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Optical and Electrical Studies of Colloidal and *F*-Aggregate Centers in Highly Pure KBr Crystals

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The optical and thermal stability of *F*, *M*, *R* bands and colloids in KBr is measured. Extensive measurements on conductivity of the additively colored crystals are reported. Excess electronic conductivity is observed; it is due to *M* centers below 150°C and to colloids between 300 and 450°C. The background divalent cation impurities suppress the excess conductivity due to *M* centers and colloids, and reduce the ionic conductivity at $\sim$300°C to a value much less than that of a similar uncolored crystal. The influence of light on the excess and the ionic conductivity in the colored KBr crystals is also discussed. OH$^-$ impurity enhances both the optical colloidal band and the excess conductivity associated with it. The results are compared with those obtained by us recently for KCl crystals.

I. INTRODUCTION

RECENT measurements of the electrical conductivity of additively colored KCl crystals[1–4] show that color centers modify the conductivity of the crystal in a remarkable manner. Some measurements of conductivity in colored KBr crystals have also been made.[5,6] The investigations on KBr crystals which corroborate the results for KCl crystals and reveal several new features are reported in this paper.

II. EXPERIMENTAL

The methods of growing the crystals, slowly cooling or quenching them, additive coloration, optical-absorption measurements, bleaching with white light, and electrical-conductivity measurements have been described earlier.[3,7–9] The crystals grown from spectrographically pure powder obtained from Johnson-Matthey and Co., Ltd., England, are designated as highly pure (H) crystals, and those grown from "pure" guaranteed reagent powder obtained from S. Merck Ltd., India, are designated as G crystals. Crystals were also grown with cadmium impurity, and these crystals are designated as D crystals. A number placed after the letter H, G, or D indicates the batch number of the colored crystal from which samples were taken for optical and electrical measurements, and therefore refers to a specific value of the excess alkali-metal concentration n_K in the crystal. The value of n_K was calculated from optical-absorption measurements on the additively colored and quenched crystals. These crystals showed mainly *F*-band and a very small *M*-band absorption. Knowing the concentrations n_F and n_M of the *F* and *M* centers from the absorption data (using the Smakula-Dexter formula[10]), n_K was calculated from the relation $n_K=n_F+2n_M$, since each *M* center consists of two *F* centers.[10] From the ionic-conductivity measurements,[11,12] the H crystals were found to contain $\sim 10^{-10}$ and G crystals $\sim 10^{-8}$ molar fractional concentration of the background divalent cation impurities. The purity of H crystals is comparable to that in crystals grown by Grundig[13] from zone-refined KBr material. The concentration of cadmium impurity in the D crystals was determined from the ionic-conductivity measurements as well as polarographically.[11,14] The crystals were heated at a rate of 1°C/min up to 200°C, and 2°C/min above 200°C for electrical-conductivity measurements at different temperatures. Reproducible and consistent results were obtained with these heating rates. Relative humidity was kept low ($\sim$20%) with the help of a Voltas dehumidifier and was increased to $\sim$80% by introducing steam into the heating furnace when desired. All results described in the paper were made at low humidity unless otherwise specified.

III. RESULTS AND DISCUSSIONS

A. Optical Studies

Properties of the color centers in KBr have been studied less thoroughly than in KCl.[10] Some results of optical-absorption studies are reported in this section.

Typical results of the decay of *F* band and growth of

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[1] L. M. Shamovskii, A. A. Dunina, and M. I. Gosteva, Fiz. Tverd. Tela **2**, 2526 (1960) [English transl.: Soviet Phys.—Solid State **2**, 2252 (1961)].

[2] S. C. Jain and G. D. Sootha, Nature **193**, 566 (1962).

[3] S. C. Jain and G. D. Sootha, J. Phys. Chem. Solids **26**, 267 (1965).

[4] S. C. Jain and G. D. Sootha, Phys. Rev. **171**, 1075 (1968); **171**, 1083 (1968).

[5] V. V. Krasnopevtsev, Fiz. Tverd. Tela **4**, 1807 (1962) [English transl.: Soviet Phys.—Solid State **4**, 1327 (1963)].

[6] J. N. Maycock, J. Appl. Phys. **35**, 1512 (1964); Research Institute for Advanced Studies Technical Report 64-2, 1964 (unpublished).

[7] S. C. Jain and P. C. Mehendru, Phys. Rev. **140**, A957 (1965).

[8] S. C. Jain and G. D. Sootha, Phys. Status Solidi **22**, 505 (1967).

[9] S. C. Jain and V. K. Jain, J. Phys. **C1**, 895 (1968).

[10] W. D. Compton and H. Rabin, Solid State Phys. **16**, 121 (1964).

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

[12] J. Rolfe, Can. J. Phys. **42**, 2195 (1964).

[13] H. Grundig, Z. Physik **182**, 477 (1965).

[14] I. M. Kolthoff and J. J. Lingane, in *Polarography* (Wiley-Interscience, Inc., New York, 1952), Vol. 2.

R and *M* bands while bleaching an additively colored H crystal, having $n_K=5.0\times10^{17}$ cm^{-3}, with white light from a 60-W incandescent lamp[9] at room temperature are shown by curves 1, 2, and 3, respectively, in Fig. 1. The *N* band could not be produced by optical bleaching alone. When a colored crystal with $n_K=3.8\times10^{17}$ cm^{-3}, optically bleached for 2 h, was kept in the dark at room temperature, optical absorption at the *F*, *R*, *M*, and *N* bands changed with time as shown by the curves 4–7, respectively, in Fig. 1. It is seen from these curves that after optical bleaching the *F* band increases for an initial period of about 20 h and the *M* band for an initial period of 40 h, and then they start decreasing; the *R* band decays and the *N* band grows continuously with time. The results obtained in case of optical bleaching with monochromatic *F* light are essentially the same as in the case of white-light bleaching except that the relative decay and growth rates of the *F*, *M*, and *R* bands are modified slightly.[9] This is due to the fact that the white-light spectrum consists of two regions of maximum intensity, one in the *F*-band region and the second in the *M*-band region of KBr, which causes simultaneous bleaching of the *M* centers in white-light bleaching.

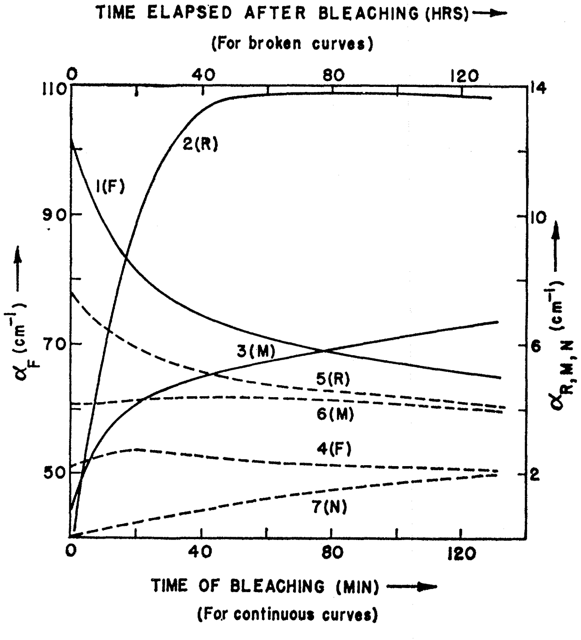

FIG. 1. Influence of optical bleaching and room-temperature annealing on the concentrations of *F* and *F*-aggregate centers in KBr. Continuous curves: changes in the absorption coefficient α at the peaks of *F*, *R*, and *M* bands with time of optical bleaching at room temperature in an additively colored H crystal ($n_K=5.0\times10^{17}$ cm^{-3}). Broken curves: changes in the values of α at the peaks of *F*, *R*, *M*, and *N* bands with time at room temperature in an additively colored H crystal ($n_K=3.8\times10^{17}$) exposed to white light for 2 h prior to optical-absorption measurements.

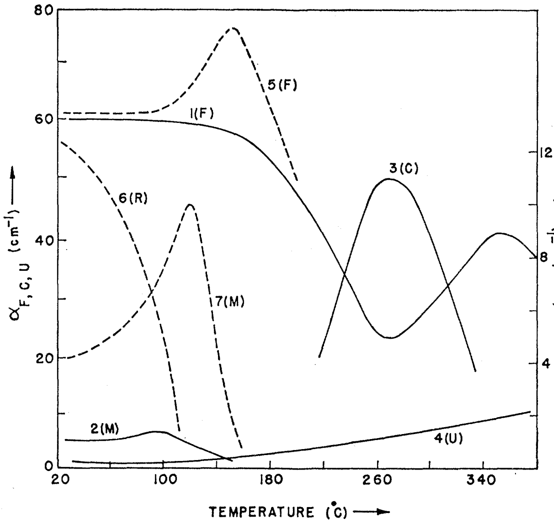

FIG. 2. Changes in the absorption coefficient α at the peaks of *F*, *M*, *C*, and *U* bands with temperature in the dark in an additively colored and quenched H crystal having $n_K=2.9\times10^{17}$ cm^{-3} (continuous curves), and at the peaks of *F*, *R*, and *M* bands with temperature in the dark for another colored H crystal ($n_K=4.1\times10^{17}$ cm^{-3}) bleached with while light at room temperature for 90 min prior to heating (broken curves) in the dark.

Figure 2 shows the changes in the concentration of the *F*, *F* aggregate, and other centers on heating the additively colored (H) crystals, in the dark and in dry atmosphere. Curves 1–4, respectively, show the changes in the absorption coefficient α (cm^{-1}) at the peaks of *F*, *M*, colloid (*C*), and *U* bands on heating a crystal having $n_K=2.9\times10^{17}$ cm^{-3} immediately after additive coloring and quenching. Curves 5–7 show the changes on heating in α at the peaks of *F*, *R*, and *M* bands, respectively, for a crystal having $n_K=4.1\times10^{17}$ cm^{-3} and bleached with white light at room temperature for 90 min prior to heating. From these results and the results of Fig. 1, the relative thermal stability of *F*, *F* aggregate, and colloidal centers can be written as follows:

$R\rightarrow F+M+N$, ($\gtrsim$room temperature)
$M\rightarrow F$, $\gtrsim$(100°C) (in crystals not exposed to white light)
$F\rightarrow C$, ($>150°$)
$C\rightarrow F$, ($>250°$C).

N centers are quite stable at room temperature and disappear completely at ~100°C. In the optically bleached crystals, which contain high concentration of the *F*-aggregate centers, the *M*-center concentration is maximum at ~120°C and it decreases fast above 120°C. At 120°C the crystal contains only *F* and *M* bands. Formation of the colloid band is aided by the presence of moisture in the atmosphere. The *U* band is due to hydride-ion impurity and is, presumably, formed by diffusion of some moisture into the crystal and its reaction with the excess alkali metal during heating. This band forms at a slow rate up to ~200°C, and its formation increases at higher temperatures.

From a detailed analysis of the absorption spectra of the crystals in different states, the peak positions and

TABLE I. Observed peak positions, half-widths, and oscillator strengths of various bands in KBr at room temperature.

Band	Peak position (nm)	Half-width (eV)	Oscillator strength
F	625	0.37	0.48[a]
M	920	0.15	0.11
$R(R_2)$	795	0.13	0.43
N	1080	0.05	0.06
C	740	0.35	...

[a] Taken from Compton and Rabin (Ref. 10).

half-widths of the F, F aggregate, and C bands were determined. These values are given in Table I. Purity of the crystals did not influence the peak positions of the F, M, R, and N bands. However, the half-widths of these bands in highly pure crystals were in general slightly smaller than those given in the table for reagent-grade pure crystals. Both the peak position and half-width of the C band were influenced by the purity of the crystal. In highly pure crystals the C band occurs at ~790 nm and has a half-width of 0.19 eV as compared to the peak position ~740 nm and half-width 0.35 eV in the reagent-grade pure crystal. This is presumably due to the formation of Scott R' centers[15] in the reagent-grade pure crystals which contain relatively larger background divalent cation impurities.

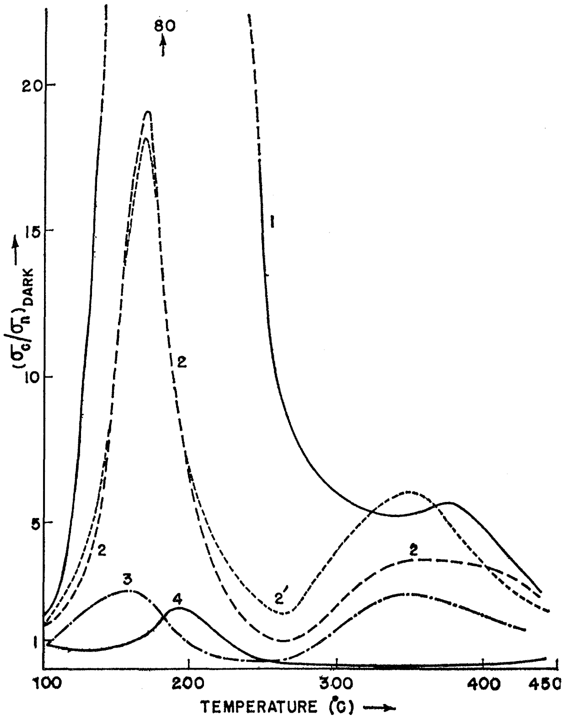

FIG. 3. Plot of the σ_c/σ_n as a function of increasing temperature for additively colored KBr crystals in the dark (humidity ~20%). Curves 1–4 are for the crystals H1, G1, G2, and D1, respectively, having $n_K = 2.9\times10^{17}$, 4.6×10^{17}, 1.7×10^{17}, and 1×10^{18} cm^{-3}. Curve 2′ is for the G1 crystal when σ_c was measured under high-humidity (~80%) conditions.

The values of the oscillator strengths of the M, R, and N centers determined[9] from these results are also given in Table I. The optical results are needed for the interpretation of the electrical-conductivity results (given in Sec. III A) and a summary of the results is given here. A more detailed account of the optical work is being published elsewhere.[9]

B. General Features of the Electrical Conductivity in the Temperature Region 100–450°C

Curve 1 in Fig. 3 shows a typical plot of the observed ratio of the conductivity σ_c of the colored crystal measured in the dark to the conductivity σ_n of the normal crystal as a function of increasing temperature for highly pure H1 crystal having excess alkali-metal concentration $n_K = 2.9\times10^{17}$ cm^{-3}. Curves 2 and 3 are for two "pure" crystals G1 and G2, having $n_K = 4.6\times10^{17}$ and 1.7×10^{17} cm^{-3}, respectively, and curve 4 is for D1 crystal doped with ~10 ppm Cd and having $n_K = 1\times10^1$ cm^{-3}. Curve 2′ is for the G1 crystal for the conductivity measurements under high-humidity conditions and will be discussed later. The ratio σ_c/σ_n is ~1 near 100°C. As the temperature is increased, the ratio increases, and after attaining a maximum value near 180°C it decreases; at still higher temperatures it attains a minimum value around 250°C, increases again, and finally shows a second maximum between 350 and 400°C. Comparison of curves 1 and 2 shows that the conductivity ratio σ_c/σ_n is smaller in the whole temperature range 100–450°C for the G crystal as compared to that for the H crystal even though the G crystal had larger excess alkali-metal concentration. Curve 4 for the cadmium-doped D1 crystal shows a large suppression in the ratio in the entire temperature range in spite of very high value of $n_K (1\times10^{18}$ cm$^{-3})$ in this crystal. The value of σ_c/σ_n around the minimum in this plot becomes 0.1, i.e., σ_c becomes $\frac{1}{10}$ of σ_n. For the same purity of the crystal, σ_c/σ_n increases with an increase in the value of n_K.

It is convenient to divide the conductivity plots of Fig. 1 into three regions: (a) region I from 100 to 250°C, where the first maximum in the conductivity plot occurs; (b) region II from 180 to 300°C, where the conductivity ratio σ_c/σ_n decreases and shows a minimum; and (c) region III from 250 to 450°C, where the ratio increases again and shows a second maximum.

C. Temperature Region 100–250°C

1. *Measurements in the Dark*

Recent work has shown that the increase in the value of σ_c/σ_n to more than unity is usually the electronic conductivity associated with the electrons ionized from the color centers and colloids in additively colored crystals.[3,4] The conductivity measurements were made with increasing temperature on additively colored H crystals with values of n_K in the range 1×10^{17} to

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[15] A. B. Scott and L. P. Bupp, Phys. Rev. **79**, 341 (1950).

9×10^{17} cm^{-3}. The peak in the σ_c/σ_n- versus-temperature plots is found to occur at the same temperature, 180°C, for crystals containing different excess concentration n_K of the alkali metal. As stated earlier, the additively colored crystals contain mainly *F* centers. The concentration of the *M* centers remains less than 2% of the concentration of *F* centers in these experiments. Higher *F*-aggregate centers are not present in these crystals.

The temperature cycle in a normal conductivity measurement on an additively colored and quenched crystal was reversed at 170°C. While the crystal was allowed to cool at a rate of 1°C/min, its conductivity was measured to see the effect of *M* centers on the conductivity, since *M* centers bleach on heating up to 170°C (Fig. 2). It was found that the conductivity during the cooling cycle was close to that during the heating cycle. If the colored crystal was heated to ~250°C in a conductivity measurement, and then the cycle was reversed, the excess conductivity and the maximum in the conductivity plot near 180°C could not be reproduced during cooling. Optically this crystal showed no *F* band, but a large C band.

These results show that the increase in the conductivity σ_c in the temperature region 100–250°C is not connected with the presence of a small *M* or other *F*-aggregate center concentration. The facts that the ratio σ_c/σ_n decreases above 180°C due to a decrease in the *F* band and that the excess conductivity disappears in crystals cooled from 250°C make it tempting to attribute the large excess conductivity in the region 100–250°C to the *F* centers. However, it seems unlikely for the following reasons.

(i) If n_K is increased, σ_c/σ_n does not increase in exact proportion to the *F*-center concentration. For H crystals taken from the same batch, it was found that when n_K was increased by a factor of about 7, σ_c/σ_n increased by a factor of only 5.

(ii) Energy of thermal ionization of an *F* center in additively colored KBr is[16] 1.78 eV, and it seems unlikely that the centers will be ionized at such a low temperature (~180°C).

(iii) Smakula[17] has measured the thermal ionization of the *F* centers in additively colored KBr in the intrinsic region above 480°C. An extrapolation of his results shows that no apprediable electron currents due to the ionization of *F* centers should be observable at or below 180°C.

The above extrapolation of the results of the intrinsic region to the extrinsic region is somewhat uncertain because the expression for the electronic conductivity due to *F* centers[16] involves a term of anion-vacancy concentration, and this concentration is not known in the extrinsic region.[11] Theoretically[11,16] the anion-vacancy concentration in the alkali-halide crystals near room temperature should be negligible ($10^{-2}-10^{-5}$ cm^{-3}). Experimental regults[7,18] on the studies of growth of *F* centers on x irradiation and on thermoluminescence of the irradiated crystals show large anion-vacancy concentration ($10^{16}-10^{17}$ cm^{-3}) at room temperature in KCl. The large anion-vacancy concentration in the extrinsic region will further suppress the conductivity due to the ionization of *F* centers. We therefore attribute the excess conductivity to electrons ionized from unknown centers of low-thermal stability.

(iv) Extensive work on KCl has not revealed any electronic conduction which can be attributed to electrons ionized from the *F* centers at these low temperatures.[4] This work supports the view that *F* centers should not give rise to appreciable number of conduction electrons below 200°C.

Logarithmic plots of the excess conductivity $\sigma_e=\sigma_c-\sigma_n$ as a function of $1/T$ for four H crystals H1, H2, H3, and H4 (having $n_K=2.9\times10^{17}$, 4.8×10^{17}, 8.7×10^{17}, and 1.4×10^{17} cm^{-3}, respectively) are found to be parallel straight lines. The slopes of these lines give a value of 1.2 eV for the thermal ionization energy of the centers responsible for the excess conductivity ($\sigma_c-\sigma_n$). If $\log(\sigma_e/T^{3/2})$ is plotted[16] in place of $\log\sigma_e$ as a function of $1/T$ to evaluate the activation energy, then the observed value of the energy is lowered by 0.05 eV.

The unknown centers are presumably formed by the electrons trapped at some shallow traps. We could not observe any optical-absorption band in the range 185–1000 nm due to the unknown centers. It is possible that the band, if any, is weak and was not detected.

2. *Effect of White Light*

If the colored crystal is exposed to light momentarily during the conductivity measurements, the conductivity near 180°C increases by a factor of ~30 at temperatures below 140°C. These results are qualitatively similar to those reported by other authors on the *F*-center photoconductivity in the alkali halides.[19,20]

Conductivity measurements were also made on additively colored crystals exposed to visible light prior to measuring the conductivity. Four neighboring slices from the colored H2 crystal having $n_K=4.8\times10^{17}$ cm^{-3} were exposed to white light at room temperature for 12, 30, 60, and 90 min, respectively, and subsequently their conductivities were measured in the dark. The σ_c/σ_n-versus-temperature plots before exposure to light and after 12, 30, 60, and 90 min exposures are shown in Fig. 4 by plots 1–5, respectively. It is seen that the excess conductivity in the colored crystal is en-

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[16] N. F. Mott and R. W. Gurney, in *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, England, 1948).

[17] A. Smakula, Gottingen Nachr. Math. Phys. K1 (NF) **1**, 85 (1934); see also R. W. Pohl, Proc. Phys. Soc. (London) **49**, 3 (1937).

[18] P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, Phys. Rev. **121**, 484 (1961).

[19] G. W. Nelson and A. B. Scott, in *Proceedings of the Conference on Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 297.

[20] F. C. Hardtke, A. B. Scott, and R. E. Woodley, Phys. Rev. **119**, 544 (1960).

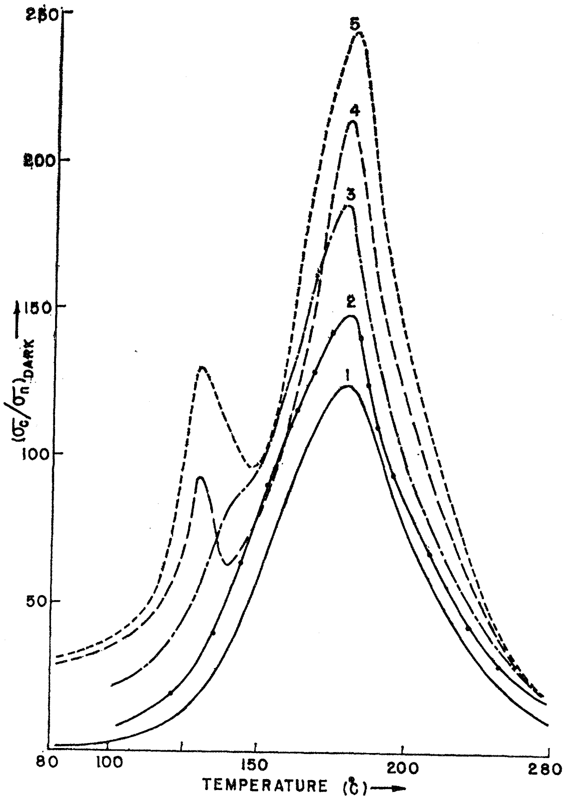

FIG. 4. σ_c/σ_n-versus-temperature plots in the dark for the H2 crystal having $n_K=4.8\times10^{17}$ cm^{-3}. Curve 1, colored and quenched crystal; curves 2–5, after exposing the colored crystal to white light at room temperature for 12, 30, 60, and 90 min, respectively, prior to conductivity measurements in the dark.

hanced in whole of the temperature region under consideration on preexposing the crystal to white light. The enhancement due to exposure to light increases with increase in the time of exposure and is more on the low-temperature side of the 180°C peak (characteristic of the crystals not exposed to visible light). A new peak appears at 130°C as the exposure time increases to 60 min. A comparison of these results with the results on the relative thermal stability of the *F* and *F*-aggregate centers in KBr (Sec. III A) shows that the enhancement in the excess conductivity in the exposed crystal in the temperature range 80–130°C is related to the *F*-aggregate centers.

It was shown in Fig. 2 that *R* centers are destroyed by heating the colored and preexposed crystal above room temperature. A colored crystal preexposed to light for 90 min was heated to 85°C, kept at this temperature for 2 h, and quenched from this temperature; its conductivity was then measured in the dark with increasing temperature. In another experiment both *R* and *M* centers were destroyed in a similar crystal by heating at 155°C for 2 h in the dark and the conductivity was measured after quenching. When only *R* centers are destroyed, the excess conductivity below 110°C is found to decrease appreciably as compared to that in the case of the exposed crystal containing *F*, *M*, and *R* centers, but the values of σ_c/σ_n at 130 and 180°C do not change. Thus, *R* centers seem to contribute to the conductivity significantly only below 110°C. When both *R* and *M* centers are destroyed, the peak at 130°C in the conductivitity plot vanishes and the excess conductivity near 180°C is also decreased considerably. In fact, the value of σ_c/σ_n at the peak of 180°C in this crystal was somewhat lower than that obtained in the additively colored crystal without any exposure to white light. We therefore conclude that the 130°C peak in the excess conductivity due to prior exposure of the colored crystal to white light is due to the presence of the *M* centers in the crystal. Since the *M* centers disappear almost completely at 180°C, the increase in the σ_c/σ_n peak in optically bleached crystals at 180°C cannot be due to *M* centers. It is possible that, on bleaching the *F* band by visible light, the number of unknown centers (discussed in Sec. III B) increases. On heating the crystal to a temperature in the range 150–180°C, some of the unknown centers seem to bleach along with the *M* centers.

It has been shown recently that optical absorption under the *M* band in KCl crystals is due to two different centers which have different thermal stabilities.[21,22] The two centers were designated as "soft" and "hard" *M* centers. In KCl, the excess conductivity due to soft *M* centers was observed in the neighborhood of 60°C. The excess conductivity due to hard *M* centers, expected at or above 120°C, could not be observed due to the complication of Scott *R′* centers which start forming at this temperature. The work on KBr shows that centers analogous to soft *M* centers are not formed in these crystals. Since the background impurity concentration in KBr crystals is much less than KCl crystals, Scott *R′* centers are now less important, and the σ_c/σ_n peak at 130°C seems to be due to hard *M* centers.

A plot of $\log(\sigma_c-\sigma_n)$ as a function of $1/T$ in the temperature region 110–130°C yields a rough value of 1.0 eV for the thermal ionization energy E_M of the hard *M* centers in KBr. The values of E_M are 1.0 and 1.2 eV for soft and hard *M* centers, respectively, in KCl. No earlier estimate of the value of E_M in KBr is available in literature.[10]

Similar experiments with G crystals show that the excess conductivity due to *M* and unknown centers is considerably suppressed by the background divalent impurities.

D. Temperature Region 180–300°C

The behavior of σ_c/σ_n in this temperature range was discussed in Sec. III B. In the temperature region 180–300°C the effects of divalent cation impurities and ordinary light on the coagulation of the *F* centers are important, and these determine the electrical effects of

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[21] S. C. Jain, P. C. Mehendru, and G. D. Sootha, J. Phys. Chem. Solids 29, 2072 (1968).

[22] G. D. Sootha, Ph.D. thesis, University of Delhi, 1967 (unpublished).

the centers in this temperature range as well as at higher temperatures. Detailed investigations reveal the following results.

(i) When a highly pure colored crystal is heated in the dark, colloids (which give rise to an optical-absorption band at ~790 nm in KBr) are mainly formed. In such crystals the value of σ_c/σ_n remains $\gtrsim 1$, even at the minimum in the σ_c/σ_n-versus-temperature plot near 300°C (curve 1 of Fig. 1).

(ii) In the presence of divalent cation impurities in the additively colored KBr crystals, the ionic conductivity decreases in the range 180–300°C and the formation of the colloids is suppressed even in the dark. A composite broad optical-absorption band, presumably a Scott R' band,[15] at a position between the F band and the pure C band is observed. When the impurity concentration is very small, the conductivity σ_c becomes less than σ_n at the minimum in the σ_c/σ_n-versus-temperature plot (curves 3 and 4 of Fig. 3). The excess conductivity due to M and other centers in the first region and due to colloids in the third region (to be discussed in Sec. III E) is also suppressed in such crystals.

(iii) In the presence of white light the conductivity is further suppressed in the impure crystals. The complex optical Scott R' band on the long-wavelength side of the F band becomes stronger.

These results are similar to those obtained by us for KCl crystals.[4,22] Since both F centers and ionic conductivity decay when Scott R' centers are formed and since background impurity ions are necessary for this to happen, the Scott R' centers must involve impurity ions, F centers, and cation vacancies. The formation of these centers is aided by visible light, presumably due to an increase in the F-center mobility by the light. More detailed investigations[11] show that the conductivity σ_c in a doped colored KBr crystal in the temperature region under consideration follows a second-order kinetics as found in case of KCl crystals.[4,22] A quanitative analysis of the results shows that the mechanism of the formation of the complex centers seems to be the same as in KCl, that is, first F centers and impurity ion-cation vacancy pairs combine to form the Scott R' center, and then, as the impurity-vacancy pairs are used up in this way, free cation vacancies and free impurity ions combine to form new pairs to maintain the equilibrium between the pairs and the free impurity ions and vacancies.[4,22] The second reaction in which the free cation vacancy concentration decreases is the rate determining process and controls the decrease in the conductivity. However, in the case of KBr crystals the growth rate of the Scott R'-type impurity centers is very fast, and the back dissociation of these centers soon becomes important.

E. Temperature Region 250–450°C

The potassium colloids, formed by heating the colored crystal up to ~250°C, give rise to excess electronic conductivity due to thermionic emission of electrons into the conduction band of the crystal from the colloids.[3,4,11] The case of thermionic emission from colloids in KCl crystals has been discussed in detail elsewhere.[3,4,22,23] Following the method discussed in these references, the value of $\phi-\chi$ (where ϕ is the work function for thermionic emission of potassium colloid into a vacuum, and χ is the electron affinity of the crystal) has been determined from the conductivity data for KBr crystals. It is found that for highly pure (H) KBr crystals $\phi-\chi$ is ~1.9 eV. Taking the value of ϕ the same as that for bulk potassium, 2.26 eV,[24] a value of 0.36 eV is obtained for the electron affinity χ of the KBr crystal.

The background divalent cation impurities concentration is found to have appreciable influence on the observed value of $\phi-\chi$ in KBr. For example, in the case of the pure G crystals, which have a background divalent cation impurity concentration larger by a factor of ~100 as compared to that in the H crystals, the value of $\phi-\chi$ is 1.3 eV. An explanation for the lower value of $\phi-\chi$ in the relatively impure crystals is not clear. Since the impurity concentration is high, some impurity cation may be adsorbed on colloid particles and reduce the work function for thermionic emission from these particles.[25]

It is well known that the presence of hydroxyl impurity in the alkali-halide crystals plays a definite role in the generation of colloids in these crystals.[26,27] The effect of heating the crystal in humid air was investigated by us in some detail. The optical studies (Sec. III A) have shown that even the presence of moisture in the atmosphere assists the coagulation of F centers into colloids in the KBr crystals. Electrical-conductivity measurements on additively colored G1 crystal in dry and in humid atmosphere (humidity 80%), (curves 2 and 2′, respectively, of Fig. 3) show that the excess conductivity due to colloids in the temperature region 250–450°C is also enhanced by the presence of moisture in the atmosphere. Thus the conductivity results support the inference drawn from the optical studies that moisture aids the formation of colloids. While comparing plots 2 and 2′ of Fig. 3, it must be pointed out that there is a slight decrease in the excess conductivity near 180°C in humid air as compared to that in dry air. This is consistent with the results that the colloids start forming at a lower temperature in humid air as compared to that in dry air,[9] and presumably causes fast decrease in the centers which give rise to excess conductivity at lower temperatures.

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[23] 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 in the equation. However, this did not cause any error in the calculations, since A was unity for the crystals used in these experiments.

[24] C. Herring and M. H. Nicholes, Rev. Mod. Phys. **21**, 185 (1949).

[25] A. J. Dekker, in *Solid State Physics* (MacMillan & Co. Ltd., London, 1958), p. 215.

[26] H. W. Etzel, Phys. Rev. **118**, 1150 (1960).

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

A comparison of the results obtained with NaCl, KCl, and KBr is interesting. Even in the purest NaCl crystals colored and kept in the dark, σ_c/σ_n is considerably suppressed in the temperature range 100–500°C, and excess conductivity due to F-aggregate centers or colloids is not observed.[11] The excess conductivity due to R, M, and colloids is significant in KCl if crystals are of high purity. The excess conductivity due to F-aggregate centers in the purest KBr crystals is larger by a factor of ~ 3 as compared to KCl crystals. The 180°C peak observed in KBr in the dark is not observed in KCl crystals. The background divalent cation impurity concentration (estimated from the conductivity data) in the best crystals used by us are 10^{-5} in NaCl, 10^{-6} in KCl, and better than 10^{-8} molar fraction in KBr. We believe that the differences in the behavior of the NaCl, KCl, or KBr are related to the differences in the concentration of background impurity in the crystals. KCl and KBr crystals containing large background impurity concentration behave like NaCl crystals.

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Normal Modes of a Semi-Infinite Ionic Crystal

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The normal modes of a semi-infinite ionic crystal bounded by a pair of (100) faces normal to the z direction but infinite in the x and y directions have been determined by a combination of analytical and numerical methods. Cyclic boundary conditions are imposed on the displacements along the x and y directions, but the presence of a pair of free surfaces is correctly incorporated into both the short-range and the long-range Coulomb contributions to the dynamical matrix. The latter contribution is made rapidly convergent by a modified Bessel-function transformation. The $6L\times 6L$ (L = number of atomic planes for the slab) eigenvalue equation for the normal-mode frequencies is solved numerically for general values of the wave vector throughout the two-dimensional first Brilluion zone. The two lowest-frequency modes are Rayleigh waves, whose degeneracy is slightly split by the presence of a pair of free surfaces. Optical surface modes are found whose limiting frequencies at infinite wavelength differ from those of the bulk LO and TO modes. The contribution to infrared absorption at infinite wavelength of the optical surface modes have been calculated and the effects of relaxing the intraplanar lattice parameter and the interplanar separations to minimize the potential energy of the slab have also been determined.

I. INTRODUCTION

The problem of determining the normal modes and their frequencies of finite or semi-infinite specimens of ionic crystals has received a good deal of theoretical attention in recent years.[1–7] Particular attention has been given to the determination of the frequencies of the long-wavelength optical modes which play a central role in determining the optical properties of ionic crystals at infrared frequencies. Inasmuch as the long-range Coulomb forces between ions make a significant contribution to the frequencies of the long-wavelength optical modes through the macroscopic fields to which they give rise, these frequencies are sensitive to the size and shape of the crystal specimens.

The limiting optical frequencies of a finite spherical crystal of the rocksalt structure were studied by Maradudin and Weiss,[2] neglecting retardation effects. These authors found that in the long-wavelength limit the frequencies of the longitudinal optical (LO) and transverse optical (TO) modes are equal, in contrast with the result obtained for infinitely extended crystals, in which these frequencies obey the Lyddane-Sachs-Teller[8] relation, $\omega_{\mathrm{LO}}/\omega_{\mathrm{TO}}=(\epsilon_0/\epsilon_\infty)^{1/2}\neq 1$, where ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants, respectively.[1] More recently, Fuchs and Kliewer[4] have examined the optical modes of an ionic crystal slab extending to infinity in the two lateral directions and of finite thickness. Neglecting retardation they found in this case that as the wave vector $\mathbf{k}\rightarrow 0$, the frequencies of the LO and TO modes are those of the infinitely extended crystal, and satisfy the Lyddane-Sachs-Teller

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[1] H. B. Rosenstock, Phys. Rev. **121**, 416 (1961).

[2] A. A. Maradudin and G. H. Weiss, Phys. Rev. **123**, 1968 (1961).

[3] T. H. K. Barron, Phys. Rev. **123**, 1995 (1961).

[4] R. Fuchs and K. L. Kliewer, Phys. Rev. **140**, A2076 (1965); K. L. Kliewer and R. Fuchs, *ibid.* **144**, 495 (1966); **150**, 573 (1966).

[5] R. Englman and R. Ruppin, Phys. Rev. Letters **16**, 898 (1966).

[6] A. A. Lucas, Phys. Rev. **162**, 801 (1967).

[7] A. A. Lucas (unpublished).

[8] R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. **59**, 673 (1941).