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Optical, Electrical, and EPR Studies of KBr Crystals Doped with Cadmium

S. C. JAIN* AND S. RADHAKRISHNA
Solid State Physics Division, National Physical Laboratory New Delhi-12, India

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The peak positions, half-widths, and oscillator strengths of Cd (and Zn) bands in KBr and other uncolored alkali halides are given. In uncolored KBr, Cd introduces three optical absorption bands at 202, 215, and 280 nm, respectively. Two new bands, D_1 and D_2, at 250 and 285 nm, respectively, are observed in the irradiated KBr:Cd crystals. The growth of absorption coefficients α_F and α_M at the peaks of F and M bands, respectively, was studied as a function of radiation dose. The value of S in the relation $\alpha_M = S\alpha_F^2$ is suppressed by a factor ~100 in crystals containing more than 20 ppm of Cd. In the crystals irradiated for short times, the M band cannot be produced even by optically bleaching the F band. The second-stage growth of the F band is also suppressed considerably by the Cd impurity, which supports the view that the second-stage F centers are necessary for the formation of M centers. The D_1 and D_2 bands observed in x-irradiated crystals are absent in the additively colored crystals. In the crystals colored additively at 460°C, an ultraviolet band at 330 nm and a band at 750 nm are observed in addition to the F band. The F band can be converted to the 750-nm band by optical or partial thermal bleaching of the crystal. In a crystal colored at 560°C the 750-nm band is absent, and only the 330-nm band and a very stable F band are present. On heating the crystals to 600°C, the 330-nm band, F band, and 750-nm band disappear, and a new band at 300 nm appears. The crystal containing the 300-nm band shows an EPR absorption line with Lorentzian shape and a g value of 1.987, and enhanced conductivity above 500°C. These results suggest that the centers responsible for this band are metallic colloidal particles of Cd. The equilibrium concentration of F centers in crystals doped with 28 ppm of Cd and colored additively at 560°C is 15% less than that in a pure crystal. At 560°C the rate of diffusion of F centers in the Cd-doped crystals is less by a factor ~5 as compared to the rate in a pure crystal, and is less by a factor ~50 as compared to rate the of diffusion of 330-nm band centers.

1. INTRODUCTION

THE optical-absorption spectra in alkali halides containing alkaline earth impurity ions[1,2] and mercury-like ions[3] have been studied in detail. Relatively little work has been done on the optical properties of alkali-halide crystals containing Cd and Zn impurities.[4,5] Results of optical and ESR absorption and electrical-conductivity measurements of uncolored and colored KBr crystals containing cadmium impurity are reported in this paper.

2. EXPERIMENTAL

Single crystals of cadmium-doped alkali halides were grown in the laboratory by the Kyropoulos method from the melt of BDH analar alkali halides containing Merck's reagent grade Cd halides. The concentration of Cd in the crystal was measured by dissolving the crystal in water and using the polarographic method.[6]

The ratio of Cd concentration in the melt to that in the KBr crystals is ~200, indicating a small solubility of Cd in KBr. The crystals were cleaved into cubes of dimension 1 cm on each side for the purpose of additive coloration and into pieces of thickness 1 mm for the purpose of x irradiation. The x irradiation was done at room temperature in the dark by a Philips PW 1009/30 x-ray diffraction unit, using a molybdenum target. Additive coloration, optical bleaching with F light or white light, thermal bleaching, optical absorption, and conductivity measurements were made in the usual manner.[7,8] The EPR measurements were made with V-4502-12 type Varian spectrometer. To measure the concentration of F centers as a function of depth from the surface of the crystal, the crystal holder plate was attached to a micrometer screw and could be moved in front of the slit of the spectrophotometer. The position of the crystal could be read correctly to 0.1 mm.

3. UNCOLORED CRYSTALS

Curves 1–4 in Fig. 1 show the absorption spectra of NaCl, KCl, KBr, and KI crystals, respectively, doped with cadmium. In each case the impurity concentration in the melt was 0.5% by weight. It can be seen from the figure that NaCl:Cd has only one absorption peak at 190 nm, KCl:Cd has one absorption peak at 190 nm and another at 278 nm, and KBr has three peaks at 202, 215, and 280 nm, respectively. The peak in KI is rather broad and is not symmetrical, suggesting that the absorption in this band is due to two absorption bands in close vicinity. Experiments with different

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* Also at the Indian Institute of Technology, Hauz Khas' New Delhi-29, India.

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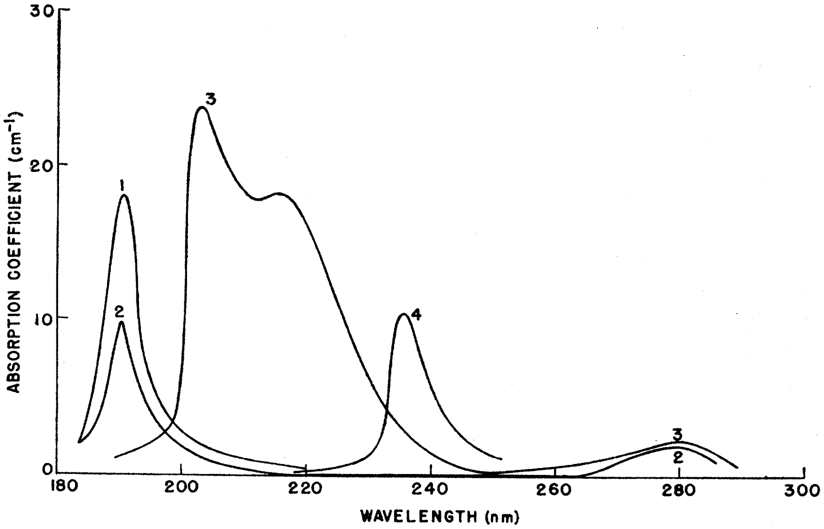

FIG. 1. Optical-absorption spectra at room temperature of (1) NaCl, (2) KCl, (3) KBr, and (4) KI grown from the melt containing 0.5% of the corresponding cadmium halide.

concentrations of the impurity were performed for all the above alkali halides. If the concentration of Cd in the crystal is less than 3 ppm, the absorption bands are so weak that they cannot be observed. No additional bands were found in the wavelength range 285–1000 nm for high Cd concentrations.

The effect of aging and temperature on the absorption bands in KBr are shown in Fig. 2. Curve 1 is the absorption spectra for the KBr crystal containing 6 ppm of Cd impurity and curve 2 is the absorption of the same crystal after aging it at room temperature for about 48 h. It is seen by comparing these two curves that the 215-nm band grows at the expense of the 202-nm band as a result of aging. This suggests that the 215-nm peak is due to an aggregate center involving more than one cadmium impurity ion. Curves 3–5 are obtained when the absorption is measured at 50, 70, and 90°C, respectively. It can be seen from the figure that the 202-nm peak becomes broad and shifts to longer wavelengths, indicating that the centers responsible for this peak are

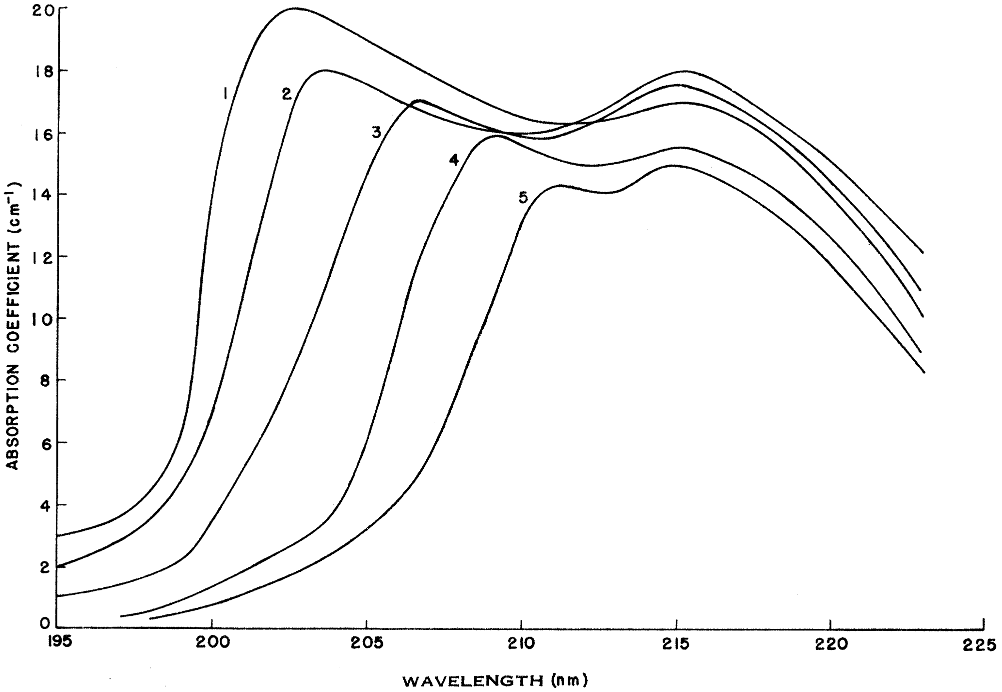

FIG. 2. Effect of aging and temperature on the Cd bands in KBr crystals. Curve 1 is for a freshly quenched crystal containing 6 ppm of cadmium impurity. Curve 2 shows the absorption bands after aging the crystal at room temperature for 48 h. Curves 3, 4, and 5 show the absorption bands at 50, 70, and 90°C, respectively.

atomically dispersed. However, the peak at 215 nm is not affected much by the temperature, as is to be expected for the aggregate centers. On increasing the cadmium concentration slowly, both the 202 and 215-nm bands increase in height in the beginning. However, when the concentration of the impurity in the crystal is larger than 30 ppm, the two peaks merge into one very broad composite band, showing that the aggregates of different sizes of the impurity are now present in the crystal.

Absorption spectra of NaCl and KBr crystals doped with 0.5% by weight of the corresponding zinc halides in the melt have also been measured.[9] The peak positions and half-widths of Cd- and Zn-impurity bands in NaCl, KCl, KBr, and KI are collected in Table I. The impurity concentration was estimated by polarographic analysis and by measuring the ionic conductivity in the "second region"[10] of the conductivity plot and comparing it with that of a crystal containing known concentrations of divalent impurity. The oscillator strengths of the bands calculated by using Smakula's formula[1] are also shown in Table I. Since the estimate of the atomically dispersed impurity concentration is not very accurate, the values of the oscillator strengths given in Table I give only orders of magnitude.

The various models of the impurity centers which can give rise to absorption band in the ultraviolet region are (1) the absorption due to the excitation of the impurity ion inside the crystal (e.g., Seitz's[11] model of Tl-doped KCl crystals), (2) charge transfer from the neighboring halide to the impurity ion (e.g., Prighsheim's[12] model of Tl-doped KCl), and (3) charge transfer from an anion, with the impurity in its first-neighbor position, to the alkali metal (analog of the α or β bands[1]).

TABLE I. Peak positions, Half-widths, and oscillator strengths of Cd and Zn bands in four alkali halides at room temperature.

Host crystal	Impurity	Peak position (nm) of the Cd and Zn bands	Peak position (nm) of the α band	Half-widths of Cd and Zn band (eV)	Approximate oscillator strengths of Cd bands
NaCl	Cd	190	174	0.19	10^{-2}
	Zn	189		0.31	···
		260		0.69	···
KCl	Cd	190	178	0.24	10^{-2}
		278		0.24	10^{-3}
KBr	Cd	202	201	0.20	10^{-1}
		215		0.67	···
		280		···	···
	Zn	202		0.23	···
		225		0.47	···
		275		0.33	···
KI	Cd	235	238	···	10^{-1}

The peak position of the absorption band closest to the fundamental band (Table I) is strongly dependent on the host crystal but is not very sensitive to the impurity. The peak positions are the same for Cd and Zn impurity in KBr and only slightly different for the two impurities in NaCl. On the other hand, it changes rapidly to longer wavelength in going from chloride through bromide to iodide. These facts suggest that this band may be due to the exciton absorption band perturbed by the neighboring[13] Cd or Zn impurity. It would be interesting to measure the absorption in KCl and NaCl doped with Cd and Zn in the region 160–180 nm to see if there are other Cd or Zn bands close to the α band.

The longer-wavelength bands may be related to crystal-field spectra of the impurities (intra-ionic transitions) as suggested by Kuwabara and Aoyagi.[4]

No EPR absorption associated with any of the bands listed in Table I could be observed. This suggests that the atomically dispersed impurities go into the lattice in the M^{2+} state (where M stands for Cd or Zn). The results of conductivity measurements[9] of uncolored KBr crystals doped with Cd and Zn are consistent with this view.

4. X-IRRADIATED CRYSTALS

A. Optical-Absorption Bands

Optical spectra of several KBr crystals doped with different concentrations of Cd and irradiated with x rays of different intensities and for different lengths of time were studied. Typical results for a pure crystal and for a crystal containing 35 ppm of Cd and irradiated for 2h are shown by curves 1 and 2 in Fig. 3. The Cd bands observed in the uncolored crystal did not change much on irradiation and have been subtracted from curve 2. It is seen that the effect of Cd impurity is to suppress the growth of the F band and change the character of the ultraviolet bands. The ultraviolet band at 236 nm in the pure crystal is the usual V_3 band with a tail on its long-wavelength side.[1,14] The tail grows relatively stronger on irradiating the crystal heavily and is presumably connected with the Br aggregate centers.[14] In the Cd-doped crystals, the ultraviolet band is at 250 nm with a shoulder at 285 nm. The heights of 250- and 285-nm bands increase with Cd concentration for the same radiation dose. On heating the crystals up to 80°C, the F band was partially bleached but the 250- and 285-nm bands were not affected in the Cd-doped crystals. The optical stability of these bands is also quite different from that of the V bands (see below). In view of these considerations, we suggest that the 250- and 285-nm bands are similar

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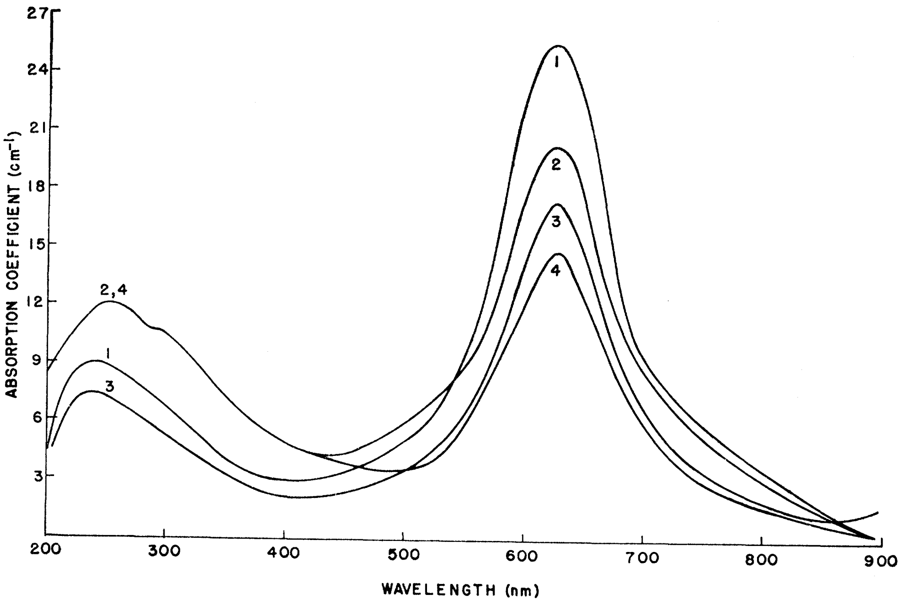

FIG. 3. Optical-absorption bands at room temperature in x-irradiated crystals. Curve 1, pure KBr crystal x-irradiated for 2 h. Curve 2, KBr crystal containing 35 ppm of cadmium impurity and x-irradiated for 2 h. *F*-light bleaching changes the absorption from curve 1 to 3 in the pure crystal and from curve 2 to 4 in the doped crystal.

to the D_1 and D_2 bands observed in KBr crystals doped with alkaline earth impurities[14] and are not the *V* bands. We hope to make dichroic studies of these bands in the near future.

The effect of optically blecahing the *F* band with *F* light for 15 min is shown by curves 3 and 4 for the pure and the Cd-doped crystals, respectively. The *F* band is bleached by comparable amounts in both cases but the *M* centers are formed only in the pure crystal and not in the doped crystal. The V_3 band is partially bleached along with the *F* band optically but the D_1 and D_2 bands cannot be bleached in this manner. In crystals doped with small amounts of Cd and x irradiated for 40 h, a very weak *M* band was produced. The strength of this band remained less than 1/100 of the *M* band produced in the pure crystals under identical conditions. The value of S in $\alpha_M = S\alpha_F^2$ becomes very small for Cd-doped crystal, a result similar to the KCl crystals containing hydrogen and calcium impurities.[15] The other aggregate bands could not be produced in the Cd-doped crystals.

B. Growth Rate of *F* Centers

The rate of growth of the *F* band in KBr crystals doped with different concentrations of Cd and irradiated with x rays of different intensities is shown in Fig. 4. The intensity of x rays was taken to be proportional to the plate current of the x-ray tube.[8] Curves 1 and 2 are for the pure crystals irradiated with x rays at 10 and 5 mA, respectively, and curve 3 for the KBr crystal containing 20 ppm of Cd impurity, irradiated with x rays at 10 mA. Curves 4–6 are for crystals containing 28-ppm Cd impurity and irradiated with x rays at 15, 10, and 5 mA, respectively. It is seen from these curves that the effect of the Cd impurity is to suppress both the early and late stages of coloration.[16]

The growth curves of Fig. 5 were analysed by the methods used by earlier workers[8,17,18] for KCl and NaCl. In addition to the linear growth of *F* centers in the late slow stage, the early stage is found to consist of two exponential components; the concentration n_F of the *F* centers can be expressed by

$$n_F = n(1-e^{-bt}) + n'(1-e^{-ct}) + at, \qquad (1)$$

where n, n', b, and c are constants, a is the slope of the linear late-stage growth of *F* centers, and t is the time of x irradiation. Both b and c decrease with impurity concentration but seem to be independent of the intensity of x irradiation in doped crystal. The value of b is about five times larger than the value of c. Comparing these results with those obtained by Mitchell *et al.*[17] and by Jain and Mehendru,[8] we identify the component $n(1-e^{-bt})$ with the first type of *F* centers and $n'(1-e^{-ct})$ with those second type of *F* centers which saturate with time. Thermoluminescence studies similar to those of Jain and Mehendru[8] have confirmed this identification.[9] The suppression of early-stage coloration is mainly due

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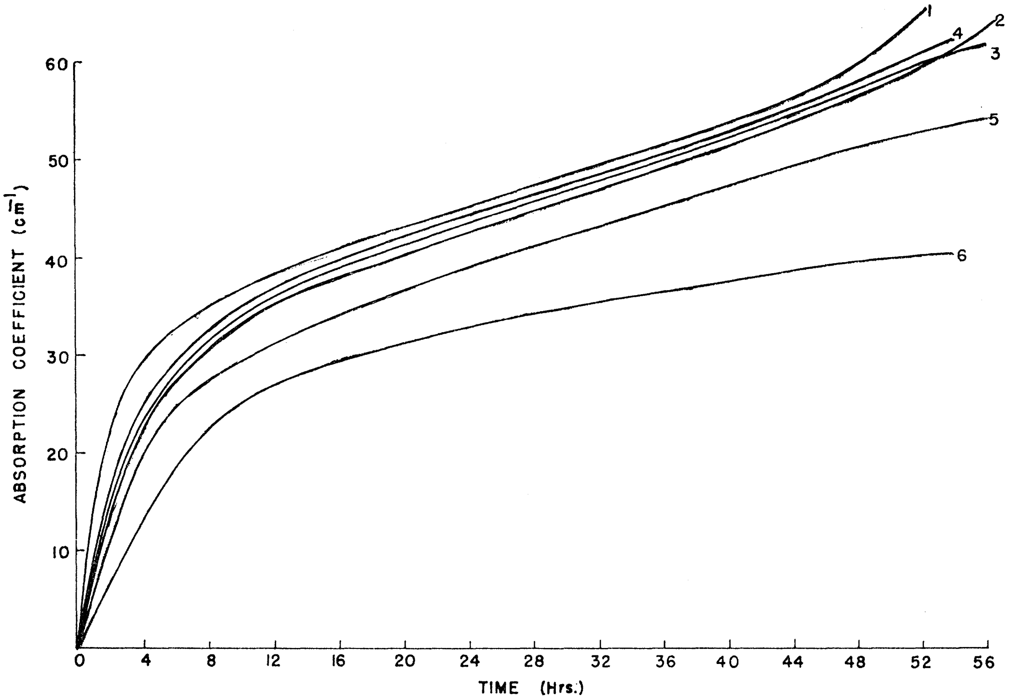

FIG. 4. Rate of growth of F band in pure and Cd-doped KBr crystals at room temperature. Curves 1 and 2 are for pure KBr crystal irradiated with x rays at 10 and 5 mA, respectively. Curve 3 is for a KBr crystal containing 20 ppm of Cd impurity and irradiated at 10 mA. Curves 4, 5, and 6 are for KBr crystals containing 28 ppm and irradiated at 15, 10, and 5 mA, respectively.

to the reduction in the values of b by the cadmium impurity.

Equations developed by Pooley[19] show that the effect of changing the x-ray intensity or the impurity concentration on the growth rate of the second stage is taken into account by a parameter $P=\text{const }(I/n_i^2)$, where I is the intensity of x irradiation and n_i is the concentration of the impurity. According to Pooley's theory, the power x of I in the equation $a\propto I^x$ should be unity for large values of P and should increase and approach a limiting value 1.5 upon decreasing the parameter P. The slopes a of the late-stage linear parts

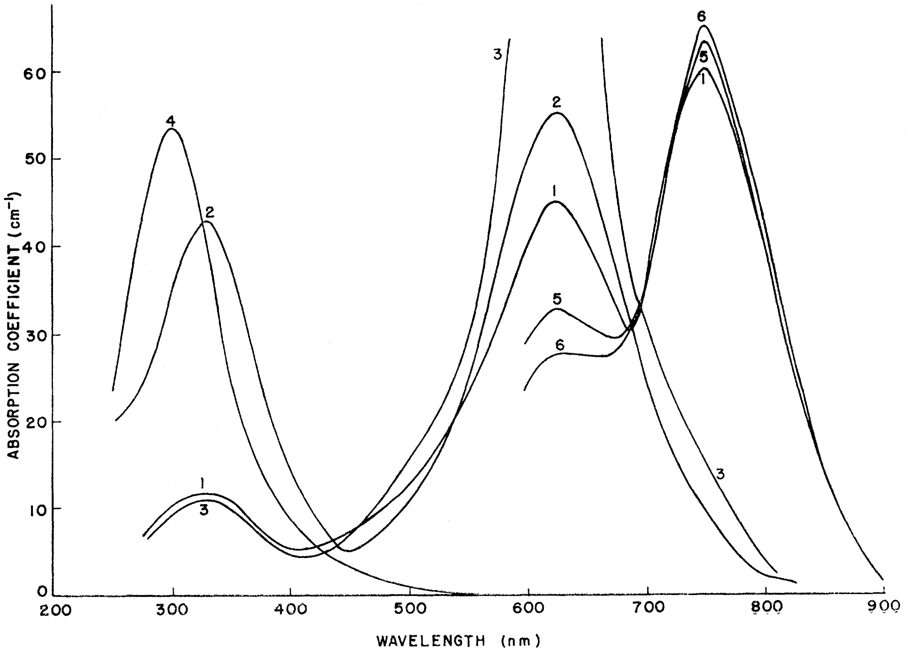

FIG. 5. Optical-absorption bands at room temperature in additively or electrolytically colored KBr crystals containing 28 ppm of Cd impurity. Curves 1 and 2 are for a crystal colored additively at 460 and 560°C, respectively. Curve 3 is for a crystal colored electrolytically at 560°C and curve 4 is for any of the above crystals after it is annealed at 600°C. Curves 5 and 6 are obtained after bleaching the crystal colored at 460°C for 15 and 30 min, respectively.

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of the growth curves were determined and a plot of $\ln a$ versus $\ln I$ was made for various crystals. An accurate analysis[17] and thermoluminescence experiments similar to those performed by Jain and Mehendru show that the first stage does not saturate upto about 50 h. The growth curves for times of irradiation larger than 50 h (some of the curves not shown in Fig. 4) were used for the determination of a. Contrary to the result of Pooley, a plot of $\ln a$ versus $\ln I$ gives $a \propto I^{0.9}$ for KBr crystals doped with 28 ppm of Cd (small value of P) and $a \propto I^{1.5}$ for a pure crystal (large value of P). The expression for the parameter P given above shows that if I is increased as the square of the impurity concentration, the value of P and hence that of a should remain practically constant. In going from curve 3 to curve 4 we have increased I in a ratio the same as that of the impurity concentrations (and not as the square of the impurity concentration) but the value of a remains nearly unchanged.

Abramson and Caspari[20] have suggested that the value of a is given by

$$a = BAI^2/(\beta + BAI)\,, \tag{2}$$

where AI is the steady-state concentration of the electrons during irradiation, BI is the rate of generation of vacancies, and β is the self-bleaching constant. For large values of I, β can be neglected and a should vary linearly with I. On the other hand, for small value of I, BAI can be neglected in comparison with β and a should vary as I^2. Sibley, Sonder, and Butler[21] have suggested that the effect of impurity is to reduce the steady-state concentration of, electrons which means reduction in the value of A in Eq. (2). As the impurity concentration is increased, the term BAI should gradually become less significant than β and the value of x should become 2, a result qualitatively the same as that obtained with Pooley's theory but not in agreement with the experimental results. It seems that in doped crystals the equilibrium concentration of electrons and anion vacancies is not proportional to I but to a very small power of I.

In the Cd-doped crystals the value of S is not only extremely small but the quadratic relationship $\alpha_M = S\alpha_F{}^0$, also is not obeyed accurately. Such deviations from the quadratic behavior have been reported for low-intensity x-ray irradiation and also in the early stage of F-center generation. Since second-stage F centers are not formed in the early stage of irradiation and since more R centers are formed with low intensity x irradiation, the deviation from a quadratic relationship may occur[15] because of the absence of second-stage F centers or because of the presence of R centers. No R centers appeared in the present work. Though the second-stage coloration was suppressed by the Cd impurity, the suppression of the growth rate of M was larger by about two orders of magnitude than the suppression of the second-stage F-center growth rate. The optical stability of F centers is considerably enhanced by the Cd impurity. It seems that Cd reduces the mobility of the F center and the formation of M is therefore suppressed.

5. ADDITIVELY COLORED KBr:Cd CRYSTALS—EXPERIMENTAL RESULTS

A. Optical-Absorption Bands

The 202-nm cadmium band due to cadmium in the uncolored KBr crystal was slightly suppressed on additive coloration. The bands at 250 and 285 nm obtained in the irradiated cadmium-doped crystals are absent in the additively colored crystals. The number and nature of optical-absorption bands obtained on additively coloring the doped crystal depend on the temperature at which the crystals are colored (the temperature of alkali metal was 20° lower) and on the subsequent heat treatment.

Typical optical-absorption bands in a KBr crystal doped with 28 ppm of Cd and colored additively at 460°C are shown by curve 1 of Fig. 5. The half-width of the F band increases from 0.36 eV in a pure crystal to 0.40 eV in the Cd-doped crystal. In addition to the F band, it shows two new bands, one at 750 nm with half-width 0.20 eV and the other broad band at 330 nm with half-width 1.15 eV. Curve 2 shows the optical absorption of a similar crystal colored at 560°C. The 750-nm band is now absent and both the 330-nm and the F bands are considerably enhanced. Curve 3 shows the optical-absorption band in a similar crystal colored electrolytically with pointed Pt cathode at 550°C. Qualitatively, the result is the same as that in additively colored crystal. The F density is now very large and the 330-nm band is suppressed considerably. Curve 4 shows the optical-absorption band in either of the crystals colored additively after the crystal is annealed at 600°C for about 3 h. 750-nm band in crystals colored at 460°C and the F and 330-nm bands disappear. A new band at 300 nm with a half-width of 0.75 eV is now observed.

B. Optical and Thermal Bleaching of the Absorption Bands

The results of bleaching the KBr crystal with 28-ppm Cd colored at 460°C with F light for 15 and 30 min is shown by curves 5 and 6, respectively, in Fig. 5. It is found that on bleaching with F light the 330-nm band is not affected, the F band decreases, and the 750-nm band increases. The F band in Cd-doped KBr crystals colored at 560°C and the 330-nm bands are very stable. Both bands remained unaffected on irradiating the crystal by F or white light for several hours. The M or other aggregate centers or colloids cannot be produced in additively colored KBr crystals

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with more than 20 ppm of Cd even on bleaching the crystals for up to 10h by *F* or white light and/or by heating the crystals.

The effect of heating and quenching the crystal in the dark from different temperatures in the range 50–620°C on the optical-absorption bands was studied. In a crystal doped with 28 ppm of Cd *and colored at 560°C* the temperature at which *F* centers start decaying rapidly in the dark is 250°C as compared to 150°C in the pure crystal. As the temperature is increased gradually from 250 to 480°C, the *F* band decays and 330-nm band increases. On heating the crystal to 600°C, the 330-nm and *F* bands completely disappear and the 300-nm band (curve 4) appears as mentioned before. On heating the crystal colored at 460°C up to 250°C, the *F* band decays, the 750-nm band becomes stronger and its peak is shifted to somewhat shorter wavelengths, and the 330-nm band remains unaffected. On heating the crystal to higher temperatures, the 730-nm band and the *F* band start decreasing. At 600°C, the *F* band, the 330-nm band, and the 730-nm band disappear and again the 300-nm band appears.

C. Distribution of Color Centers in Cd-Doped KBr Crystals

The relative heights of the 330- *F*, and the 750-nm bands in a crystal slice depend on the distance of the slice from the surface of the crystal through which diffusion had taken place, on the Cd concentration, and on the temperature and time of coloration. The optical absorption at the peak positions of 330- *F*, and 750-nm band was measured as a function of distance from the surface along the line EF in the slice ABCD (see inset in Fig. 6) taken from the middle of the crystals colored at 460°C as well as 560°C, for 2h, 12h, 96h, and 15 days. Both pure crystals and crystals doped with different concentrations of Cd were used. Curve 1 in Fig. 6 shows the height of the *F* band in a pure crystal colored at 560°C for 2h. Curves 2 and 3 show the heights of the *F* and the 330-nm bands in a crystal (14.0 mm long) with 28 ppm of Cd and colored at the same temperature and for the same time. It can be seen from these curves that the *F* band decreases and becomes negligible at a distance of 5.5 mm from the surface in the pure crystal and at a distance of 0.3 mm in the doped crystal. The 330-nm band increases as the distance from the surface increases up to 5.5 mm, becomes constant for about 0.3 mm, and then starts decreasing rapidly. The region where the *F* density decreases rapidly is shown by broken line in the figure. In the crystal colored at 460°C, the 750-nm band also decreases with the *F* band in moving towards the center of the slice. Curves 4 and 5 in Fig. 6 give the heights of *F* and 330-nm bands in crystals (6 mm long) colored at 560°C for 15 days.

D. Effect of Cd Concentration on the *F* and 330-nm Bands

The effect of Cd concentrations on the strengths of *F* and 330-nm bands was studied in six KBr crystals containing six different concentrations of Cd and

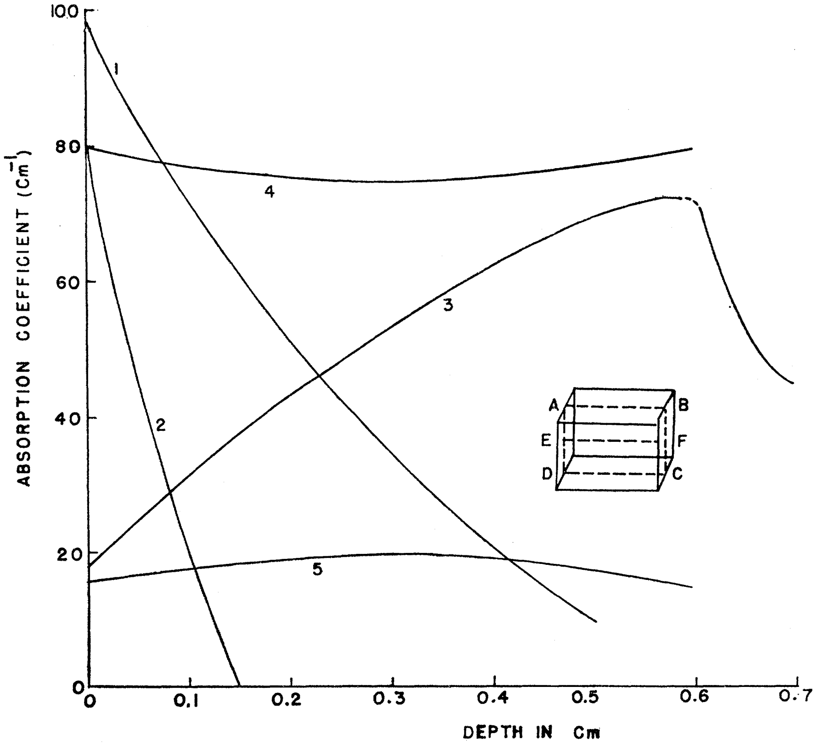


FIG. 6. Variation of concentration of color centers with distance from the surface through which diffusion of color centers takes place. Curve 1 shows height of the *F* band in a pure KBr crystal colored at 560°C for 2 h. Curves 2 and 3 show the heights of *F* and 330 nm bands in a KBr crystal (14-mm long) containing 28 ppm of cadmium and colored at 560°C for 2 h. Curves 4 and 5 show the height of *F* and the 330-nm bands in a crystal (6-mm long) containing 28 ppm and colored at 560°C for 15 days. Optical-absorption measurements were made at room temperature.

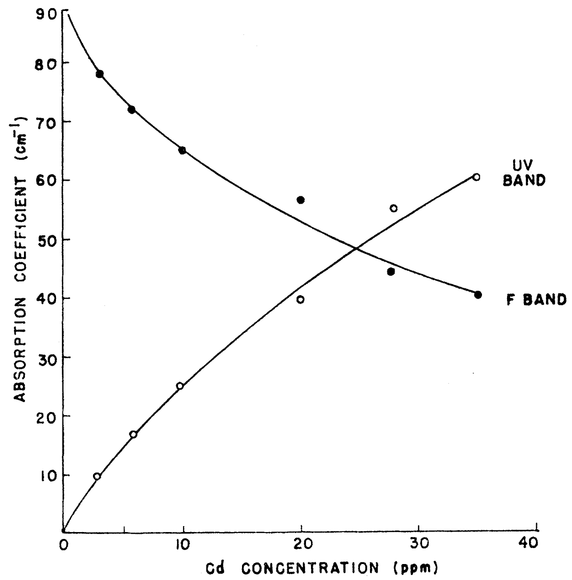


FIG. 7. The variation of the heights of F and the 330-nm bands with concentration of Cd in KBr crystals at a distance of 4 mm from the surface. The crystals were colored at 560°C for 96 h. If the time of coloration is increased, the height of the F band increases and that of 330-nm band decreases in the interior of the crystal.

additively colored at 560°C. In each case, the optical spectra in a small crystal taken from a distance of 3 mm from the point E (inset in Fig. 6) on the surface of the crystal were measured. Curves 1 and 2 in Fig. 7 show that the 330-nm band rises and the F band is suppressed as the Cd concentration increases. However, the increase in 330-nm band height is not proportional to the cadmium concentration but increases somewhat slowly.

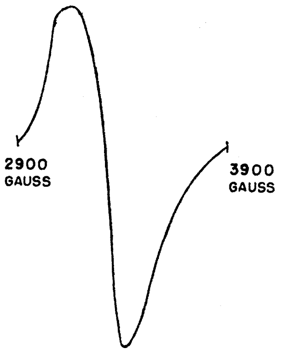


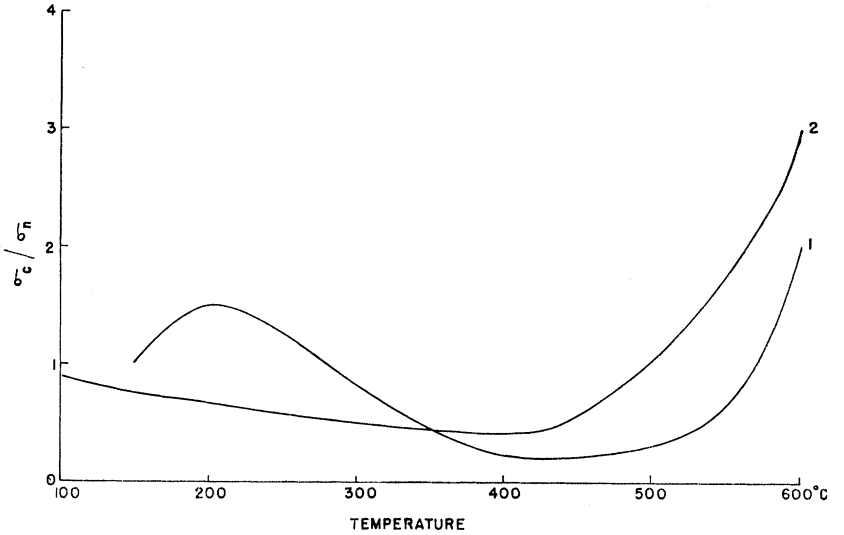
FIG. 8. EPR absorption line at room temperature associated with the 300-nm band in additively colored Cd-doped KBr crystals annealed at 600°C.

E. EPR and Conductivity Measurements

No EPR absorption which could be associated with the 330-band or the 750-nm band was observed. The EPR of the F center was not influenced by the cadmium impurity and the usual linewidth of 125 G and a g value of 1.988 for the EPR line characteristic of the F band were obtained.[22] Typical EPR results for a crystal containing 28 ppm of cadmium colored at 560°C and subsequently annealed at 600°C in air is shown in Fig. 8. Optically, only the 300-nm band (curve 4 in Fig. 5) is present in the crystal as discussed above. A Lorentzian EPR absorption line with half-width of 200 G and a g value 1.987 is now observed. To make sure that the 300-nm band and the associated EPR are not due to oxygen or other impurities which might diffuse into the crystal from the ambient atmosphere, several Cd-doped and colored crystals were annealed at 600°C in vacuum. The same 300-nm band and EPR line were observed in these crystals also.

The electrical conductivity of Cd-doped and colored KBr crystals is shown in Fig. 9. Curve 1 is the plot of σ_c/σ_n(σ_c and σ_n are the conductivities of the colored

FIG. 9. A plot of σ_c/σ_n(σ_c is the conductivity of an additively colored crystal and σ_n is the conductivity of an uncolored crystal) as a function of temperature. Curve 1 is for the colored KBr crystal containing 20 ppm of Cd and curve 2 is for the same crystal annealed at 600°C.



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[22] H. Seidel and H. C. Wolf, Phys. Status Solidi 11, 3 (1965).

and the uncolored crystals) versus temperature for a crystal containing about 20 ppm of Cd and colored at 560°C. It is seen from the figure that curve 1 has one maximum at 200°C. As the temperature increases, the ratio σ_c/σ_n decreases, attains a minimum value <1, and then starts increasing again. Curve 2 shows the conductivity of the same crystal after annealing at 600°C. σ_c/σ_n becomes less than unity below 500°C but increases to a value of more than unity at higher temperatures. This increase is found to be more prominent in the crystals with larger cadmium concentration. Since in the doped and colored crystals heated to 600°C only the 300-nm band is prominent, the decrease in the value of σ_c/σ_n below 500°C and increase in its value at higher temperatures must be associated with the 300-nm band centers.

6. RESULTS OBTAINED WITH ADDITIVELY COLORED KBr:Cd CRYSTALS

A. 750- and 330-nm Bands

Since the height of the 750-nm band increases on bleaching by *F* light, the band seems to be due to electron-excess centers. The 750-nm band is not formed if the crystal is colored at higher temperatures, suggesting that the 750-nm band centers themselves or the defects which capture the electrons and become the centers are not stable at high temperatures. It seems that pairs of Cd^{++} ions and cation vacancies are involved in the 750-nm band centers. The number of such pairs will decrease rapidly at high temperatures and this would explain the absence of these centers in crystals colored at 560°C. The 750-nm band cannot be formed in crystals colored at 560°C even by subsequent optical bleaching of the *F* band. It is possible that on coloring the crystal at 460°C, and quenching it from this temperature, an appreciable number of impurity vacancy pairs are frozen in the crystal and the pairs are absent if the crystals are colored and quenched from 560°C. The band is not formed in KBr:Cd crystals on x irradiation or on subsequent optical bleaching of the *F* band in the irradiated crystals. It seems that in uncolored crystals most of the impurity vacancy pairs are present as trimers (or as higher aggregates) promoting the growth of D_1 and D_2 bands[14] on x irradiation.

The observed fact that a strong 330-nm band is formed if the crystal is colored at higher temperatures suggests that the centers responsible for this band are formed by the capture of electrons by single cadmium ions. The large half-width of the band and the shift in the peak position to longer wavelengths on increasing the cadmium concentration suggest that some of the centers are perturbed by *F* centers or other defects in the close neighborhood. It is possible that when Cd concentration is very high, centers involving two or more cadmium ions are also formed.

No EPR absorption associated with the 750-nm band and the 330-nm band was observed. However, since the *F* band is always present along with these bands in the crystal, the strong EPR line due to *F* centers may mask any weak signal due to these bands; we cannot be sure of the negative result without more detailed work. Since the cation vacancy needed to maintain the charge neutrality will not remain in the crystal when Cd^{2+} is converted to Cd^{+}, the conductivity of the crystal should decrease as the 330-nm band is formed. However, the conductivity results are complicated because electrons ionized from the *F* centers enhance the conductivity[23] and definite conclusions cannot be drawn from the conductivity measurements.

The high optical stability of the *F* band in these crystals suggests that the mobility of *F* centers is considerably suppressed by the 330-nm band. This result is similar to that obtained in KCl crystal containing hydrogen impurity.[15]

In spite of the extensive studies of the *Z* bands in alkali halides doped with alkaline earth impurities, the models of the *Z* centers are still not clear.[2] Considerable further work is necessary before the nature of the 750- and 330-nm band centers is clearly understood.

B. 300-nm Band

We now discuss the 300-nm band observed in colored KBr:Cd crystals annealed at about 600°C. The peak position and half-widths of this band are reproducible in crystals heated in air or in a vacuum and do not depend upon the initial *F* concentration in the crystal. The height of the band is also insensitive to the initial *F* concentration but increases with the increase in Cd concentration. Once this band is formed at 600°C in the crystal, it was impossible to bleach it by optical or thermal bleaching of the crystal. A similar band at 320 nm has been observed recently in additively colored KCl:Cd crystals annealed at high temperatures.[5] We tentatively suggest that this band is due to metallic colloids of Cd. Since the height of the band does not depend on the initial *F* concentration in the crystal, it appears that the *F* centers only assist or accelerate the formation of Cd colloids and the relative concentration of potassium atoms must be very small in the colloidal particles. The Lorentzian shape of the EPR line is consistent with the colloidal nature of the EPR centers.[24] Similar EPR lines due to alkali metal particles have also been observed in NaCl,[25] Kcl,[26] and KBr[9] crystals.

In a pure crystal, ionized *F* centers give rise to enhanced conductivity and a large peak in the value at 160°C.[23] Since the thermal stability of the *F* centers in Cd-doped crystals is high, this peak is observed at about 200°C (curve 1, Fig. 9) in the Cd-doped crystals.

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[23] V. K. Jain, Ph.D. thesis, Delhi University, 1967 (unpublished).

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[25] A. A. Bugai, M. O. Deign, M. A. Rubat, and A. A. Shatalov, Phys. Probl. Spectry. **11**, 116 (1960).

[26] S. C. Jain and G. D. Sootha, Phys. Rev. **171**, 1075 (1968).

At higher temperatures F centers interact with Cd^{2+} ions, the ions and the F centers seem to go out of the solid solution, and the ratio σ_c/σ_n becomes less than unity. The increase in the value σ_c/σ_n near 600°C to more than unity again suggests the presence of Cd colloids. On cooling this crystal and measuring the conductivity again at different temperatures the value σ_c/σ_n remains less than unity below 500°C and becomes more at higher temperatures. Since Cd is eliminated from the solid solution and the F centers which act as donors are not present in the crystal in appreciable concentration, the conductivity ratio σ_c/σ_n is suppressed to a value less than unity at lower temperatures. The Cd metallic particles emit[7] electrons thermally into the conduction band of the crystal at higher temperatures and give rise to the excess electronic conductivity. A plot of $\ln[(\sigma_c-\sigma_n)/\Delta T^{3/2}]$ versus $1/kT$ (Δ is the area under the 300-nm band) gives a straight line with a slope of 3.24 eV. Interpreting these results as being due to thermionic emission of electrons from the metallic cadmium particles embedded in KBr, the value of the slope must correspond to $\phi-\chi$, where ϕ is the work function of metal particles and χ the electron affinity of KBr crystals.[7] Jain has obtained[23] a value 0.36 eV for χ for KBr which gives $\varphi\sim4$ eV, a value close[27] to 4.1 eV for the work function of bulk cadmium. This lends a strong support to the suggestion that the 300-nm band centers are Cd colloidal particles.

A more detailed study of the EPR and conductivity of the crystals containing the 300-nm band and the variation of half-width of the band with temperature supporting this assignment will be published later.[9]

7. DIFFUSION AND CONCENTRATION OF *F* CENTERS IN Cd-DOPED KBr CRYSTALS

A. Concentration of *F* Centers

Mott and Gurney[28] have derived an expression for the concentration n_F of F centers in equilibrium with the vapor of alkali metal at high temperatures. According to this expression, n_F is completely independent of the concentration of vacancies, impurities, or other defects in the crystal and is proportional to the density of alkali atoms in the vapor in equilibrium with the crystal. On the other hand, Shibanov[29] has suggested that a thin metal layer is formed on the crystal surface heated in saturated vapors of the metal and therefore there is equilibrium between the colored crystal and the bulk metal in contact with each other. Now the equilibrium F concentration will be such that the Fermi level in the crystal is the same as in the metal and the value of n_F is given by

$$n_F=N_v^+\exp\left(\frac{E_F+\chi-\varphi}{kT}\right), \tag{3}$$

where E_F is the energy of ionization of the F center, φ is the work function of the metal, and χ is the width of the conduction band. According to this expression, n_F should depend upon the anion vacancy concentration and hence on the divalent impurity concentration which suppresses the anion vacancy concentration.

We can see in Fig. 7 that in a KBr crystal containing 28 ppm of impurity colored in K vapors in a sealed glass tube for 15 days, the maximum F concentration is 85% of that obtained in a pure crystal under identical conditions. Since Cd^{++} suppresses the anion vacancy concentration, this result supports the view that the equilibrium F-center density depends on the anion vacancy concentration. A quantitative comparison of Eq. (3) with the experiment is not possible since the valence state of all the Cd ions in a colored crystal is not known.

B. Diffusion of Color Centers in Cd-Doped Crystals

We have seen that the rate at which F color diffuses into the crystal is considerably suppressed in the Cd-doped crystals. A pure crystal ($10\times10\times10$ mm^3) colored at 560°C acquired a uniform equilibrium color center density in 12 h. A crystal of the same dimensions containing 28 ppm of cadmium could not be colored uniformly at 560°C even after several days.

Tamai[30] and Shibanov[31] have discussed the solution of equation of diffusion of color centers in crystals doped with impurities. They have found that the impurity band centers or color centers diffuse up to a distance X in time t such that[31]

$$X=2\frac{n_S}{(\sqrt{\pi})^{n_i}}(Dt)^{1/2}=2\lambda(Dt)^{1/2} \tag{4}$$

for the case of large impurity concentration. Here n_s is the surface concentration of color centers and n_i is the impurity concentration. The concentration of color centers at time t and distance x is given by

$$n=\frac{n_s}{\operatorname{erf}\lambda}\left[\operatorname{erf}\lambda-\operatorname{erf}\frac{x}{2(Dt)^{1/2}}\right], \tag{5}$$

where D is the diffusion coefficient of the color center under consideration.

In the interior of the crystal where the F-center density is negligible, Eq. (5) can be fitted quantitatively with the distribution of 330-nm band centers and the energy of activation for the migration of the uv band centers is found to be close to that needed for the migra-

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[27] *Handbook of Chemistry and Physics*, edited by Charles G. Hodgman (Chemical Rubber Publishing Co., Cleveland, Ohio, 1964).

[28] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Dover Publications, Inc., New York, 1964).

[29] A. S. Shibanov, Fiz. Tverd. Tela **7**, 312 (1965) [English transl.: Soviet Phys.—Solid State **7**, 249 (1965)].

[30] T. Tamai, J. Phys. Soc. Japan **16**, 2463 (1961).

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tion of the cation vacancies. The F- and 750-nm band distribution curves could not be fitted with Eq. (5) with a constant diffusion coefficient. The process of migration of F centers in a doped crystal seems to be more complicated than the mechanism postulated by Shibanov.[31]

It is not clear as to why the 330-nm band decreases as the F concentration increases. There is a region of yellow color between the outer F-band region and the inner transparent region of the crystal containing the 330-nm band. It is possible that other complex centers are formed by the interaction of the F- and 330-nm band centers and the complex centers do not give absorption in the wavelength region studied in this work

8. COMPARISON WITH THE PROPERTIES OF CRYSTALS DOPED WITH ALKALINE-EARTH IMPURITIES

The electrical conductivity of alkali halides doped with alkaline-earth impurities Cd, Ni, and Co show that the general behavior of all divalent cation impurities is the same.[10,32–35] Dielectric properties appear to be sensitive to the size of the impurity ions.[36,37] Extensive work on the optical bands introduced by the divalent cation impurities in colored alkali halides has been done only with alkaline-earth impurities.[2,38,39] A comparison of the optical and EPR results obtained with Cd impurity in the present paper with those obtained by adding alkaline-earth impurities by earlier workers is interesting.

(1) Unlike Ca, Sr, and Ba impurities, Cd introduces new bands in uncolored crystals in the range 185–300 nm.

(2) The short-wavelength D_1 and D_2 bands observed by us in x-irradiated KBr:Cd crystals seem to be similar to the corresponding bands obtained by Ishii and Rolfe[14] in KBr doped with alkaline-earth impurities. In this respect the behavior of the two classes of the impurities is the same.

(3) Ca enhances the growth of the first stage of the F band and suppresses[40] the second stage of growth while Cd is found to suppress both the first and second stages. This has been confirmed by thermoluminescence experiments such as those performed by Jain and Mehendru.[8] Both Ca[40] and Cd suppress the growth rate of M centers.

(4) Bands similar to the Z bands on the long-wave length side of the F band observed in crystals doped with alkaline-earth impurities are not formed in crystals doped with Cd. On the other hand, Cd introduces new bands near 300 nm on additive or electrolytic coloration. The terminal stability of the Z bands in alkaline-earth–doped crystals is smaller compared to that of the Cd band in the colored alkali halides.

(5) Optical, electrical, and EPR results show that colloids of Cd metal are formed when additively colored Cd-doped crystals of KBr are heated near 600°C. Such evidence of the formation of metallic colloids of Ca, Sr, and Ba in alkali halides has not been obtained.

(6) Though there is considerable evidence that Z_1 center has Bushnell's model, models for other Z centers are not known. Considerable further work is necessary before specific models of Cd centers can be suggested.

(7) Cd suppresses the rate of diffusion of F centers during additive coloration process. Alkaline-earth impurities seem to enhance this rate.

ACKNOWLEDGMENT

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