

## Optical, Electron-Spin-Resonance, and Electrical Studies of Colloidal and *F*-Aggregate Centers in Highly Pure KCl Crystals. I. Colloidal Centers

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In additively colored highly pure *H* and "pure" *B* crystals (background impurity concentration  $\sim 1$  and  $\sim 10$  ppm, respectively) quenched from  $300^\circ\text{C}$  in the dark, a colloidal optical absorption band is formed. The peak position (730 nm) and half-width (0.25 eV) of the band do not change with heat treatment in the dark in the *H* crystals. In *B* crystals the colloidal band has a larger half-width (0.30 eV) and moves to longer wavelengths on heating the crystal to higher temperatures. On quenching the crystals from 150 to  $250^\circ\text{C}$  in light, the *F* band decreases, and a new *X* band in the *H* crystals at 700–710 nm and the Scott *R'* band in the *B* crystals at the same wavelengths are formed. Most of the *X* centers and some of the Scott *R'* centers are converted to colloidal centers at  $300^\circ\text{C}$ . The colloidal band in *H* crystals and the composite colloidal and Scott *R'* bands in *B* crystals move rapidly to longer wavelengths and increase in half-width on heating the crystals to higher temperatures in light. A narrow symmetrical ESR line due to colloidal centers, superimposed on the well-known ESR line due to *F* centers, is observed in crystals containing the colloids. The line is Lorentzian in shape, has a half-width of 2.5 G at room temperature, and has a *g* value of 1.9998. This value of *g* agrees with the value obtained theoretically by Beinenstock and Brooks for potassium-metal conduction electrons neglecting "polarization correction" and including the "Hartree term." A rough upper limit of 700 atoms on the size of the colloidal particles is obtained by the observed symmetrical shape and half-width of the CESR line. In the *B* crystals, only a small fraction of the absorption under the "colloidal band" is found to be due to colloidal particles. Even in the *H* crystals, a part of the optical absorption under the "colloidal band" is due to residual background impurity present in the crystals. No colloids are formed in crystals containing large concentrations of Ba or Cd. The *X* band does not influence the electrical conductivity, the Scott *R'* band suppresses the conductivity by a large factor, and colloids enhance the conductivity at higher temperatures. The results show that the colloidal nature of the centers, investigated by Scott, Smith, and Thompson, is essentially correct, and contradictory results were obtained by several subsequent workers because it is not possible to understand the effect of light and background impurity on the optical absorption bands by optical measurements alone.

### I. INTRODUCTION

ADDITIVELY colored alkali-halide crystals, when quenched rapidly from the coloring temperature to room temperature in the dark, contain pure *F* centers.<sup>1,2</sup> If the crystals containing *F* centers are now heated to  $150$ – $450^\circ\text{C}$ , the *F* band diminishes and the optical absorption bands peaking on the long-wavelength side of the *F* band (between 700 and 820 nm for KCl) with different half-widths are formed<sup>1–3</sup>. We shall denote this family of bands in KCl as infrared (IR) bands. Scott *et al.*,<sup>3</sup> Doyle,<sup>4</sup> and Penley and Witte<sup>5</sup> have identified the centers responsible for the IR bands with the small colloidal particles of the potassium metal embedded in the crystal lattice. On the other hand, Shatalov,<sup>1</sup> Bugai *et al.*,<sup>6</sup> Sonder,<sup>7</sup> and others<sup>1</sup> have obtained results which are not consistent with the colloidal nature of the centers.

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<sup>1</sup> *Color Centers in Solids*, edited by J. H. Schulman and W. D. Compton (Pergamon Press, Inc., New York, 1962).

<sup>2</sup> G. D. Sootha, thesis, University of Delhi, 1967 (unpublished).

<sup>3</sup> A. B. Scott and W. A. Smith, *Phys. Rev.* **83**, 982 (1951); A. B. Scott, W. A. Smith, and M. A. Thompson, *J. Phys. Chem.* **57**, 757 (1953).

<sup>4</sup> W. T. Doyle, *Phys. Rev.* **111**, 1067 (1958); *Proc. Phys. Soc. (London)* **75**, 649 (1960).

<sup>5</sup> J. C. Penley and R. S. Witte, *J. Appl. Phys.* **33**, 2875 (1962).

<sup>6</sup> A. A. Bugai, M. O. Deigen, M. A. Rubat, and A. A. Shatalov, *Phys. Probl. Spectry. (Moscow)* **11**, 116 (1960).

<sup>7</sup> E. Sonder, *Phys. Rev.* **125**, 1203 (1962).

In this paper, results of optical, electron-spin-resonance (ESR), and electrical studies of KCl crystals containing different centers responsible for the IR bands in highly pure KCl crystals are reported. In particular, the effect of exposure of the crystals to visible light and of the background and deliberately doped divalent cation impurities are investigated. These results show that the absorption under the IR bands, obtained in KCl crystals quenched from 150 to  $450^\circ\text{C}$  is due to a variety of centers, and optical studies alone cannot distinguish between the different kinds of centers.

### II. EXPERIMENTAL DETAILS

Single crystals from spectroscopically pure KCl powder obtained from Johnson, Matthey, and Co., Ltd., London, were grown by the Kyropoulos method.<sup>2</sup> These crystals contain less than 1 ppm of background divalent cation impurity<sup>2,8</sup> and are designated as highly pure (*H*) crystals. Crystals grown from BDH Analar powder contain about 10 ppm of divalent cation impurity and are designated as *B* crystals.<sup>8</sup> Crystals doped with Ba and Cd impurities, grown from the melt, are designated as *D* crystals. The crystals were cleaved in rectangular blocks of approximate dimensions  $15 \times 15 \times 15$  mm. A number placed after the letter *H*, *B*, or *D* indicates the batch from which the crystals were

<sup>8</sup> S. C. Jain and P. C. Mehendru, *Phys. Rev.* **A140**, 957 (1965).

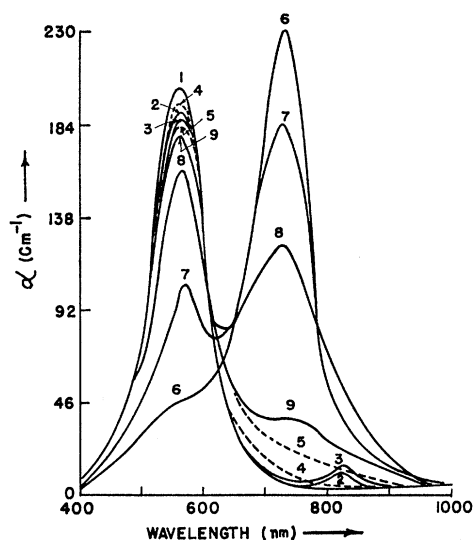


FIG. 1. Absorption spectra of an additively colored *H1* crystal containing  $9.0 \times 10^{17} \text{ cm}^{-3}$  excess potassium atoms and quenched from different temperatures to room temperature *in the dark*. Curve 1 is for the crystal quenched from the coloring temperature (580°C). Curves 2–9 correspond to the quenching temperatures 80, 120, 150, 200, 280, 350, 400, and 450°C, respectively.

cleaved. The cleaved blocks were then additively colored in the usual manner.<sup>1,2,9</sup> Care was taken to keep the crystals in complete darkness during the coloring and the cleaving process and during the subsequent measurements. The method of heating and quenching the crystals, measuring the optical absorption, the electrical conductivity, and the thermal and optical bleaching were the same as described earlier.<sup>2,8,9</sup> Initial *F*-center concentration in quenched crystals, which is taken to be equal to the concentration of the excess potassium metal, is calculated using the Smakula-Dexter equation and taking the oscillator strength  $f=0.5$  for KCl.<sup>10</sup> The crystals were heated at the rate of 1.5°C/min.

The ESR spectra of additively colored KCl crystals were measured at different temperatures with an X-band standard Varian V-4502-12 EPR spectrometer, the variable-temperature accessory V-4557, and the temperature-controller accessory V-4540 of the Varian spectrometer. The accuracy of measured  $g$  values is  $\pm 0.0003$ .

### III. EXPERIMENTAL RESULTS AND DISCUSSION

#### A. Optical-Absorption Measurements

##### 1. Highly Pure Crystals

In Fig. 1 are shown the optical absorption results obtained after quenching an additively colored highly

pure *H1* crystal from different temperatures to room temperature in complete darkness. Curve 1 is for the crystal quenched from the coloring temperature 580°C. The concentration  $N_F$  of the initial *F* centers or of the excess potassium metal in this crystal is  $9.0 \times 10^{17} \text{ cm}^{-3}$ . Changes in the optical absorption in the *F* and IR band regions on quenching the *H1* crystal in dark from 80, 120, 150, and 200°C are shown by curves 2 to 5, respectively. It is seen from these curves that except for aggregation of a small number of *F* centers into *M* centers below 120°C, the *F*-center concentration remains nearly constant up to 200°C. The results obtained on quenching the crystal from temperatures in the range 200 to 300°C (not shown in the figure) depend upon the heating rate used. On quenching the crystal from 300°C, *F*-center concentration becomes very small and a new IR band peaking at 730 nm is formed (curve 6). Curves 7, 8, and 9 were obtained after quenching the same crystal from 350, 400, and 450°C, respectively, and show that the number of centers responsible for the 730-nm IR band decreases and that of the *F* centers increases on heating the crystal to temperatures higher than 300°C.

Experiments were also performed on crystals containing different concentrations of excess alkali metal. It was found that the 730-nm band could not be developed in *H* crystals containing less than  $5 \times 10^{16} \text{ cm}^{-3}$  excess alkali atoms and heated in the dark. The crystals containing higher concentrations of excess alkali metal showed that there is a heterogeneous equilibrium<sup>3</sup> in the temperature range 300–450°C between the *F* centers and centers responsible for the 730-nm band, suggesting that the 730-nm band is due to potassium colloidal particles.<sup>1,3</sup> The peak position 730 nm and half-width 0.25 eV of the IR band observed in the present work did not change with heat treatment in dark in the highly pure crystals, a result different from those obtained by earlier workers.<sup>1,3,5</sup>

The effect of combination of heat and visible light on the coagulation of *F* centers in another highly pure *H2* crystal containing the same ( $9.0 \times 10^{17} \text{ cm}^{-3}$ ) excess alkali atoms is shown in Fig. 2. The *R*, *M*, and *N* centers are formed at 50°C (curve 1), but on quenching the crystal from 70°C, the *R* centers disappear and the *M* and *N* concentration increases (curve 2). Curves 3, 4, and 5 show the effect of quenching the crystals from 150, 200, and 250°C, respectively. The *F*-center concentration becomes small at 200°C and an IR band with a half-width of 0.4 eV, designated as *X* band, is observed at 700 nm.

On quenching the crystal from 280°C, in light, this band shifts to 730 nm and a small *F* band is also formed (curve 6). The half-width of the 730-nm band is now 0.28 eV. The band again showed a heterogeneous equilibrium with the *F* band, and is therefore identical with the colloidal band.

On quenching the crystal from 350, 380, and 450°C, curves 7, 8, and 9 show that the colloidal band decreases

<sup>9</sup> S. C. Jain and G. D. Sootha, *J. Phys. Chem. Solids* **26**, 267 (1965).

<sup>10</sup> W. D. Compton and H. Rabin, *Solid State Phys.* **16**, 121 (1964).

in intensity and shifts continuously to longer wavelengths, and its half-width increases. The area under the band is sensitive to the heating rate and the intensity of visible light used.

### 2. Crystals With Background Impurity and Deliberately Doped Barium Impurity

Experiments similar to those performed on *H1* and *H2* crystals were also performed on *B* crystals containing about 10 ppm of background divalent cation impurity and  $10^{16}$ – $10^{18}$ - $\text{cm}^{-3}$  *F* centers. The results obtained with *B* crystals heated in the dark are qualitatively similar to those obtained with the *H* crystals. *F* centers are stable below 200°C; the heterogeneous equilibrium between the IR band and the *F* band was observed in the temperature range 300–450°C, indicating the colloidal nature of the centers giving absorption under the IR band. However, in *B* crystals the peak position of the colloidal band changes<sup>11</sup> from 730 to 745 nm on increasing the temperature of quenching from 300 to 450°C. The half-width of the band is 0.30 eV as compared with 0.25 eV for *H* crystals heated in the dark.

Apparently the behavior of *B* crystals heated in light and quenched from temperatures below 250°C is the same as that of the *H* crystals heated and quenched similarly. However, the conductivity results show that the IR band in the *B* crystals is not the same as the *X* band obtained in the *H2* crystal (curves 3, 4, and 5 of Fig. 2). The band in *B* crystals is sensitive to the background impurity and is presumably a Scott *R'* band.<sup>12,13</sup> ESR measurements to be described later in this paper show that at 300°C a part of Scott *R'* centers are converted into colloidal centers. The composite colloidal and Scott *R'* band move to longer wavelengths and become broad on heating the crystal to temperatures higher than 300°C.

The behavior of the *D* crystals doped with Ba or Cd impurity is very different. A strong IR band at 730 nm of half-width 0.35 eV and a large decrease in *F* band are observed in *D1* crystal containing 40 ppm of Ba impurity when heated in dark to 200°C. It will be shown later that the absorption under this band is partly due to colloidal centers and partly due to Scott *R'*-type or other complex centers. On increasing the temperature, the composite IR band becomes weak and moves to the longer wavelengths and finally disappears at  $\sim 400^\circ\text{C}$ . A broad IR band at 820 nm was formed in *D2* crystal containing the same Ba concentration but heated in

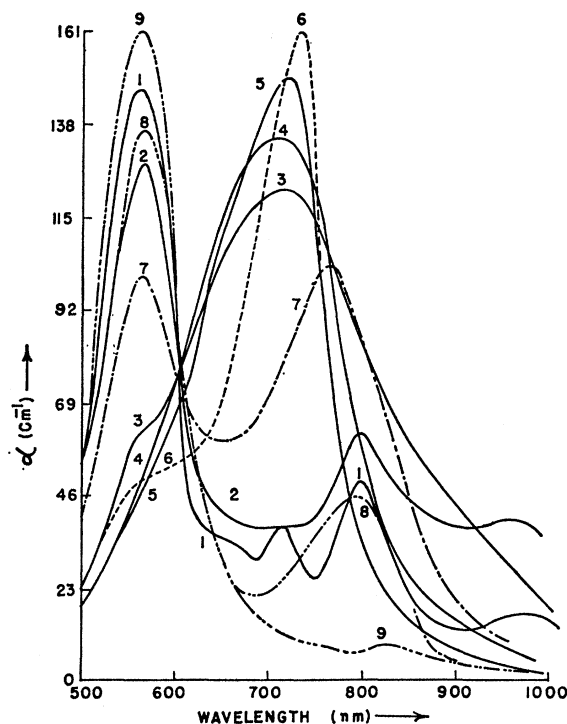


Fig. 2. Absorption spectra of an additively colored *H2* crystal containing  $9.0 \times 10^{17}$   $\text{cm}^{-3}$  excess potassium atoms and quenched from different temperatures to room temperature in light. Curves 1–9 correspond to quenching temperatures 50, 70, 150, 200, 250, 280, 350, 380, and 450°C, respectively.

light to temperatures in the range 100–400°C. *D3* crystal containing 80 ppm of Ba and heated in light or dark behaved in a manner similar to *D2* crystal. In addition to the possible absorption due to *X*, Scott *R'*, and colloidal centers, the *D* crystals have further complication because of the absorption by the *Z* centers.<sup>1</sup> Kojima<sup>14</sup> has shown that the *Z*<sub>2</sub> band in Ba-doped KC1 crystals has a component at 800 nm also.

Experiments were also performed on *D4* crystals containing 30 ppm of cadmium impurity. No IR bands (including *R*, *M*, and *N* bands) could be formed in this crystal. Optical absorption bands on the short-wavelength side of the *F* band observed in the cadmium-doped crystals<sup>2</sup> will be discussed in paper II<sup>15</sup> and in detail in a later publication.<sup>16</sup>

## B. ESR Measurements

### 1. Highly Pure Crystals

The ESR absorption measurements were made on several highly pure II crystals containing different concentrations of excess potassium metal. The quenched

<sup>11</sup> Our earlier results (Ref. 9) indicated that the peak position of the IR band in crystals grown from BDH material heated in dark was constant. Presumably, the batch from which those crystals were grown was purer than the *B* crystals used here.

<sup>12</sup> A. B. Scott and L. P. Bupp, Phys. Rev. **79**, 341 (1950). The notation *R'* has also been used to denote the center formed by the capture of an electron by the *R* center (Ref. 10). To avoid confusion, we shall designate the present band as the Scott *R'* band.

<sup>13</sup> T. Ikeda and S. Yeshida, J. Phys. Soc. Japan **22**, 138 (1967).

<sup>14</sup> K. Kojima, J. Phys. Soc. Japan **19**, 868 (1964).

<sup>15</sup> S. C. Jain and G. D. Sootha, following paper, Phys. Rev. **171**, 1083 (1968).

<sup>16</sup> S. C. Jain, G. D. Sootha, and R. K. Jain (to be published).

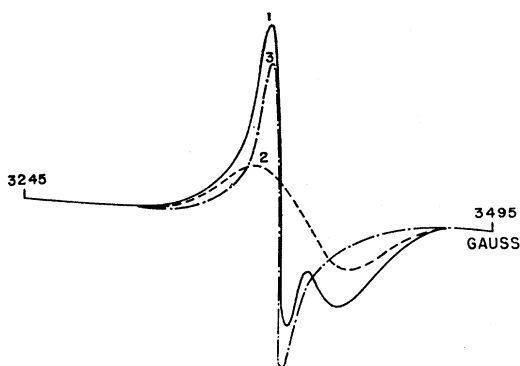


FIG. 3. Curve 1 is the first-derivative trace of the ESR spectra taken from the recorder chart, at room temperature for additively colored *H1* crystal ( $N_f = 9.0 \times 10^{17} \text{ cm}^{-3}$ ) after quenching from  $300^\circ\text{C}$  in dark. Curve 2 is the expected *F*-center ESR absorption for this crystal (see text). Curve 3, obtained after subtracting curve 2 from the composite curve 1, is the CESR line due to metal colloidal particles embedded in KCl crystal.

crystals containing only *F* centers gave a Gaussian ESR line with a half-width of 46 G and a *g* factor of 1.9957, in agreement with the well-known ESR absorption characteristic of the *F* centers in KCl crystals.<sup>1,17</sup> On quenching the crystals in the dark from temperatures below  $200^\circ\text{C}$ , the same ESR line with an intensity proportional to the *F*-center density was observed. The results obtained after quenching the crystals, containing more than  $5 \times 10^{16} \text{ cm}^{-3}$  excess potassium metal initially, from  $300^\circ\text{C}$  are most interesting. Now a narrow ESR line superimposed on the broad *F*-center ESR line is obtained. A typical trace, taken from the recorder, chart, obtained after quenching the *H1* crystal from  $300^\circ\text{C}$  to room temperature in the dark, is shown by curve 1 in Fig. 3. The optical absorption results for this crystal were given in Fig. 1. The intensity of the narrow ESR absorption line decreases on quenching the crystal from temperatures greater than  $300^\circ\text{C}$  and the *F*-center ESR absorption intensity increases. The narrow ESR line superimposed on the broad *F*-center ESR line disappears on quenching the crystals from  $450^\circ\text{C}$  or above.

A comparison of the ESR results with the optical absorption results shown in Fig. 1 shows that the optical absorption band of half-width 0.25 eV at 730 nm due to colloids and the narrow ESR absorption line appear and disappear at the same temperature and suggests that the narrow ESR line is due to the conduction ESR in the colloidal particles of potassium metal.

In order to separate the narrow ESR line from the composite spectra, the dependence of the intensity of the *F*-band ESR line on the *F*-center density was studied. The exact number of *F* centers present in the crystal quenched from  $300^\circ\text{C}$  was determined from the optical absorption measurements, and the expected ESR absorption line due purely to *F* centers was drawn (curve 2 in Fig. 3) and subtracted from the composite

curve 1 of Fig. 3. The narrow ESR absorption line (curve 3 in Fig. 3) thus separated from the composite spectra at room temperature is found to be Lorentzian in shape with a half-width of  $2.5 \pm 0.2$  G and a *g* value of 1.9998. The half-width of the ESR line was found to decrease from 2.5 G at room temperature to 2.0 G at liquid-nitrogen temperature. No change in the line shape and *g* value was observed at liquid-nitrogen temperature.

Bienenstock and Brooks<sup>18</sup> have calculated the *g* shift in different alkali-metal particles, (1) with and without the polarization correction and (2) with and without a term in the potential corresponding to an approximate self-consistent Hartree field due to the presence of other conduction electrons within the Wigner-Seitz sphere. The authors found that the best agreement with experiment for several alkali metals is obtained when the "polarization correction" is neglected and the Hartree term is included. Our value of 1.9998 for *g* is identical with that evaluated by these authors neglecting polarization correction and including the Hartree term for potassium metal, and is also in approximate agreement with, the value of 1.9997 recently observed by Walsh, Rupp, and Schmidt<sup>19</sup> for potassium metal. These results suggest independently that the narrow ESR absorption is due to potassium colloidal particles. The observed Lorentzian shape is also consistent with the metallic nature of the centers.<sup>19-23</sup>

Previous theoretical<sup>20</sup> and experimental<sup>19,21-23</sup> work on ESR absorption due to metallic conduction electrons has shown that the symmetry and half-width of the line changes with the particle size. Dyson<sup>20</sup> has discussed the effect of particle size on the symmetry of the CESR spectra and has shown that the line is symmetrical and Lorentzian if the size is smaller than the skin depth and in this case  $A/B = 1$ , where *A* and *B* are the maximum amplitudes of the first derivative of the ESR absorption on either side of the base line. In the present work, the ratio *A/B* remained close to unity even at liquid-nitrogen temperature. This therefore puts an upper limit of about 700 atoms on the size of the colloidal particles in KCl crystals. Rough estimate of the size of colloidal particles made from the observed half-width of CESR line<sup>24,25</sup> gives a value between 10 to 30 atoms per colloid. These values of colloidal size are within the limiting values estimated by Scott *et al.*,<sup>3</sup> from the optical work on additively colored KCl crystals.

It was found earlier that the optical absorption peak due to potassium colloids remains at 730 nm when the *H* crystals are quenched from  $300$ – $450^\circ\text{C}$  in the dark.

<sup>18</sup> A. Bienenstock and H. Brooks, *Phys. Rev.* **A136**, 784 (1964).

<sup>19</sup> W. M. Walsh, Jr., L. W. Rupp, Jr., and P. H. Schmidt, *Phys. Rev.* **142**, 414 (1966).

<sup>20</sup> F. J. Dyson, *Phys. Rev.* **98**, 349 (1955).

<sup>21</sup> G. Feher and A. F. Kip, *Phys. Rev.* **98**, 337 (1955).

<sup>22</sup> R. Catterall, *J. Chem. Phys.* **43**, 2262 (1965).

<sup>23</sup> R. J. Pressley and H. L. Berk, *Phys. Rev.* **140**, A1207 (1965).

<sup>24</sup> R. J. Elliott, *Phys. Rev.* **96**, 280 (1954); **96**, 2660 (1954).

<sup>25</sup> R. C. McMillan, *J. Phys. Chem. Solids* **25**, 773 (1964).

<sup>17</sup> H. Seidel and H. C. Wolf, *Phys. Status Solidi* **11**, 3 (1965).

The half-width of the optical absorption band as well as the CESR absorption line remains constant under these conditions. This shows that the colloidal size remains constant in the *H* crystals heated in the dark.

The area under the CESR absorption is compared with the area under the corresponding IR optical absorption band in Fig. 4. It is seen that the observed points for *H*1 crystal heated in dark lie on a straight line, indicating that the CESR absorption intensity increases linearly with the area under the colloidal band. The straight line does not pass through the origin but cuts the *x* axis at a finite value of the area. This suggests that all of the optical absorption under the IR band is not due to pure colloids even when the crystal is highly pure and is heated in the dark. The area of the optical band corresponding to the intercept made by the straight line on the *x* axis is about half of the area under the maximum IR band formed in the crystal quenched from 300°C in the dark. The area that does not correspond to the colloids is found to be independent of the initial *F*-center concentration and is mainly determined by the background impurity concentration present in the crystal.

## 2. Effect of Light and Impurity on ESR Absorption

The effects of visible light and background or doped divalent cation impurities on the ESR absorption in additively colored KCl crystals are summarized in Fig. 4 and are discussed below.

(1) Exposure of additively colored crystals to visible light produced the well-known<sup>17</sup> narrowing of the *F*-center ESR line. KCl crystals doped with 30 ppm of Cd behaved in a similar manner, even though no *F*-aggregate centers could be produced in these crystals. Barium-doped KCl crystals were not studied in detail because of the complication due to the absorption by the *Z* centers.<sup>1,26</sup>

(2) Point 250H2 in Fig. 4 shows that no ESR absorption due to *X* centers present in *H* crystals (see Sec. III A) is observed and that the *X* centers are different from the colloidal centers.

(3) The points 280H2 and 350H2 in Fig. 4, for crystals heated in light, lie close to the straight line obtained earlier for the *H* crystals heated in the dark. This shows that the fraction of the absorption under the colloidal band which is not due to colloidal centers is the same in *H* crystals heated to 280°C or more, in light or in dark. However, both the area of the optical colloidal band and the CESR line are considerably reduced on heating the crystal in light. Presumably, under the combined action of heat and light, the excess alkali metal diffuses out of the crystal faster. The half-width of the CESR line is now 3 G as compared with 2.5 G observed with crystals

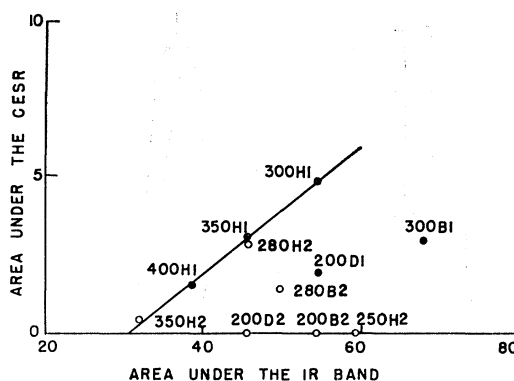


Fig. 4. Plot of the area under the CESR absorption due to potassium colloidal centers as a function of the area under the corresponding IR bands in KCl crystals quenched from different temperatures. The letters *H*, *B*, and *D* indicate highly pure, "pure," and doped crystals. The numbers placed before and after each letter indicate, respectively, the temperature in °C from which the crystal was quenched and the batch number from which the crystal was taken. ●, heating and quenching done *in the dark*; ○, heating and quenching done *in light*.

heated in the dark, suggesting that the shift of the optical colloidal band (curve 7, Fig. 2) to longer wavelengths is due to the increase in the size of the colloids under the combined action of heat and light.

(4) On quenching in dark, from 300°C, the *B* crystals containing ~10 ppm divalent cation impurities and more than  $1.0 \times 10^{17} \text{ cm}^{-3}$  excess potassium atoms gave a very weak CESR absorption line with slightly greater half-width (3.0 G) but the same *g* value. The point 300B1 for *B*1 crystal with  $7.0 \times 10^{17} \text{ cm}^{-3}$  excess alkali atoms in Fig. 4 shows that the ratio of the area under the CESR line to the area under the IR band is about  $\frac{1}{3}$  of the value expected from the straight line between the two areas for the *H* crystal. The part of the optical absorption not related to the colloidal centers increases rapidly with the increase in the background impurity concentration. This gives support to the conclusion arrived at earlier, that the area under the IR band given by the intercept made by the straight-line plot on the *x* axis in Fig. 4 is due to centers involving residual background impurity present in the *H* crystals. No colloidal centers are formed in crystals containing *F*-center concentration equal to or less than the concentration of background divalent cation impurity.

(5) The optical work discussed earlier showed that a strong IR band designated as the Scott *R'* band is formed in *B* crystals heated in the range 150–250°C. The point 200B2 for the *B*2 crystal containing  $7.0 \times 10^{17} \text{ cm}^{-3}$  excess potassium atoms shows that Scott *R'* centers do not give ESR absorption. When the *B* crystals heated in light and containing *R'* centers are quenched from 280°C, a very weak CESR line is observed, as shown by the point 280B2 in Fig. 4. A small part of Scott *R'* centers is converted to colloidal centers at 280°C.

<sup>26</sup> G. E. Conklin and R. J. Friauf, Phys. Rev. **132**, 189 (1963).

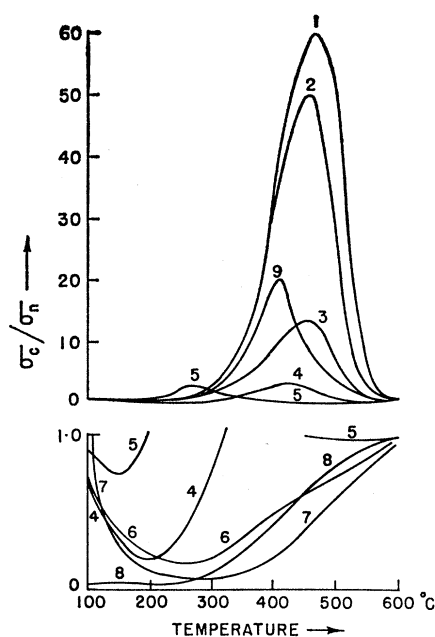


FIG. 5. Plot of  $\sigma_c/\sigma_n$  as a function of increasing temperature for additively colored *H*, *B*, and *D* crystals. Curves 1 and 9 are for *H1* and *H3* crystals containing  $1.5 \times 10^{18}$  and  $4.0 \times 10^{17}$   $\text{cm}^{-3}$ , respectively, of excess potassium-metal concentration initially and heated in dark. Curve 2 is for the *H2* crystal, identical to the *H1* crystal, heated in visible light. Curves 3 and 4 are for *B1* and *B2* crystals containing  $1.0 \times 10^{17}$   $\text{cm}^{-3}$  of excess potassium-metal concentration and heated in dark and light, respectively. Curves 5 and 6 are for *D1* and *D2* crystals doped with 40 ppm of Ba and heated in dark and light, respectively. Curve 7 is for the *D3* crystal doped with 80 ppm of Ba and heated in dark. Curve 8 is for the *D4* crystal doped with 30 ppm of Cd and heated in dark.

(6) Point 200D1 in Fig. 4 shows that *D1* crystal containing  $\sim 40$  ppm Ba concentration and  $\sim 10^{18}$   $\text{cm}^{-3}$  *F* centers gives a weak CESR line after quenching the crystal from  $200^\circ\text{C}$  in the dark. It is seen that though the optical absorption under the IR band in *H1* and *D1* crystals is the same, the ESR absorption under the CESR line, in *D1* crystal, is much smaller. The half-width of the CESR line is now 4 G as compared with 2.5 G in *H1* and 3 G in *B* crystals, in the dark. On increasing the Ba concentration further ( $\sim 50$  ppm), colloids cannot be formed, because no CESR is observed at any temperature. On heating the *D2* crystals doped with 40-ppm Ba in the temperature range  $30$ – $400^\circ\text{C}$  in light, no CESR could be observed. The point 200D2 in Fig. 4 shows the result obtained after quenching the crystal from  $200^\circ\text{C}$  in light. *D4* crystals containing 30 ppm or more of Cd impurity did not give CESR whether heated in light or in the dark. No optical absorption in the IR region was observed in this crystal.

The *g* value in all cases where CESR is observed is the same and the shape of the line Lorentzian. The increase in half-width in *H* crystals heated in light may be due either to larger size of the colloids formed in the presence of light or to inclusion of impurity atoms in the colloids in *B* and *D* crystals.

### C. Electrical Conductivity Associated with Colloidal Particles, and Effect of Light and Background Impurity

Curve 1 in Fig. 5 shows the plot of the ratio  $\sigma_c/\sigma_n$  ( $\sigma_c$  is the conductivity of the colored crystal and  $\sigma_n$  that of the uncolored crystal) versus temperature for the *H3* crystal containing  $1.5 \times 10^{18}$   $\text{cm}^{-3}$  excess potassium atoms and heated in the dark. It is seen from the plot that the ratio  $\sigma_c/\sigma_n$  remains unity up to  $\sim 250^\circ\text{C}$  and starts increasing at higher temperatures. After attaining a maximum value 60 at  $465^\circ\text{C}$ , it starts decreasing and becomes unity at  $\sim 600^\circ\text{C}$ . These results are in qualitative agreement with the results obtained earlier with *B* crystals in the dark.<sup>9</sup> Curve 2 gives the results for an identical crystal *H4* heated in light. It is seen that the conductivity near the peak is suppressed from 60 to 50 in the presence of light. The maximum area under the optical or ESR colloidal band is obtained at  $300^\circ\text{C}$  in dark and  $280^\circ\text{C}$  in light. By comparing curve 6 in Fig. 1 with curve 6 in Fig. 2, it can be seen that the maximum area of the colloidal band in the crystal heated in light is about 20% less as compared with that in crystal heated in the dark. Thus the reductions in the maximum colloidal-band area and in the peak value of  $\sigma_c/\sigma_n$  on heating the *H* crystal in the dark and in light are in the same ratio. It was pointed out earlier that in the presence of light, a part of the excess alkali metal present in the crystal diffuses out.

The results for *B3* and *B4* crystals containing  $1.0 \times 10^{18}$   $\text{cm}^{-3}$  excess potassium metal and heated in the dark and in light, respectively, are shown by curves 3 and 4. The lower portion of Fig. 5 shows the plot of conductivity ratio  $\sigma_c/\sigma_n$  between zero and unity on an enlarged scale. The peak value of the conductivity ratio is reduced from 14 to 3.5 and the peak position changes from  $450$  to  $430^\circ\text{C}$  when the heating is done in light. Thus the effect of light is more pronounced in the *B* crystals than in the *H* crystals. Curve 5 for the conductivity ratio of the *D1* crystal doped with 40 ppm of barium and containing  $10^{18}$   $\text{cm}^{-3}$  *F* centers and heated in the dark shows a peak at about  $260^\circ\text{C}$ . The value of  $\sigma_c/\sigma_n$  at the peak is 3. Curve 6 shows that  $\sigma_c/\sigma_n$  is suppressed considerably in the whole temperature range when the *D2* crystal containing 40 ppm of barium is heated in light. Curves 7 and 8 show that similar results are obtained with *D3* and *D4* crystals doped with 80 ppm of Ba and 30 ppm of Cd, respectively, even when heated in the dark.

The effect of background impurity on the conductivity in the colloidal region can be seen by comparing curve 1 for *H3* crystal with curve 3 for *B3* crystal. The concentration of excess potassium metal in the *B3* crystal is about  $\frac{2}{3}$  of that in the *H3* crystal, but the peak value of the conductivity ratio in *B3* crystal heated in dark is 14, less than  $\frac{1}{4}$  of the peak value in *H3* crystal heated similarly. Curve 9 for *H5* crystal containing  $4.0 \times 10^{17}$   $\text{cm}^{-3}$  excess potassium metal and heated in

the dark further emphasizes the effect of background impurity on the excess conductivity. Though the concentration of excess metal in this crystal is less than half of that in *B3* crystal, the peak value of the conductivity ratio in the *H5* crystal is still 50% larger as compared with that in the *B3* crystal.

Both the concentration of colloids and the excess conductivity due to the colloids are considerably reduced by exposure of the crystal to light or by the background impurity, and the effect becomes more pronounced by the combination of the two. The values of  $\sigma_e/\sigma_n < 1$  observed with impure crystals will be discussed in detail in paper II.

In earlier works,<sup>2,9</sup> the observed excess conductivity ( $\sigma_e - \sigma_n$ ) in the temperature range 300–500°C in KCl was attributed to electrons emitted thermally by the potassium-metal particles into the conduction band of the salt crystal. On this model, the temperature variation of the excess conductivity ( $\sigma_e - \sigma_n$ ) is given by

$$\sigma_e = \sigma_e - \sigma_n = CT^{3/2}F(T)e^{-(\varphi - \chi)/kT}, \quad (1)$$

where  $\varphi$  is the thermionic work function of potassium particles for emission of electrons into vacuum,  $\chi$  is the electron affinity of KCl,  $F(T)$  is a function of the concentration of colloids and therefore depends on the temperature, and  $C$  is a constant.

In the earlier work,  $F(T)$  was taken to be proportional to the area under the IR optical absorption band. The value of  $\varphi - \chi$ , and hence of  $\chi$ , has been reevaluated by taking  $F(T)$  proportional to the area under the CESR line as suggested by the results of Fig. 4. The value of  $\chi$  for KCl now comes out to be 0.23 eV as against 0.32 eV reported previously.<sup>9</sup>

The detailed theory of ionization of metal particles embedded in a crystal has not been worked out. Einbinder,<sup>27</sup> Smith,<sup>28</sup> and Sodha<sup>29</sup> have discussed the electron density in equilibrium with solid particles suspended in a gas at high temperatures. If the maximum ionization is one electron per particle, the electron density will be given by Saha's equation,<sup>28,30</sup> and for small densities the temperature variation of electron density will be governed by an exponential term with energy  $\frac{1}{2}\varphi$ . On the other hand, if multiple ionization takes place, the energy in the exponential term may be considerably more than  $\varphi$ , since the small particles are charged as the emission of electrons proceeds and the work function increases. The work function may also change because the colloids are in the molten state at these high temperatures. However, recent work has shown that the saturation of  $F$ -center density in a crystal colored additively at higher temperatures is controlled by the work function of the alkali metal, and the experiment suggests that the work function in the molten state is not

much different from that in the solid state.<sup>31</sup> In any case, the value of  $\chi$  obtained by this method should be regarded as only a rough estimate.

The shift in peak position  $T_0$  with excess potassium concentration  $n_K$  is given by<sup>2,9</sup>

$$n_K = De^{-\Delta Hc/kT_0}, \quad (2)$$

where  $\Delta Hc$  is the energy required to take one atom from the colloidal particle and convert it into an  $F$  center. Present work has confirmed that in identical crystals, heated in the dark, the observed shift in peak position is given by Eq. (2), with  $\Delta Hc = 0.8$  eV.

Attempts have also been made to correlate the preexponential factor  $CF(T)$  in expression (1) for ( $\sigma_e - \sigma_n$ ) with the total number of colloids present in the crystal.<sup>32</sup> Assuming that the colloids are effectively plane emitters, that their surfaces are perpendicular to the applied electric field, that the total volume of colloids present in the crystal is a small fraction of the volume of the crystal itself, and that the applied field is large enough so that the space-charge effects can be neglected, Kothari and Jain<sup>32</sup> have written expression (1) in the form

$$\sigma_e = (\sigma_e - \sigma_n) = 2ev \left( \frac{2\pi mkT}{A} \right)^{3/2} e^{-(\varphi - \chi)/kT}, \quad (3)$$

where  $A$  is the area of the crystal surface and  $S$  is an area related to the concentration of colloids, both areas being perpendicular to the applied field. Comparing the preexponential factor with the observed value and assuming a reasonable value for the electron mobility  $v$ , the authors have obtained the value of  $n$ , the number of atoms in each colloid.<sup>32</sup> However, the procedure is extremely rough and calculations of free-electron density in the crystal such as those made for particles suspended in gases<sup>28,29</sup> will be very valuable.

Before concluding this section, we would like to make some comments on the nature of  $X$  and  $R'$  centers. The  $X$  band seems to be due to atomically dispersed centers. It is also found in crystals which are exposed to light and heated in the dark.<sup>15</sup> Fischer<sup>33</sup> has suggested that the centers responsible for this may be one-dimensional needles or two-dimensional platelets of potassium atoms. Such needles and platelets of impurities in KCl crystals doped with  $KO_2$  have been observed by Fischer. However, EPR expected from such centers<sup>34</sup> could not be observed by us.  $X$  centers have no influence on the conductivity of the crystal.<sup>15</sup> Scott  $R'$  centers, though

<sup>31</sup> A. S. Shibanov, *Fiz. Tverd. Tela* **7**, 312 (1965) [English transl.: *Soviet Phys.—Solid State* **7**, 249 (1965)].

<sup>32</sup> D. S. Kothari and S. C. Jain, *Phys. Letters* **13**, 203 (1964). There is an error in Eq. (1) of this paper. The factor  $A$  has been omitted in the denominator of the preexponential factor on the right-hand side of the equation. However, this did not cause any error in the calculations, since  $A$  was unity for crystals used in those experiments.

<sup>33</sup> F. Fischer (private communication).

<sup>34</sup> A. Guinier and M. Lambert, in *Cluster Conference Proceedings*, Harwell, 1966, p. 281 (unpublished).

<sup>27</sup> H. Einbinder, *J. Chem. Phys.* **26**, 948 (1957).

<sup>28</sup> F. T. Smith, *J. Chem. Phys.* **28**, 746 (1958).

<sup>29</sup> M. S. Sodha, *Brit. J. Appl. Phys.* **14**, 172 (1963).

<sup>30</sup> M. N. Saha, *Phil. Mag.* **40**, 472 (1920).

optically similar to the  $X$  centers, decrease the conductivity of the crystal by a large factor.<sup>15</sup>

#### D. Experiments of Other Workers on Colloids in Alkali Halides

(1) Our results on the effect of barium and cadmium impurity on the formation of colloids are in qualitative agreement with the optical work of earlier authors.<sup>35,36</sup> Low concentration of barium reduces the maximum concentration of colloids that can be formed and high concentration of barium suppresses the colloidal band completely. 30 ppm of cadmium impurity suppress completely the formation of the colloidal and all other  $F$ -aggregate bands on the long-wavelength side of the  $F$  band.

(2) Penley and Witte<sup>5</sup> have found that the half-width of the "colloidal band" in KCl crystals heated in the dark was more than that which would correspond to Mie theory<sup>1</sup> and that in two cases the peak position was 800 nm as compared with all other cases, where the peak position was between 715 and 725 nm, Nadeau<sup>37</sup> has observed two components of the "colloidal band" at 735 and 769 nm in KCl crystals annealed at 290°C. In a few cases, we observed two such components in "pure crystals" containing unknown background impurity and in crystals doped with barium. The work reported here shows that the large half-width structure in IR band and shift in peak position of the IR band observed by earlier workers are related to the unknown background impurity present in the crystal and to the effect of the exposure of the crystal to light.

(3) Etzel<sup>38</sup> has found that the width of the "colloidal band" in NaCl increases with temperature and concluded that the so-called colloidal band must be due to atomically dispersed centers. Though the work similar to that reported here has not been performed on NaCl crystals, one would expect that the effect of heat and light will be the same on KCl and NaCl crystals, and

the band observed by Etzel was similar to the  $X$  band observed by us. Sastry<sup>39</sup> has confirmed that the width of the colloidal band developed in additively colored NaCl crystals in the dark is temperature-insensitive.

(4) Bugai *et al.*<sup>6</sup> were able to measure ESR absorption due to colloids in sodium-chloride crystals, but they found that the "colloidal band" in potassium-chloride crystals did not give the ESR absorption. Recently, Sonder<sup>7</sup> has measured the magnetic susceptibility associated with the color centers in KCl and has come to the conclusion that the "colloidal centers" are not magnetic. These authors heated the additively colored potassium-chloride crystals in visible light at or below 280°C to produce the "colloidal band." The results of these authors are in agreement with the results discussed in this paper, since in none of the  $H$  or  $B$  crystals heated in light below 280°C could colloids be formed. The bands observed by these authors must have been  $X$  or Scott  $R'$  type of bands.

(5) Berge and co-workers<sup>40</sup> have found that the conductivity of lithium-fluoride crystals irradiated by heavy doses of neutrons ( $\gtrsim 10^{18}$  nV) is considerably enhanced. The effect was more pronounced in highly pure LiF crystals. In these crystals conductivity could be increased by a factor of up to  $10^3$ . ESR<sup>17,41</sup> and NMR<sup>42</sup> absorption measurements and microthermal and x-ray analysis<sup>34</sup> have shown that the same high doses of neutrons ( $\gtrsim 10^{18}$  nV) produce precipitates of small lithium-metal particles in LiF crystals. We suggest that the enhanced conductivity observed by Berge and co-workers<sup>40</sup> is due to electrons thermally emitted by lithium particles into the conduction band of the salt crystal. This interpretation is supported by the fact that the effect of background impurity and the general behavior of enhanced conductivity in LiF are similar to those observed by us in KCl in the colloidal region. A rough analysis of the data of Berge and co-workers yields  $\chi = 1.18$  eV for LiF crystals.

<sup>39</sup> P. V. Sastry (private communication).

<sup>40</sup> P. Berge and G. Blanc, *Bull. Soc. Franc. Mineral. Crist.* **83**, 257 (1960); M. Dubois, P. Berge, and G. Blanc, *Discussions Faraday Soc.* **31**, 167 (1961).

<sup>41</sup> R. Kaplan and F. J. Bray, *Phys. Rev.* **129**, 1919 (1963).

<sup>42</sup> A. Van Den Bosch, *J. Phys. Chem. Solids* **25**, 1293 (1964).

<sup>35</sup> L. R. Watson and A. B. Scott, *J. Chem. Phys.* **30**, 342 (1959).

<sup>36</sup> N. A. Tsal and M. V. Pashkovskii, *Fiz. Tverd. Tela* **6**, 780 (1964) [English transl.: *Soviet Phys.—Solid State* **6**, 607 (1964)].

<sup>37</sup> J. S. Nadeau, *J. Appl. Phys.* **34**, 2248 (1963).

<sup>38</sup> H. W. Etzel, in Ref. 1, p. 266.