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Reaction of Mercury Ions in Potassium Halide Lattices

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Single crystals of potassium halides grown from the melt doped with Hg(II) halides contain mainly Hg(II), and only small amounts of the Hg(I) species formed by partial decomposition. When the alkalihalides are doped with Hg(I), species found in the KI crystal are mainly Hg(I); both Hg(I) and Hg(II) in KBr, but in KCl the monovalent mercury salt decomposes almost completely to its elements. The different species were identified by a study of the spectra of the doped single crystals, before and after additive coloration, and the spectra of the pure alkalihalides coated with the respective mercury halide at room temperature.

Introduction

Among the group II_B elements, mercury is unique in having both mono and divalent ions in aqueous solution. Monovalent mercury dimerizes as a rule by the formation of a metal–metal bond, i.e., Hg^+–Hg^+. Hence mercury ions will undergo a variety of reactions depending on the concentration of the components, the matrix, and the temperature. Two equations presenting interconversion of the mercury ions are of interest in this work:

$$HgX_2 \overset{\text{matrix}}{\rightleftharpoons} Hg^+ + X^- + \tfrac{1}{2}X_2, \qquad (1)$$

$$Hg^{2+} \overset{\Delta}{\rightleftharpoons} Hg^0 + Hg^{2+}. \qquad (2)$$

In a former study (*1*) some difficulties were encountered in identifying the different species of mercury present in KCl crystals. The present investigation was undertaken in order to elucidate these difficulties by extending the scope of our investigations. KBr and KI as well as KCl matrices were used. Also experimental evidence of spectra obtained by coating the pure single crystals of the alkalihalides with the respective mercury salts at room temperature has been included.

Experimental

Single crystals were grown from the melt of Baker's analysed reagent grade material by the Stockbarger method. The amount of impurity added to the melt varied from 0.1–1.0 wt %. The crystals were reheated and quenched after growth in order to get homogenous transparent samples. Additive coloration was performed in Pyrex containers (*2*) in vacuum at 500°C, for times varying from 1 to 10 hr. The optical absorption was recorded on a Perkin–Elmer model 137 uv Spectrophotometer or on a Cary 14. A special holder with 0.5 mm slit was used in the sample beam which enabled moving a crystal plate, cut from the colored cube, in front of the slit so that the spectrum could be recorded from the surface towards the interior.

Coating of pure alkalihalide crystals with mercury salts was performed in the following manner. A small amount of the appropriate mercury salt was dispersed on a piece of paper and a plate of the alkalihalide was rubbed against it until some powder adhered to the crystal surface. Diffusion at room temperature was very fast when using Hg(II) salts, but rather slow or ineffective with Hg(I) salts.

The impurity was determined by dissolving a representative part of the doped crystal in water and measuring its absorbance in the ultraviolet. From a suitable calibration curve the impurity content was calculated (*3*). In Table I the concentration of mercury in some of our more concentrated samples are listed. Using Smakula's formula (*4*) as corrected by Dexter (*5*), the oscillator strength *f* of the mercury bands in the different alkalihalides was also calculated.

The values obtained appear to be reasonable when compared to that of other similar elements

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TABLE I

CONCENTRATION AND OSCILLATOR STRENGTH OF MERCURY DOPED ALKALIHALIDE BANDS

Crystal	No. of centers/cm^3	Band peak in nm	αmax/cm	Half width in ev	f
KCl:Hg(II)	9.5×10^{17}	245	6.93	0.89	5.1×10^{-2}
KBr:Hg(II)	3.0×10^{17}	300	3.40	0.53	3.5×10^{-2}
KI:Hg(II)	3.4×10^{17}	347	3.26	0.59	3.4×10^{-2}
KI:Hg(I)	3.4×10^{17}	450	1.32	0.50	1.2×10^{-2}

recorded in the literature (cf., the oscillator strength for Ag^+ in NaCl is of the order of a few hundredths at room temperature (*6*). All concentrations given in the text refer to the amount of mercury salt added to the melt.

Results

A. Mercury in KI

A solution of HgI_2 in conc KI shows the spectrum of $[HgI_4]^{2-}$, characterized by a band peaking at 350 nm and a shoulder at ~280 nm. Single crystals of KI doped with HgI_2 are slightly yellow and show also two bands peaking at 350 nm and at ~275 nm. An additional weak band is obtained at ~455 nm and the broadened appearance of the ~275 nm band indicates the presence of at least one more component. After heat treatment the 455-nm band completely disappears and the 275 nm band is considerably narrowed, see Fig. 1 (*a*), (*b*).

Single crystals of KI doped with Hg_2I_2 are distinctly yellow, show a prominent band peaking at ~455 nm, and two more distinct bands peaking at 260 nm and at ~280 nm. A shoulder just below 350 nm, and another one at ~290 nm was often observed, see Fig. 1 (*c*).

Comparing these two spectra we conclude that the band at ~350 nm is due to Hg(II) and the band at ~455 nm is due to Hg(I). Moreover, when doping with Hg(II) some Hg(I) is formed by decomposition, and vice versa. The complex of bands in the 260–290-nm region belongs to both species as indicated by further experiments. A KI crystal was grown by doping with Hg(II) and an approximately equimolar amount of elemental mercury, Fig. 1 (d). The two characteristic bands at 455 nm [Hg(I)] and at 350 nm [Hg(II)] were prominent in the spectrum of this crystal, and in the short wavelength region a resolved doublet appeared at ~260 and at ~290 nm.

The spectrum of KI coated with Hg(II) showed the 350-nm band and a wide band at ~275 nm with a shoulder at 290 nm superimposed on it. The spectrum of KI coated with Hg(I) was shallow in comparison. Also, free mercury was detected in the rubbed powder, hence some of the bands probably belong to Hg(II) owing to the disproportionation reaction see Fig. 2 (a), (b).

Thus the various absorption bands of mercury on KI can be safely identified as follows:

~260 nm	~275 nm	~280 nm
Hg(I)	Hg(II)	Hg(I)
(~290 nm)	~350 nm	~455 nm
$(\mathrm{Hg(II)}_w$	Hg(II)	Hg(I)

The 275-nm band in KI:Hg(II) is mostly broad with a blunt peak being overlapped by the 260- and

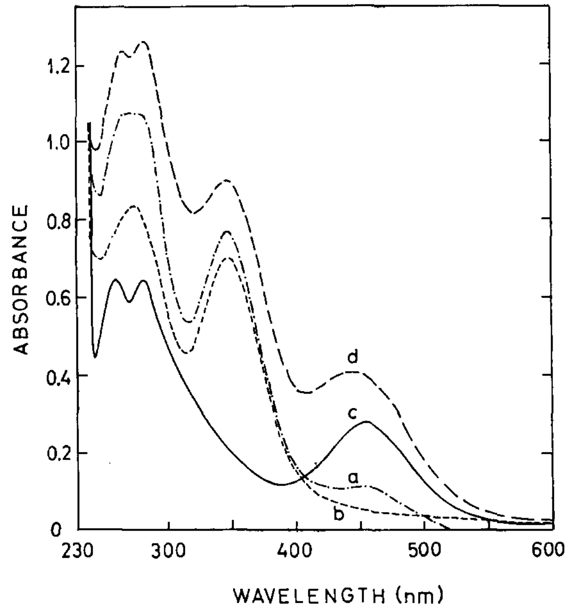


FIG. 1. Spectra of mercury doped KI. (a) KI:Hg^{2+} 0.48 wt % as grown; (b) KI:Hg^{2+} 0.48 wt % after thermal treatment; (c) KI:Hg^{2+} 0.52 wt % as grown; (d) KI:Hg^{2+} as grown.

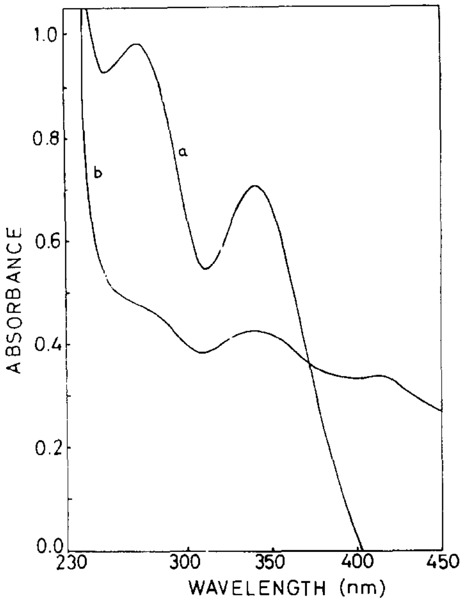
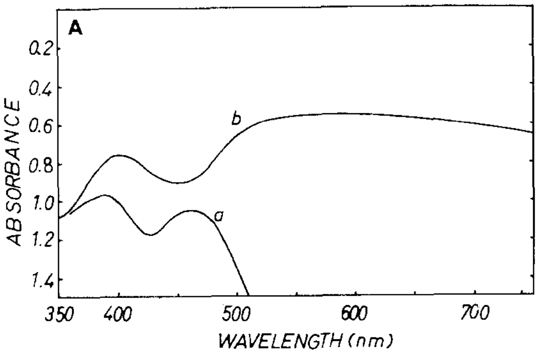


FIG. 2. Spectra of KI crystals coated with iodides of mercury. (a) KI coated with HgI_2; (b) KI coated with Hg_2I_2.



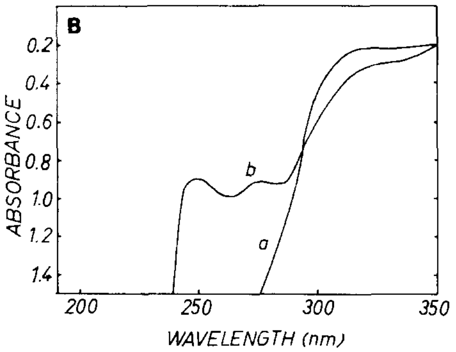


FIG. 3A. Visible spectra of additively colored KI:Hg^{2+} (0.48 wt %) crystals. (a) Strongly colored zone; (b) Inner zone, uncolored.

FIG. 3B. uv spectra of additively colored KI:Hg^{2+} (0.48 wt %) crystals. (a) Strongly colored zone; (b) Inner zone, uncolored.

280-nm bands on both sides and the weak 290-nm band superimposed on it as a shoulder. The intensity of the bands due to the monovalent species is, however, always greater in the crystals doped with Hg(I) than in those doped with Hg(II).

These assignments of the monovalent mercury spectrum were proved correct by additive coloration of divalent mercury doped KI crystals; the 350 nm and the ~275 nm band both greatly diminish as a result of coloration while the 260, the 280, and the 455 nm bands become prominent. When the F coloration is strong a new band peaking at 425 nm appears in addition. In fact, only the latter band is observed in portions of the crystal plate where coloration is very strong, while the bands due to Hg(I) appear exclusively in portions of the plate where F coloration has not penetrated see Figs. (3A), visible and (3B), uv. These observations suggest, that the 425-nm band should be identified with atomic mercury Hg^0 substituted in the lattice. This assignment is supported by Fig. 4, where the absorbance of the various bands as a function of distance from the surface of the colored crystal is plotted. The reduction of intensity of the Hg^0 band follows a similar pattern to that of the F band. This behavior is well known from former studies (*1*, *7*). In Fig. 4 one can also follow the formation and disappearance of the Hg(I) species (455 nm) and the persistance of the ~350 nm band, Hg(II), in the interior.

B. Mercury in KBr

KBr crystals doped with Hg(II) do not show distinct absorption spectra after growth. The spectra

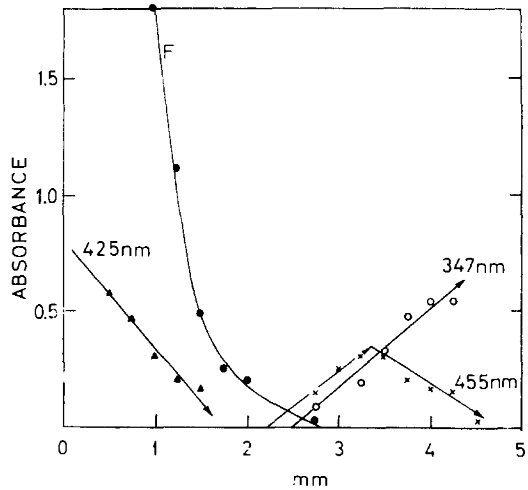


FIG. 4. Intensity of absorption bands as a function of distance (in mm) from the exposed crystal face in additively colored KI:Hg^{2+} crystals. 425 nm-Hg^0; 455 nm-Hg(I); 347 nm-Hg(II); F-band.

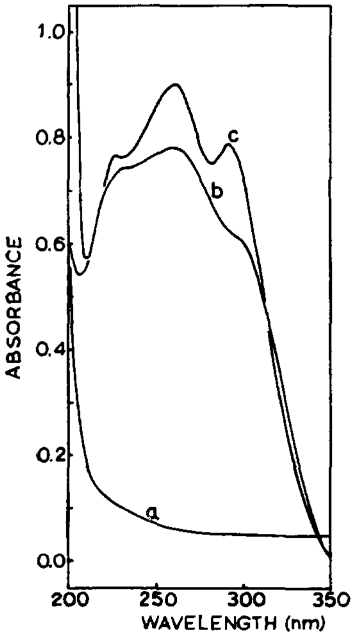


FIG. 5. Spectra of KBr:Hg^{2+} (0.4 wt %) crystals. (a) as grown; (b) after thermal treatment; (c) as (b), measured at l.n.t.

recorded after heat treatment and quenching have two bands peaking at 265 and at ~300 nm. There is a shoulder at ~315 and probably another absorption band at shorter wavelengths (around 220 nm), Fig. 5. The 265 nm band is rather broad.

Drops of mercury were observed in the ampoules in which KBr crystals doped with Hg(I) were grown; some disproportionation according to

$$Hg_2^{2+} \rightarrow Hg^0 + Hg^{2+}$$

has probably occurred. Hence one would expect to see absorption bands due to both Hg(I) and Hg(II). The spectra show absorption bands at ~300 nm and 315 nm, a very broad band between 260–275 nm, and a steep rise towards the shorter wavelength region, see Fig. 6. Evidently the spectra of the monovalent mercury- and divalent mercury-doped crystals resemble each other rather closely. However, two bands, at 260 and 315 nm, are more prominent in KBr:Hg(I) than in KBr:Hg(II) crystals and these very bands were found to be in thermal equilibrium with each other. Thus

$$260\text{ nm} \underset{\text{annealed}}{\overset{\text{quenched}}{\rightleftharpoons}} 315\text{ nm.}$$

Therefore the most probable assignment corresponding to this equilibrium would be

$$\text{Hg(I) monomer} \rightleftharpoons \text{Hg(I) dimer}$$

or $$2Hg^{+} \rightleftharpoons Hg_2^{2+}.$$

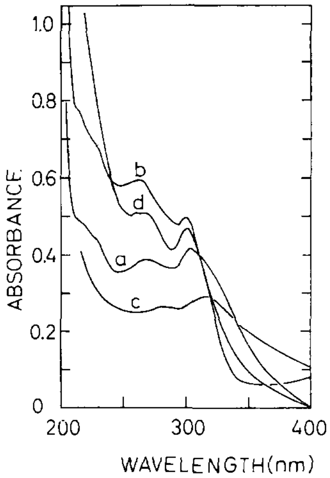


FIG. 6. Spectra of KBr:Hg_2^{2+} (0.3 wt %) crystals. (a) as grown and annealed; (b) after quenching; (c) after thermal treatment and quenching; (d) after prolonged thermal treatment, quenching and measured at l.n.t.

KBr crystals coated with Hg(II) show two bands peaking at ~300 nm and ~275 nm. A significant surface diffusion reaction was observed in this case; the absorbance at the peak wavelengths increased with time soon after the application of the coat as shown in Fig. 7. When coating with Hg(I) there is a distinct weak band at ~315 nm and a very weak absorption at ~260 nm. From the experimental data these assignments follow:

~260 nm	~275 nm	~300 nm	~315 nm
Hg(I) monomer	Hg(II)	Hg(II)	Hg(I) dimer

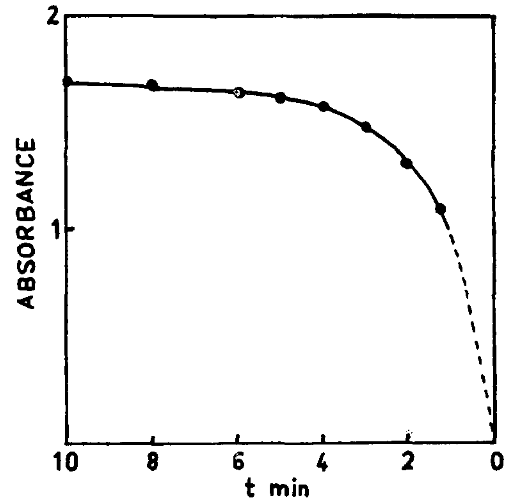


FIG. 7. Absorbance of KBr crystal coated with $HgBr_2$ as function of time (in min).

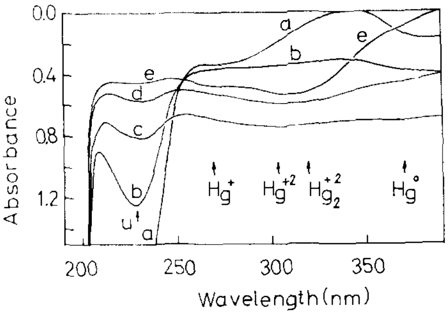


FIG. 8. Spectra of additively colored KBr: Hg^{2+} (0.4 wt %) crystals. (a)–(e) are successive spectra recorded from the outer side of the crystal towards its interior.

On intense additive coloration of KBr: Hg(II) crystals the ~300-nm band completely disappears and simultaneously a band at 260 nm, Hg(I), and a new band at 380 nm appear, see Fig. 8. Using considerations similar to those in the case of the additive coloration of KI: Hg(II), we wish to identify this new band as a Hg^0 center. In Fig. 9 one can follow the reduction in intensity of this band and the formation of the 315 nm band in the interior of the crystals, a behaviour which affords further proof to the above assignment.

C. Mercury in KCl

In a previous study (*1*) of the spectra of $HgCl_2$-doped KCl crystals two absorption bands at 245 and 265 nm in thermal equilibrium were observed. When additively colored, another band peaking at 290 nm was detected, but the assignments were doubtful and should now be revised in the light of further observations and comparison to the spectra of mercury in KBr and KI crystals.

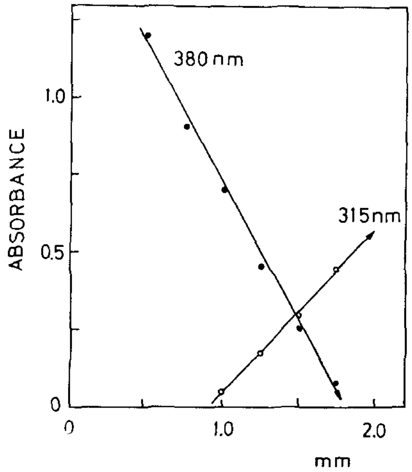


FIG. 9. Intensity of absorption bands as a function of distance (in mm) from the exposed crystal face in additively colored KBr: Hg^{2+} crystals. 380 nm–Hg^0; 315 nm–Hg(I).

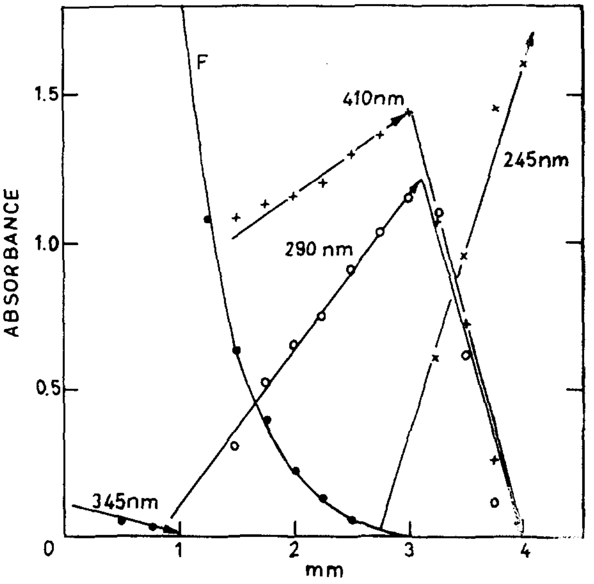


FIG. 10. Intensity of absorption bands as a function of distance (in mm) from the exposed crystal face in additively colored KCl: Hg^{2+} (0.5 wt %) crystals. 345 nm–Hg^0; 290 nm & 410 nm–Hg(I); 245 nm–Hg(II).

On comparing the spectrum of KCl coated with $HgCl_2$ with that of the doped crystal (after heat treatment) it was found that they both show the 245-nm band. The spectra of KCl coated with Hg_2Cl_2 on the other hand showed a distinct band at 290 nm. This same band had been observed on additive coloration of Hg(II)-doped KCl together with a band at 410 nm.

KCl crystals doped with mercury color with great difficulty and it was surmised that because of this difficulty the doubly reduced species had not been obtained in the prior study. After 10 hr additive coloration followed by heat treatment for 30 min, a new band at 345 nm was formed at the expense of both the divalent and monovalent species.

Figure 10 shows the change in absorbance as a function of distance, from the outer side towards the interior of the additively colored crystal plate for the several peaks mentioned, 345 nm (Hg^0), 290 nm and 410 nm (Hg(I)), and 245 nm (Hg(II)), as well as that of the F band. Thus the assignments of the band spectra of mercury in KCl should be as follows:

$$\begin{array}{ccc} 245\text{ nm} & & 265\text{ nm} \\ \text{Hg(II) monomer} & \leftrightarrow & \text{Hg(II) dimer} \end{array}$$

$$\begin{array}{ccc} 290\text{ nm} & 345\text{ nm} & 410\text{ nm} \\ \text{Hg(I)} & \text{Hg}^0 & \text{Hg(I)} \end{array}$$

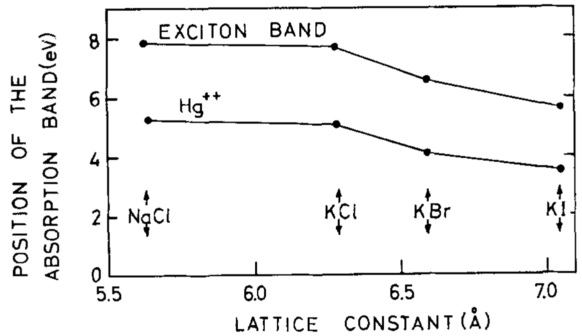


FIG. 11. Exciton band energies of the Hg(II) doped and the pure alkalihalides.

Discussion

In the literature no spectra of mercury[1] in alkalihalide lattices had been reported prior to the studies carried out in this laboratory (*1*, *8*). It is plausible that the coating of crystals with an impurity will affect the valency to a lesser extent than the drastic conditions and stresses imposed by crystal growth. Therefore, we assume that during coating followed by impurity diffusion no change in the valency of the impurity has occurred and the spectra recorded are those of the impurities in their initial state. The similarity between the spectra of the coated crystals (and pressed discs) and those of the doped crystals is thus the basis of our assignments of the divalent mercury species.

Plotting the peak energy of the short wavelength Hg(II) bands as a function of the lattice constants of the various alkalihalides, one obtains a curve that parallels the curve of the respective exciton bands, see Fig. 11. Hence the spectra of Hg(II) in the alkalihalides is due to charge-transfer from the halogen ion to the cation substituted in the lattice. Further it has been observed that the energy difference between the two Hg(II) bands in the various lattices was in good agreement with the known energy difference of the halogen doublets (*10*). See Table II.

Owing to the small energy difference of the doublet in chlorine atom the two bands overlap and cannot be resolved in the case of KCl:Hg(II).

The spectrum of KI:Hg_2^{2+} is quite different from that of KI:Hg^{2+} and one can easily distinguish the bands due to monovalent mercury from the weak divalent-bands, present in these crystals owing to slight disproportionation. Distinct monovalent bands are obtained in KBr after additive coloration. The partial disproportionation of Hg_2^{2+} to Hg^{2+} is larger in the case of the KBr melt, as can be deduced from the visible amounts of elemental mercury appearing in the ampoule after crystal growth.

TABLE II

ENERGY DIFFERENCE OF MERCURY(II) HALIDES DOUBLETS, $2p_{3/2}$—$2p_{1/2}$, IN cm^{-1}

	Δ halogen	Δ in single crystal	Δ in coated crystal
KI	7603	7500	7300
KBr	3085	3000	3000
KCl	881	—	—

In the case of KCl doped with Hg_2Cl_2, most samples completely decomposed; while in one or two experiments a weak spectrum very similar to that of the divalent mercury was obtained. Thus, the influence of the potassium halide lattices on the monovalent divalent mercury equilibrium can be summarized as follows:

$$Hg^+ + Hg^+ \underset{KI}{\overset{KCl}{\rightleftharpoons}} Hg^0 + Hg^{2+}.$$

KBr shows an intermediate behavior.

Our identification of the Hg^0 centers is based largely on the peak intensity diagrams, Figs. 7, 9, and 10.

These centers appear only at portions of the crystal plate of high F-center concentration; the concentration gradient of Hg^0 follows the same pattern as that of the F centers. The intensity diagrams actually trace the electron penetration into the crystal in additive coloring, and are in excellent agreement with the assignments of all the absorption bands observed in this work to the various species of mercury in the lattice.

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[1] Lushchik et al. (*9*) published a series of studies on "mercury-like" ions in alkalihalides but none dealt with mercury itself.