in this experiment the 2.45-eV emission is still observed. However, this is due to the excitation source. The excitation energy from the $N_2$ laser is at 3.67 eV. This is at the center of the excitation band of the 2.45-eV emission, but only at the low-energy side of the excitation band of the 1.85-eV emission. This fact, together with the high intensity of the laser excitation, makes it possible to observe the 2.45-eV emission even at 160 K. At the moment of the laser pulse only the 2.45-eV emission is observed (Fig. 8a). At a time of about 50 nsec after the laser pulse the 1.85-eV emission is observed, while the intensity of the 2.45-eV emission has de-

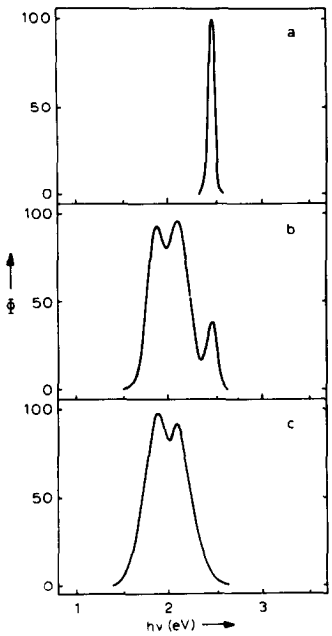


FIG. 8. Time-resolved emission spectra of $CsCdBr_3$–$Pb^{2+}$ at 160 K, (a) at the laser pulse, (b) 50 nsec after the laser pulse, (c) 200 nsec after the laser pulse. Excitation energy was 3.67 eV ($N_2$ laser).

creased (Fig. 8b). At about 200 nsec after the laser pulse the intensity of the 1.85-eV emission is not increased further, while the 2.45-eV emission is completely quenched (Fig. 8c). In addition to the 1.85-eV $Pb^{2+}$ emission we observed a similar emission at somewhat higher energy (Fig. 8). It might be that the $N_2$ laser, which excites into the tail of the excitation band, excites some special types of stacking faults which contain slightly different $Pb^{2+}$ ions.

Figure 8 seems to suggest energy transfer from the 2.45-eV-emitting $Pb^{2+}$ center to the 1.85-eV-emitting $Pb^{2+}$ center. Figure 7 shows that this is not the case, because the total $Pb^{2+}$ output is not independent of temperature. There is a pronounced minimum around 130 K and the RT output is much larger than the LHeT output. The buildup of the 1.85-eV emission agrees with the model sketched above in which the bound exciton becomes mobile above 80 K. The results show that transfer of the excitation energy to the $Pb^{2+}$ ions is a fast process, the excitation energy being transferred within 50 nsec.

The temperature change of the 1.85-eV $Pb^{2+}$ emission is rather drastic (Fig. 6b). The increase of the halfwidth points to a vibrational frequency involved of some 120 $cm^{-1}$, which seems to be reasonable. A shift to higher energy has been observed before for $s^2$ ions with large Stoke shifts (*20, 21*).

It can be concluded that at low temperatures luminescence is observed from $Pb^{2+}$ ions on a regular lattice site. At temperatures above 100 K luminescence is observed from $Pb^{2+}$ ions in a slightly distorted environment. This distortion is probably a consequence of stacking faults of the bromine ions and may be enhanced by the presence of the $Pb^{2+}$ ions. Excitation occurs in the bromine system and rapid energy transfer to the $Pb^{2+}$ ions is observed.

Finally we note that we found similar results for $Sn^{2+}$ ions in $CsCdBr_3$. The luminescence intensities were considerably lower than for $Pb^{2+}$, so that the $Sn^{2+}$ emissions were not studied any further.

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