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Reactions of Mercury-Like Ions in Potassium Halide Lattices

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Cadmium and zinc enter the alkali halide matrices as M^{2+} ions and exhibit characteristic absorption bands in the uv. Often these divalent species aggregate to form dimers (and polymers). After additive coloration of the doped single crystals, reduction occurs and monovalent monomers or dimers, and neutral atomary centers are formed. The monovalent dimers exhibit a broad ESR signal with a g value of ~2.2.

Introduction

The spectra of single crystals of cadmium chloride, bromide, and iodide and of zinc iodide were studied by Fesefeld (*1*). Two absorption bands were found for each system as shown in Table I. Butkov et al. (*2*) studied the spectra of these crystals and interpreted them as electron transfer from the halide to the metal ion, the intermediate being the halogen atom in an excited state.

Fromherz (*3*) studied the spectra of halide complexes of Zn^{2+} and Cd^{2+} in solution. These spectra were compared with those of the individual cations and anions and it was concluded that the spectra of the complexes stem from electron transfer from the halide to the divalent cation. Hilsch (*4*) pointed out the striking similarities in spectra between concentrated halide solutions and doped crystals, indicating the identity of the species present in the solid with the known $[MX_n]^{(n-2)-}$ complex in solution.

Monovalent Zn^+ and Cd^+ ions contain s as well as d electrons: $(n-1)d^{10}\,ns$, hence the spectra could stem from excited states of the metallic ion and should be more complicated than the electron transfer spectra of the divalent complexes.

TABLE I

PEAKS IN NANOMETERS OF SINGLE CRYSTALS OF HALIDES OF Zn^{2+} AND Cd^{2+}

	I^-	Br^-	Cl^-
Cd^{2+}	238; 320	212; 230	166; 194
Zn^{2+}	~220; 270	—	—

Reduced species of Zn^+ and Cd^+ were obtained in solution by flash photolysis by Baxendale et al. (*5–7*) and also in molten salts by Corbett et al. (*8, 9*), who recognized the existence of the dimer Cd_2^{2+} (a species well known in the case of mercury) both in aqueous solutions and in the solid state (*10, 11*). Reduction can also be affected by reaction of the divalent impurity in the alkali halide matrix with F centers initially formed by additive or radiative coloration, according to

$$M^{2+} + F \rightarrow M^{+} + - \quad \text{(an anion vacancy).}$$

The identification of the reduced species in solution was not unambiguous, owing to their instability and very short lifetime. In the solid the stability is much higher, but even then the identification is not easy and its confirmation is based upon a great deal of experimental data and reasoning by analogy. In former studies (*10, 11*) we reported the reactions of mercury ions in several potassium halide lattices and those of Zn^{2+}, Cd^{2+}, and Hg^{2+} in KCl. The present work reports the completion of this series of investigations, and deals with the reactions of Zn^{2+} and Cd^{2+} ions in KBr and KI matrices in relation to the results reported earlier.

Experimental

(*a*) *Materials and Instruments*

Single crystals were grown from the melt by the Stockbarger method starting with Baker's analyzed reagent grade materials. The dehydrated salts $CdBr_2$ and $ZnBr_2$ were prepared by heating the respective hydrates overnight to 75°C, and then at low pressure and 100°C with continuous pumping down to 10^{-5}

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Torr. ZnI_2 was prepared by the solid–solid reaction $Zn + HgI_2 \rightarrow ZnI_2 + Hg$, and the mercury produced was distilled off. Additive coloration with potassium vapor was performed in Pyrex containers (*12*) in vacuum at 500°C for times varying from 1 to 10 hr. The optical absorption was recorded either on a Perkin–Elmer Model 137 uv spectrophotometer or on a Cary 14. In all cases the crystals were opaque after growth, displaying a two-phase system. However, all the crystals became completely transparent and homogeneous after being reheated to 500°C in newly evacuated ampoules and quenched. The identical optical spectra of different slices of the boule attested to its homogeneity.

More extensive experimental details are given in Refs. (*10*) and (*11*).

(*b*) *Analysis*

The contents of the zinc and cadmium in the crystals thus grown was determined by atomic absorption spectrometry using a Perkin–Elmer Model 303. The doped crystals were reheated after growth for 10 min at 500°C in order to dissolve large aggregates, and quenched to 77°K. The optical absorption at 298°K of cleaved plates was determined first, and then the atomic absorption of the dissolved crystals; the concentration of the impurity was calculated on the basis of a suitable calibration curve. Using Smakula's formula (*13*) as corrected by Dexter (*14*):

$$Nf = 0.87 \times 10^{17}[n/(n^2+2)^2]\,\alpha_{\max}\,\omega$$

the oscillator strength f of the impurity bands in KI and KBr was thus calculated. The oscillator strengths of the A bands are summarized in Table II. These f values are smaller than those found for mercury-doped alkali halides (*11*).

Results

(*a*) *Cadmium in Potassium Halides*

CdI_2-doped KI crystals are yellow; they show a band, designated X in this article for the sake of reference, peaking at 288 nm, and a steep rise towards the short wavelength region. Thermal treatment followed by measurement of the spectrum at 77°K reveals the existence of thermal equilibrium for the X band:

$$292\ \text{nm} \underset{\text{annealed}}{\overset{\text{quenched}}{\rightleftharpoons}} 275\ \text{nm},$$

and a distinct shoulder at ~235 nm (see Fig. 1). A probable assignment for these bands is: Cd^{2+} for both A (275 nm) and C (235 nm) bands, and Cd^{2+} dimer or higher aggregate for the X band, in analogy with the behavior found for mercury (*11*).

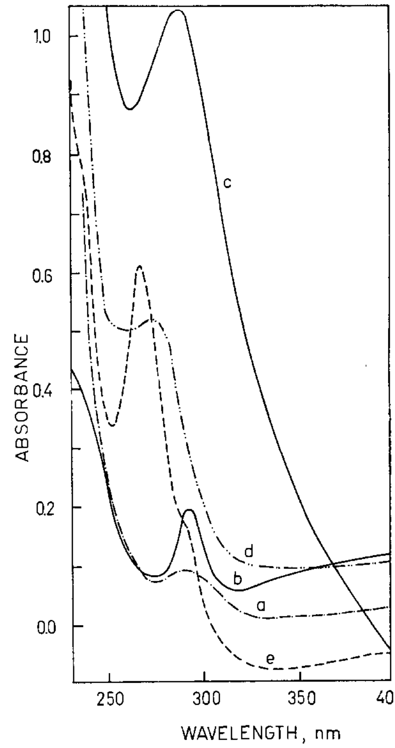

FIG. 1. Spectra of $KI:Cd^{2+}$ (0.5 wt%) crystals: (a) as grown; (b) after thermal treatment; (c) a thick (b) sample measured at 77°K; (d) as (b) after prolonged thermal treatment; (e) as (d) measured at 77°K.

TABLE II

CONCENTRATION AND OSCILLATOR STRENGTH OF CADMIUM- AND ZINC-DOPED ALKALI HALIDE BANDS

Crystal	N (No. of centers/cm^3)	n (Refractive index) (12)	Band peak (in nm)	$\alpha_{\max}$/cm	Width (in eV) at half-height ω	f
$KI:CdI_2$	6.7×10^{18}	1.91	275	4.53	0.57	2×10^{-3}
$KBr:CdBr_2$	5.2×10^{18}	1.73	250	16.40	0.53	9×10^{-3}(?)
$KI:ZnI_2$	2.2×10^{18}	2.09	245	2.12	0.46	2×10^{-3}
$KBr:ZnBr_2$	2.1×10^{19}	1.91	212	2.78	0.42	2×10^{-4}

Such a Cd-doped crystal when additively colored for 1 hr becomes intensely colored (~10^{19} *F* centers/cm^3) to a depth of about 4 mm. Besides the *F* band, a band peaking at 510 nm and a third band at 355 nm, more towards the interior of the plate, appear. In the innermost region of the cleaved plate where the latter bands cannot be observed, or where they are greatly reduced in intensity, the 292 nm Cd^{2+} *X* band develops (see Figs. 2A and 2B). Figure 3 shows a plot of the absorbance of the various bands as a function of distance from the edge of the plate exposed to coloration. A study of this plot makes the following assignments seem adequate: (a) The 510 nm band is a Cd^0 atomary center appearing in the *F*-band region of the plate, its intensity decreasing along with that of the *F* band; (b) the 355 nm band is a Cd^+ center, being a partly reduced species appearing further inside the plate with a maximum intensity at about 2.5 mm from the edge; and (c) the *X* band, peaking at ~290 nm, appearing in the region into which *F* diffusion has not reached, is a divalent cadmium species.

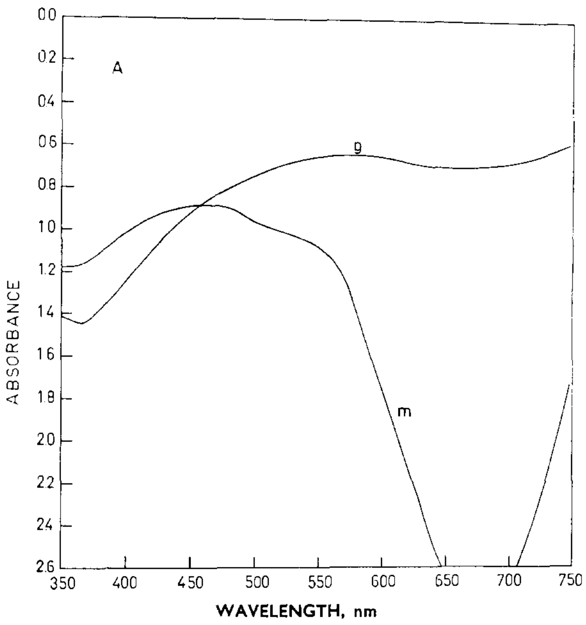

FIG. 2A. Visible spectra of additively colored KI:Cd^{2+} (0.5 wt%) crystals; (g) weakly colored zone; (m) strongly colored zone.

Our identification for the M^0 atomary centers is based on two facts: (1) The length of coloration time and/or pressure of potassium vapor during coloration has to be high if this double-reduced species is to appear. (2) The intensity of these centers decreases along with the *F*-band intensity in the outer region of the plate, as was noted previously (*10*, *11*). The formation of an F_A center is inconceivable since this band is only a slight perturbation of the *F* band caused, e.g., by a Na^+ ion in a K^+ lattice, and it should appear within a few nm of the *F* band or sometimes as a superimposed shoulder on it (*12*). In our case, the M^0 center is a distinct band *ca.* 200 nm away from the *F* band. The intensity of the *K* and *L* bands is 10^{-2}–10^{-3} that of the *F* band in the same crystal, and they can be observed only in extremely highly colored crystals (*12*). In our case, the intensity of M^0 atomary centers is of the same order of magnitude as that of the *F* center. Moreover, the M^0 bands persist even after complete thermal bleaching of the *F* band, proving that they stem from a distinct center depending on the impurity. This discussion rules out the possibility of these centers being F_A, *K*, or *L* centers.

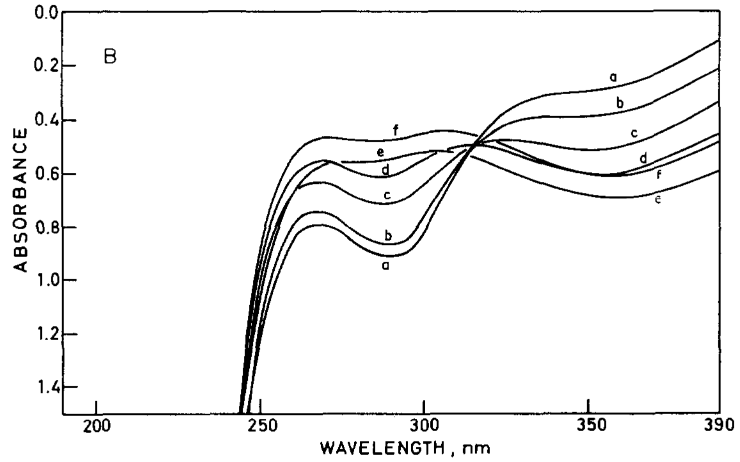

FIG. 2B. Ultraviolet spectra of additively colored KI:Cd^{2+} (0.5 wt%) crystals: (a)–(f) are successive spectra recorded from the *interior* of the crystal towards the outer face.

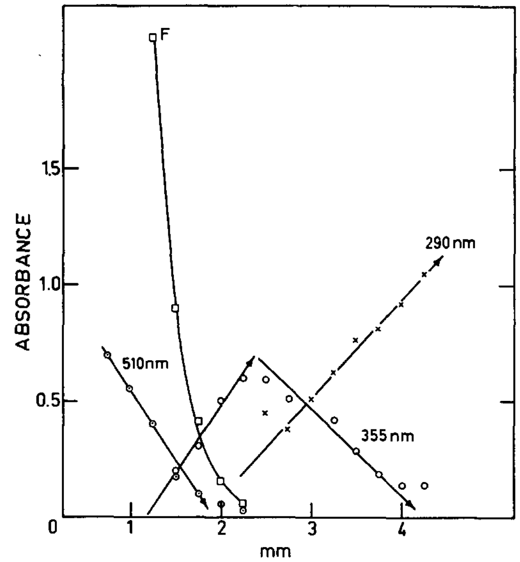

FIG. 3. Intensity of absorption bands as a function of distance (in mm) from the exposed crystal face in additively colored KI:Cd^{2+} crystals: 510 nm—Cd^0; 355 nm—Cd^+; 290 nm—Cd^{2+} (*X* band); *F* center.

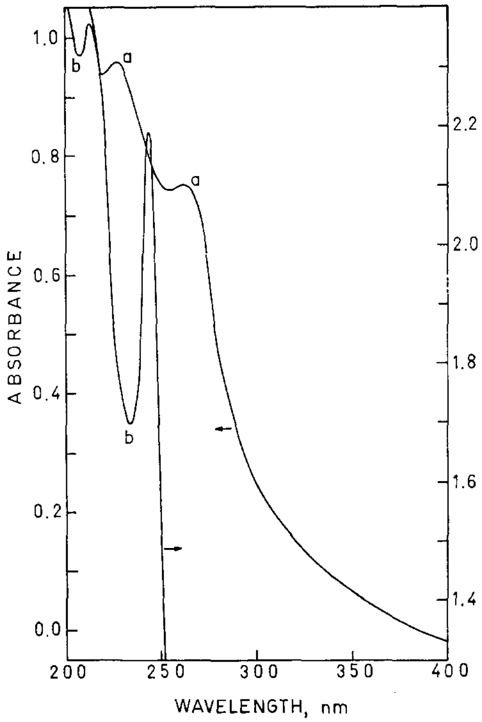

FIG. 4. Spectra of KBr:Cd^{2+} (0.3 wt%) crystals: (a) after thermal treatment; (b) as (a) measured at 77°K.

$CdBr_2$-doped KBr crystals show after thermal treatment an absorption spectrum composed of two bands: one peaking at 263 nm (*Y* band) and another one at 227 nm (see Fig. 4). Both bands are shifted simultaneously to shorter wavelengths, 250 and 212 nm, respectively, after prolonged thermal treatment of the doped crystals, or when the concentration of the impurity is reduced. It is suggested that this shift towards shorter wavelengths is due to the dissociation of the proposed dimer $(Cd^{2+})_2$ into monomers, as observed above with KI. The 227 and 212 nm bands are distinct and well separated; on the other hand, the *Y* band is, in fact, composed of two overlapping bands: one at shorter wavelength (~250 nm) and one at a longer wavelength (>263 nm). Owing to their closeness, complete resolution could not be effected and the peak position of the longer wavelength band could not be ascertained. This double band spectrum in both KI and KBr has also been observed by Fesefeld (*1*).

The additively colored KBr:Cd crystal shows three very broad bands in the range 280–370 nm. These bands can be distinguished from each other and their peak positions fixed at 280, 300, and 365 nm (see Fig. 5) after thermal annealing and recording of the spectra at varying distances from the outer surface of the plate. In the outer layers, the most prominent band is the one peaking at 280 nm; on advancing inwards, the peak shifts gradually to ~320 nm while the intensity of the absorption increases (see Fig. 5a–d). In the innermost zone, a band peaking at 365 nm appears with the simultaneous reappearance of the Cd^{2+} *Y* band peaking at ~260 nm (see Fig. 5e). To account for the relative position of these bands in the crystal plate, we propose the following assignments: (a) The 280 nm band is Cd^+; (b) the 300 nm band is due to a monovalent dimer $(Cd^+)_2$; (c) the 365 nm band is Cd^0, formed by disproportionation of the monovalent $(Cd^+)_2$ species. After prolonged thermal treatment the *F* band is bleached out and with it both the longer and shorter wavelength bands observed in the additively colored crystal plate, with the exception of the 300 nm band which is stabilized (see Fig. 5h–f). High temperature could cause the ionization of the Cd^0 centers (365 nm) to form monovalent cadmium ions (300 nm); while aging at 298°K might cause this reduced species to disproportionate

$$(Cd^+)_2 = Cd^0 + Cd^{2+}.$$

The appearance of Cd^0 together with Cd^{2+} ions in the interior of the crystal is thus explained. This disproportionation reaction has already been observed in $CdCl_2$-doped KCl (*10*). In addition, Cappelletti (*15*), studying the additive—and X-ray—coloration of Cd^{2+}-doped NaCl, identified two bands

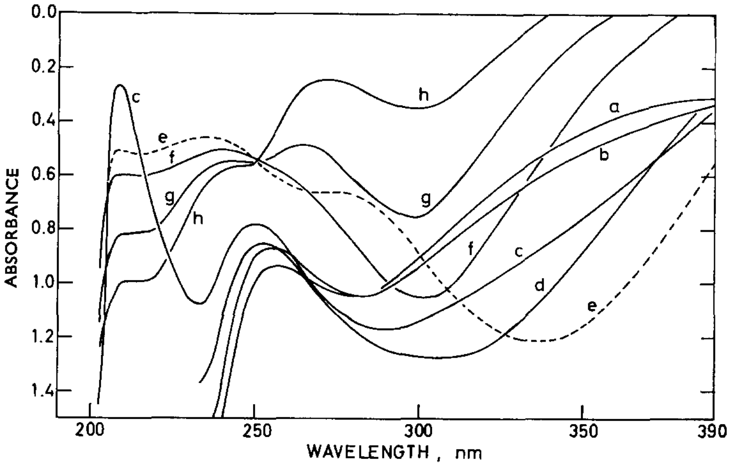

FIG. 5. Spectra of additively colored KBr:Cd^{2+} (0.3 wt%) crystals: (a)–(e) are successive spectra recorded from the outer side of the crystal towards its interior; (f)–(h) show the effect of thermal treatment on the interior region.

peaking at 278 and 295 nm as Cd^+ and Cd^0 centers, respectively. Other absorption bands observed in the same region (270–340 nm) were not identified. Since impurities behave alike in NaCl and KCl matrices, Cappelletti's results afford further proof for the assignments proposed by us (*10*). Earlier studies (*16*, *17*) on X-irradiated doped NaCl crystals also conform with this interpretation.

(*b*) *Zinc in Potassium Halides*

The spectrum of ZnI_2-doped KI crystals show an absorption band peaking at 245 nm. This band is probably somewhat distorted by overlap of the fundamental KI absorption. After additive coloration of the doped crystals, the cleaved crystal plate displays two colored zones, instead of the usual three which were observed in all other cases: an outer blue zone (*F* centers) and an inner colorless zone. In the outer zone, a 440 nm band appears besides the *F* band, and, somewhat more towards the interior, a band peaking at 330 nm can be observed. Both bands are rather weak. We suggest that they be identified as Zn^0 and Zn^+, respectively. It is nearly impossible to observe the original Zn^{2+} band in the inner colorless zone because of the overlap by an intense *U* band.

A $ZnBr_2$-doped KBr crystal shows no absorption bands after growth in the uv range investigated by us. However, after thermal treatment a faint shoulder superimposed on the fundamental KBr band can be observed at ~212 nm. The additively colored plate exhibits, again, only two zones. In the outer colored zone a band peaking at 275 nm is observed, and when the crystal is very intensely colored a second band peaking at 370 nm appears in the same zone. These observations, together with the change of intensity of the bands plotted vs. distance from the edge of the cleaved plate (see Fig. 6) suggest the following assignments: the 370 nm band is Zn^0; the 275 nm band is Zn^+; and the ~212 nm band is Zn^{2+}.

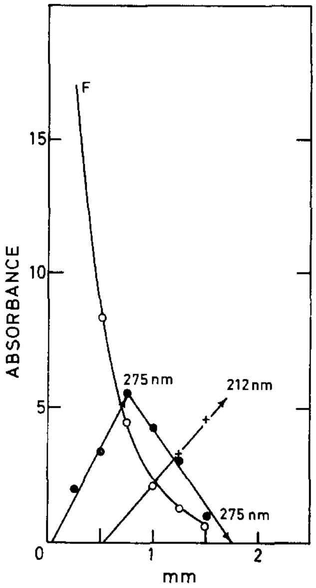

FIG. 6. Intensity of absorption bands as a function of distance (in mm) from the exposed crystal face in additively colored KBr:Zn^{2+} (0.4 wt%) crystals: 275 nm—Zn^+; 212—Zn^{2+}; *F* center.

Table III summarizes the results obtained with the four doped crystals studied in this work.

TABLE III

IDENTIFICATION OF ABSORPTION BANDS IN KI AND KBr CRYSTALS DOPED WITH Cd^{2+} OR Zn^{2+}

a. Before coloration

	KI		KBr	
	M^{2+} (nm)	$(M^{2+})_2$ (nm)	M^{2+} (nm)	$(M^{2+})_2$ (nm)
Cd^{2+}	235, 275	292	212, 250	227, >263
Zn^{2+}	245		212	

b. After coloration

	KI		KBr	
	M^+ (nm)	M° (nm)	M^+ (nm)	M° (nm)
Cd	355	510	280 (300 = $(M^+)_2$)	365
Zn	330	440	275	370

Discussion

Following our success with HgX_2 (*11*), the coating of undoped alkali halide single crystals (Harshaw) with cadmium and zinc salts by a rubbing-in process was attempted. At the most, only very shallow spectra could be observed after prolonged treatment, and hence the band assignments could generally not be confirmed by this method, except for KBr coated with $CdBr_2$. These crystals do indeed show a spectrum similar to that of the doped single crystals. Recently, Cd^{2+}- and Zn^{2+}-doped alkali halides were also studied by Jain et al. (*18*, *19*). Their observations, summarized in Table IV, agree only partly with ours (compare with Table IIIa). This discrepancy can be explained as follows. The concentration of impurities in Jain's samples was about one-fourth of that present in our crystals, due to the crystal growth technique employed: Jain's crystals were grown by the Kyropulous method in open vessels and probably lost by volatilization a large part of the material added to the melt. As a result of the lower concentration, the very weak long wavelength bands in the Cd-doped KI crystals were not observed. (Those in KBr are also rather weak.) On the other hand, Jain's spectra of the KBr crystals doped by Cd^{2+} are surprisingly similar to those doped by Zn^{2+} and it should not be precluded that they may stem from a common impurity which polluted the system during crystal growth.

TABLE IV

ABSORPTION BANDS (IN NANOMETERS) OF Cd^{2+}- OR Zn^{2+}-DOPED KBr AND KI (REPORTED BY JAIN)

	KI	KBr		
Cd^{2+}	235	202	215	280
Zn^{2+}	—	202	225	275

The divalent ion spectra observed in this work become narrower and shift to higher energies when taken at 77°K. Also, the energy difference Δ between the alkali halide exciton band and the impurity band is fairly constant for each impurity ion (see Table V), suggesting that the M^{2+} spectra stem from charge transfer from a halogen ion to an alkali ion adjacent to the impurity center. The same interpretation has been adopted for the spectra of alkali halides doped with mercury ions (*11*).

It should be mentioned here that the apparent oscillator strength of Cd^{2+} in KI was found to be smaller than that of Cd^{2+} in KBr (see Table III). This reversal of the expected values may arise from the monomer $\rightleftarrows$ dimer equilibrium; whereas in the case of the KI-doped crystals, two distinct peaks could be observed and conversion to one of the species was affected quantitatively, in the case of the KBr crystals the closeness of the peaks did not make their quantitative separation possible. We believe that the true oscillator strength for $KI:Cd^{2+}$ should be equal to, or higher than, that for $KBr:Cd^{2+}$.

The absorbance of the monovalent cadmium centers (produced by additive coloration) grows more intense from the outer surface of the crystal plate inwards, reaches a maximum value and then weakens. Crystals containing such centers (355 nm in KI and ~300 nm in KBr) give a very broad resonance signal and a high g value: 2.2. This high g value and the thermal stability of the centers suggest the presence of dimers (as well as monomers) of the monovalent species in the crystal. Two Cd^+ ions in neighboring sites, ⟨110⟩, may interact by an exchange of electrons affecting the ESR signal in this fashion. Otherwise, this anomalous observation

TABLE V

ENERGY (IN ELECTRONVOLTS) OF THE ALKALI HALIDE EXCITONS AND OF THE FIRST IMPURITY BANDS

	KI	Δ	KBr	Δ
Exciton	5.7	—	6.6	—
Zn^{2+}	5.0	0.7	5.8	0.8
Cd^{2+}	4.5	1.2	5.0	1.6
Hg^{2+}	3.6	2.1	4.1	2.5

may be due to a magnetic interaction of the moments. The experimental data on the behavior of such ions in the alkali halide lattice is rather scarce. However, the phenomenon is consistent and reproducible in the case of the Zn–Cd–Hg group of ions. In fact, in the case of freshly grown uncolored monovalent mercury-doped KI crystals, which exhibited a band just below 300 nm attributed to Hg(I) (*11*), the same broad resonance signal with the same g value was obtained. Indeed no ESR signal appeared *unless* the optical spectra showed the existence of those centers assigned by us to the monovalent species.

The ESR signal diminished in the case of a KBr crystal kept in the desiccator for two months, and its absorption band shifted to longer wavelengths: 300 nm → 365 nm. Conversely, the 365-nm band is converted to the 300-nm band after thermal treatment. These observations support our assignments, i.e., that the 300-nm band stems from the dimer of the monovalent cadmium centers, and the 365-nm band from atomary neutral cadmium centers in the KBr lattice.

The observations of Jain et al. on additively colored KBr:Cd crystals were similar, except that the longer wavelength band is stated to peak at 330 nm and the ESR signal associated with the 300 nm band is stated to have a normal g value equal to 2. These authors suggested that the latter band is due to a colloidal cadmium center, $(Cd^0)_n$, although its band maximum is positioned at a shorter wavelength (300 nm) than the 330 nm band assigned to the atomary cadmium center. We cannot offer any explanation for this difference in the reported g values, but the experimental evidence indicates that the 300-nm band is a monovalent cadmium species, as shown above.

Additive coloration of zinc-doped alkali halides causes reduction in the intensity of the original M^{2+} absorption bands, and the appearance of three rather weak bands. These reduced zinc centers are partially bleached after thermal treatment, which indicates that they are less stable than the reduced cadmium species. Their thermal stability in the KI matrix is higher than in the KBr matrix.

Crystals which show absorption bands assigned to monovalent Zn^+ species (330 nm in KI and 275 nm in KBr) give an ESR signal similar to that of monovalent cadmium. Again the signal is broad and the g value is larger than 2, thus stressing the similarity in behavior of the monovalent species of zinc, cadmium, and mercury.

A short study was made on the effects of X-irradiation on the doped crystals, from which the following was concluded:

(a) The intensity of F coloration is much lower in the doped crystals than in the pure alkali halides.

(b) The stability of the new centers formed is different from that of V centers, which are easily bleached optically and thermally.

(c) The bands can be divided into two categories:

- (i) bands specific to the matrix (F and V bands), and
- (ii) new bands specific to the impurity.

The first category of bands are similar to some of those reported by Jain and designated D bands, while the others are similar to the bands produced by additive coloration in this study, although their thermal and optical stability is low. The fleeting appearance of these bands is further proof of the formation of M^+ (monomer and dimer) and M^0 centers as by-products of the coloration of Zn^{2+}- or Cd^{2+}-doped alkali halides.

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