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

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The absorption under the M band in KCl is found to be due to two different centers, designated as M_S and M_H centers. At room temperature, the peak positions of the M_S and M_H bands are near 845 and 820 nm, respectively. The M_S band is generated along with the M_H band by bleaching the additively colored crystal with white light for times up to 15 min; it then decays on increasing the time of bleaching, leaving only the M_H band. The M_S band disappears at 70°C but the M_H band is stable up to 120°C. The Cd-doped, additively colored crystals show a band at 310 nm in addition to the F band. On heating the crystals to 600°C, the F and 310-nm bands disappear, and a band at 275 nm appears. The 275-nm band centers give a Lorentzian ESR absorption line with half-width 150 G. The plot of the ratio σ_c/σ_n (σ_c is the conductivity of the colored crystal, and σ_n that of the identical uncolored crystal) as a function of temperature shows three interesting regions. In the region from room temperature to 100°C, M_S centers act as donors with an ionization energy of about 1.0 eV, and give rise to excess conductivity and a peak in the σ_c/σ_n-versus-temperature plot at 60°C. R and N centers contribute to the conductivity near room temperature. In the second region, 150–300°C, the ratio σ_c/σ_n becomes less than unity in crystals containing background or deliberately added divalent impurity, presumably because of the aggregation of F centers with cation vacancies and impurities. The effect is more pronounced and the ratio becomes very small ($\sim$0.02) if the crystals are optically bleached before or during the heating process. The reaction controlling the decrease of conductivity is bimolecular and the energy of activation is close to the energy of migration of a cation vacancy. These results are similar to to those obtained by Ingham and Smoluchowski in γ-irradiated NaCl crystals. In the third region, 300–500°C, investigated in the preceding paper, a large excess conductivity is observed if the crystal contains colloids.

I. INTRODUCTION

THE electrical conductivity of KCl crystals containing potassium colloidal particles was studied earlier by the present authors.[1] The effect of background impurity and deliberately doped divalent cation impurity, as well as that of exposure of the crystal to visible light on the colloidal band and the excess conductivity associated with it, has been discussed in the preceding paper[2] (hereafter referred to as I). In this paper, we report the results of electron-spin-resonance (ESR), optical, and electrical studies of the M, R, X, and Scott R' centers in highly pure, "pure," and doped KCl crystals.

II. EXPERIMENTAL

The methods of growing the crystals, quenching or slowly cooling them, additive coloration, optical bleaching, measuring the electrical conductivity, optical absorption, thermal stability, and ESR absorption have been described earlier.[1,3,4] As in I, highly pure crystals are designated as H crystals, crystals of ordinary purity as B crystals, and crystals doped with barium or cadmium impurities as D crystals. A number placed after the letters H, B, or D indicates the batch number of the colored crystal from which the crystals were cleaved. The crystals were quenched and all experimental work was done *in the dark* after additive coloration unless otherwise stated. H crystals contain $\sim$1 ppm, and B crystals, $\sim$10 ppm of background divalent impurity.[2,4]

It was difficult to measure the conductivity near room temperature in ordinary atmosphere, because of moisture in the air. The use of Volta's dehumidifier somewhat improved the results. The best results were obtained when measurements from room temperature up to 150°C were made in vacuum. Crystals were heated at the rate of 1.5°C/min for conductivity measurements.

III. RESULTS AND DISCUSSION

A. Different Regions in Conductivity-Temperature Plots

The effects of background divalent impurity, deliberately doped barium impurity, and exposure of the crystals to visible light on the electrical conductivity of the additively colored KCl crystals are shown in Fig. 1. Curve 1 is the same as curve 9 in Fig. 5 of I and shows the plot of σ_c/σ_n in dark for $H3$ crystal containing 4.0×10^{17} cm^{-3} F centers. The value of σ_c/σ_n remains less than but close to unity from room temperature up to about 300°C for these crystals. The actual value is 0.9 when the crystal contains 4.0×10^{17} cm^{-3} centers and unity for the crystal containing 1.5×10^{18} cm^{-3} F centers. Curve 2 is for $H4$ crystal containing the same concentration of F centers but heated in light. A new peak in σ_c/σ_n-versus-temperature plot is now observed at

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

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

[3] S. C. Jain and S. L. Dahake, Indian J. Pure Appl. Phys. **2**, 71 (1964).

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

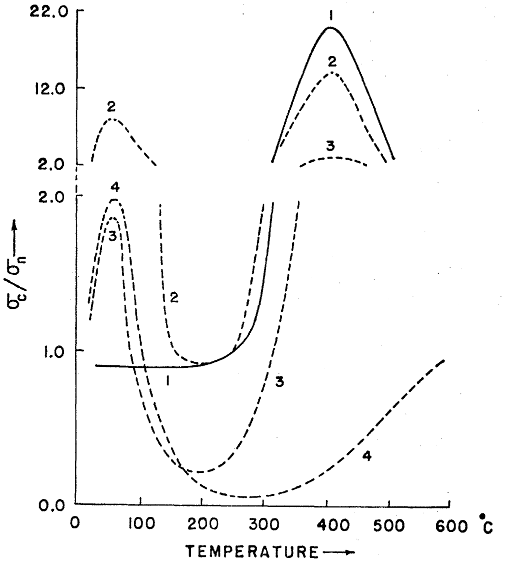

FIG. 1. Plot of σ_c/σ_n as a function of temperature for additively colored highly pure (curves 1,2), "pure" (curve 3), and 40 ppm barium-doped (curve 4) crystals. Solid curve, crystals heated in dark; broken curves, crystals heated in light.

60°C. The value of σ_c/σ_n at this peak is 8. However, the value of σ_c/σ_n at the peak near 400°C is now reduced from 21 (in dark in curve 1) to 14. Curve 3 shows the combined influence of light and background impurity on the conductivity σ_c in the quenched crystal $B2$ containing 1.0×10^{18} cm^{-3} F centers. Though the F-center density in $B2$ crystal is more than twice the value in $H3$ or $H4$ crystal, the value of σ_c/σ_n is considerably reduced in the whole temperature range. The values at the 60 and 400°C peaks are only 2 and 3.5, respectively, as compared with the corresponding values 8 and 14 for the $H4$ crystal. At the minimum near 200°C the value of σ_c/σ_n now becomes 0.2.

The effect of deliberately doping the $D2$ crystal with 10^{18} cm^{-3} centers and 40 ppm of Ba^{2+} impurity and heating the crystal in light on the conductivity ratio σ_c/σ_n is shown by curve 4. The ratio σ_c/σ_n now becomes very small near 200°C and continues to be less than unity in the region 300 to 500°C also.

The influence of slowly cooling the H and B crystals from the coloring temperature on σ_c/σ_n was also studied (results are not shown in the figure). It was found that even in the presence of light the first maximum now disappears and the ratio σ_c/σ_n in the higher-temperature region is considerably suppressed. Optical and ESR measurements showed that the F centers had coagulated into Scott R' [5] and colloidal center in these crystals.[4]

There are three distinct regions of interest in the σ_c/σ_n-temperature plots in Fig. 1: (1) the region from 25 to about 150°C, where the excess conductivity is observed in crystals exposed to light during or prior to heating for conductivity measurements; (2) the region from 150 to 250°C, where σ_c is usually smaller than σ_n and the ratio σ_c/σ_n becomes much less than unity in crystals containing impurity and/or exposed to light; and (3) the colloidal region from 300 to about 500°C investigated previously.[1,2]

B. *F*-Aggregate Centers and Electrical Effects Associated with them in the First Region

1. *Optical Studies: Two Types of M Bands*

Typical curves showing the changes in the absorption coefficient (α cm^{-1}) at the peak positions of F, R_2, M, and N peaks in H and B crystals as a function of time of exposure of the crystal to visible light were qualitatively similar to those observed by earlier workers[5,6] and will not be discussed in detail here. Curves 1 and 2 in Fig. 2 show the absorption coefficient α_M at the peak and the peak position of the composite M band, respectively, as a function of time of exposure of the crystal to white light at room temperature (RT). The peak position in a quenched crystal (not exposed to any light) is 820 nm and the absorption coefficient at the peak is 2.0 cm^{-1} in this crystal. Curve 2 shows that the peak changes from 820 to 835 nm during the 15 min of exposure of the crystal to visible light. This shift in peak position is in qualitative agreement with the shift from 800 to 820 nm observed by Kanzaki[5,7] and also by Van Doorn[5,8] at liquid-nitrogen temperature. However, at RT, as the crystal is exposed to light for larger times, the M peak gradually returns to shorter wavelengths. After about 60 min of exposure, the peak has nearly returned to the original wavelength 820 nm. It is interesting that the maximum of curve 2 showing the peak position and the maximum of curve 1 showing the growth of M band occur for approximately the same value of time t of exposure of the crystal to visible light. Curve 3 shows that the half-width of the composite M band increases from an initial value 0.10 eV to a maximum value ~0.14 eV after 8 min of white-light bleaching, and then decreases gradually to ~0.11 eV as time of white-light bleaching increases.

If the crystal exposed to visible light for 15 min and containing the maximum centers showing peak at 835 nm is warmed, the peak position of the M band again returns gradually to 820 nm at 70°C, as shown by curve 4 in Fig. 2. The values of α_M (measured at the actual high temperatures) decrease slowly on heating the crystal up to 70°C (curve 5 in Fig. 2; the total decrease at 70°C is about 10%) and then remain practically constant up to 120°C. If the crystal is exposed to light for more than 30 min before it is heated, M concentra-

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[5] W. D. Compton and H. Rabin, Solid State Phys. **16**, 121 (1964); J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, Inc., New York, 1962).

[6] E. Agathonikou-Rokofyllons, A. Costikas, and C. Manos, J. Phys. Chem. Solids **28**, 367 (1967).

[7] H. Kanzaki, Phys. Rev. **110**, 1063 (1958).

[8] Van Doorn, Philips Res. Rept. Suppl. 4 (1962).

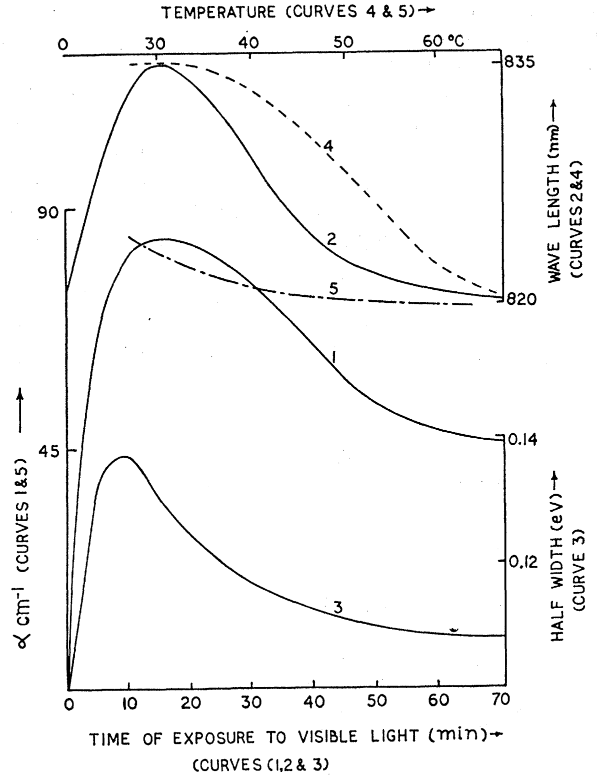

FIG. 2. Curves 1, 2, and 3 show the effect of exposure of an additively colored ($n_F = 1.5 \times 10^{18}$ cm^{-3}) highly pure KCl crystal to visible light on the absorption coefficient α cm^{-1} at the peak, the peak position and the half-width, respectively, of the composite M band at room temperature. Curves 4 and 5 show the effect of heating in dark an additively colored highly pure crystal exposed to visible light for 15 min at room temperature on the peak position and absorption coefficient at the peak of the composite M band, respectively.

tion increases slightly on heating the crystal up to 70°C and then remains constant up to 120°C.

The shift in peak position from 820 to 835 nm on bleaching the crystals up to about 15 min, the return to 820 nm on bleaching the crystal for larger values of time (curve 2) or heating it up to 70°C (curve 4), and the maxima in the M growth (curve 1) and half-width (curve 3) all suggest that the absorption under the M band is due to two different kinds of centers giving absorptions at 820 and near 835 nm, respectively. We shall designate them by M_H, the hard M centers, and M_S, the soft M centers. Since the half-width is maximum after 8 min of white-light bleaching, the two M bands must be comparable in magnitude in this crystal. A rough analysis shows that the M_H- and M_S-band peaks are at 820 and 845 nm, respectively. The M_S band is thermally less stable and cannot be observed in crystals quenched from temperatures higher than 70°C. This explains the fact that the M peak in quenched crystals is always at 820 nm. The M_S band grows relatively rapidly on optically bleaching the crystal and the observed peak shifts towards 835 nm as the relative strength of the M_S band increases. On warming the crystal, the M_S band decays first and the peak returns to 820 nm. However, it is not clear why the M_S band decays on optically bleaching the crystal for larger values of time and peak returns to 820 nm. It seems that after a certain minimum number of M centers is formed, nucleation of R centers starts and then M_S centers decay rapidly, presumably into R and N centers on longer bleaching by white or F light.

2. *R, X, and Cadmium Bands*

The peak position of the R_2 band also changes from 730 nm for a crystal irradiated with white light for 5 min to 750 nm after about 2 h of white-light irradiation (results not shown in Fig. 2). R_1 and R_2 bands decay monotonically on heating the crystal to temperatures higher than RT.

In pure crystals exposed to visible light and then heated in dark, the X band at 710 nm discussed in I develops at 70°C and keeps on rising up to 250°C. On additively coloring the Cd-doped KCl crystals, the concentration of F centers decreases and a new band at 310 nm appears. The intensity of the 310-nm band is roughly proportional to the concentration of $CdCl_2$ added to the KCl melt for growing the cadmium-doped crystals. The half-width of this band is 1.4 eV. The F centers cannot be bleached by exposing the Cd-doped colored crystals to F or white light. Colloidal centers, X centers, Scott R' centers, or F-aggregate centers giving bands on the long-wavelength side of the F band cannot be formed by heating the cadmium-doped colored crystals in the range RT–500°C in the dark or in light. Above 500°C, the 310-nm band started shifting towards the shorter wavelengths. On quenching the crystal from temperatures in the range 520–600°C, the F band and 310-nm band disappear completely and a new band at 275 nm appears.[4,9] The intensity of the 275-nm band is maximum in crystals quenched from 600°C. The half-width of this band is 0.70 eV. The growth of F-aggregate centers in crystals doped with barium impurity could not be studied quantitatively because of the complications introduced by the presence of Z bands.[5]

3. *ESR Studies*

In crystals irradiated with white light, the well-known[10] narrowing of the F-center ESR absorption line was observed. No ESR absorption due to R centers was observed, since the crystals were not strained to align the R centers in one direction.[11] The results of ESR absorption due to X, Scott R', and colloid bands have been discussed in I.

Additively colored, quenched KCl crystals doped with

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[9] L. Ben Dor, A. Glasner, and S. Zolotov, Phys. Status Solidi **18**, 593 (1966).

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

[11] D. C. Krupka and R. H. Silsbee, Phys. Rev. Letters **12**, 193 (1964); Phys. Rev. **152**, 816 (1966).

cadmium did not give any new ESR absorption. The F-center ESR half-width and the g factor remained unchanged even in crystals doped with 2% of $CdCl_2$ in the melt. A new ESR absorption line associated with the 275-nm optical absorption band is observed (Fig. 3) in crystals quenched from temperatures in the range 520–600°C. The F-center ESR decreases in intensity in proportion with the F band and disappears completely at 600°C, and the intensity of the new ESR line now becomes maximum. The half-width of the ESR line is 150 G, the g value is 1.990, and the shape is Lorentzian. The Lorentzian shape of the ESR line and its g value close to the free-electron value suggest that the ESR line may be due to the conduction electrons in metallic colloidal particles of cadmium. The electronic conductivity due to thermionic emission of electrons from these cadmium colloidal particles has also been studied at high temperatures and results similar to those obtained by Jain and Sootha[1,2] for potassium colloids have been obtained.[12] These results yield a value ~4 eV for the work function ϕ of the metal particles. This value is close to $\phi=4.1$ eV for cadmium-metal work function[13] and strongly supports the view that 275-nm band centers are Cd colloidal particles.

4. *Electrical Conductivity Associated with M Centers*

Curves 1, 2, and 3 in Fig. 4 show the plots of σ_c/σ_n as a function of temperature in an H crystal containing 1.5×10^{18} cm^{-3} F centers and exposed to white light for 2, 5, and 15 min, respectively, prior to conductivity measurements in the dark. Starting from room temperature, the conductivity ratio increases rapidly, obtains a maximum at 60°C, and then decreases and becomes practically unity at about 120°C. On increasing the time of exposure to white light for 30, 45, and 60 min, the results shown by curves 4, 5, and 6 are obtained. Though there is a maximum in these three curves at 60°C, the value of the ratio at the maximum at 60°C now decreases as the time of exposure to white light is further increased. The ratio σ_c/σ_n starts increasing below 40°C.

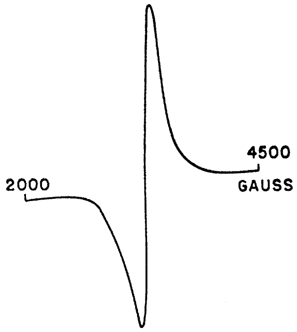

FIG. 3. First-derivative trace of the ESR spectra, taken from the recorder chart, at room temperature for an additively colored $D4$ crystal doped with 30 ppm cadmium after quenching from 600°C.

Curve 7 shows a similar plot for a B crystal containing 1.0×10^{18} cm^{-3} excess potassium atoms and exposed to white light for 15 min. The absorption coefficient at the M peak in this crystal is 70, a value comparable with the value 85 in the H crystal, but the excess conductivity in the B crystal (curve 7) is much smaller as compared with that in the H crystal (curve 3).

Since the increase in σ_c/σ_n below 100°C is observed only in crystals which have received visible-light exposure before the conductivity is measured in the dark, the excess conductivity must be related to the presence of F-aggregate centers. After 2 min of exposure of the crystal to light, the N centers are not formed and the R-center density is negligible. Both the M-center density and the 60°C peak value of σ_c/σ_n increase with time of exposure of the crystal to visible light. The maximum value of the peak at 60°C and the maximum concentration of the M centers occur for the same time of white-light irradiation. When the time of white-light irradiation is more than 15 min, both the M-center concentration and the 60°C peak value of σ_c/σ_n start decreasing. On increasing the time of white-light exposure from 15 to 30 min, the R-center density increases by a factor of

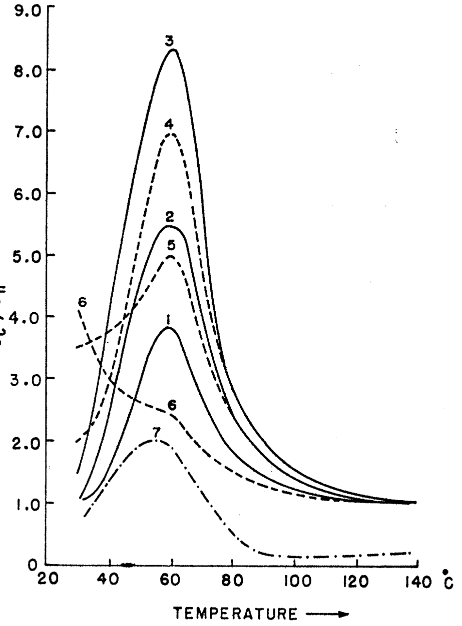

FIG. 4. Plot of σ_c/σ_n as a function of temperature for additively colored quenched highly pure and "pure" KCl crystals, in dark. Curves 1 to 6 were obtained after exposing six identical slices of highly pure H crystal ($n_F=1.5\times10^{18}$ cm^{-3}) to visible light at room temperature for 2, 5, 15, 30, 45, and 60 min, respectively, prior to conductivity measurements in dark. Curve 7 was obtained after exposing a "pure" B crystal ($n_F=1.0\times10^{18}$ cm^{-3}) to visible light for 15 min at room temperature prior to conductivity measurements in dark.

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[12] S. C. Jain and S. Radhakrishna (to be published).

[13] See, for example, A. J. Dekker, *Solid State Physics* (Macmillan and Company, Ltd., London, 1963), p. 223.

1.5 but the 60°C peak value of σ_c/σ_n decreases by a factor of 4. The 60°C peak of σ_c/σ_n in Fig. 4 must therefore be attributed to the M centers present in the crystal.

After 60 min of white-light irradiation, the value of α_M is the same as the value after about 2 min of white-light exposure, but in the former case, the peak value of σ_c/σ_n at 60°C is about half (curve 6) of the value (curve 2) obtained in the latter case. It can be seen by comparing the decay of σ_c/σ_n with the thermal decay of the M centers with temperature that though the concentration of M centers decreases only by $\sim 10\%$ up to 120°C, the excess conductivity almost completely disappears at this temperature. These results indicate that a simple interpretation of the excess conductivity in terms of the electrons provided by all of the M centers is not possible.

Evidence was presented earlier that all optical absorption under the M band is not due to one kind of M centers. The above results can be understood if we assume that only the soft M_S centers generated in the initial stages of optical bleaching contribute to the excess conductivity. On increasing the time of white-light irradiation to more than 15 min, the M_S centers decay and M_H centers grow which do not contribute to the electrical conductivity at these low temperatures. After 60 min of white-light irradiation, α_M approaches a constant value ~ 50 and the maximum value of σ_c/σ_n at 60°C decreases to a value of ~ 2, since now most of M centers are M_H centers. σ_c/σ_n becomes unity near ~ 100°C even when α_M is very large, since only M_H centers are stable above 70°C.

Unlike that in crystals containing colloids,[1,2,4] the maximum in σ_c/σ_n as a function of temperature in crystals containing different M_S-center concentrations always occurs at 60°C and is consistent with the atomically dispersed nature of M centers.

An approximate value of the energy of thermal ionization of M_S centers can be obtained in the following manner. The composite M band for any time of white-light irradiation is resolved into M_H and M_S bands and a rough value of α_{M_S} for M_S band is obtained. A plot of the logarithm of the excess conductivity σ_e divided by the corresponding value of α_{M_S} as a function of reciprocal of absolute temperature for the crystal preexposed for 15 min to visible light at room temperature is shown in Fig. 5. It is seen from the figure that all the points lie close to a straight line. Similar plots for crystals preexposed for less than 15 min gave straight lines parallel to the line given in Fig. 5. The slope of the straight line yields the energy $E_M = 1.0$ eV for the thermal ionization of an M_S center.

The thermal ionization energy of 1 eV for the M center is slightly less than the value 1.2 eV given by Tomiki[5,14] from the study of decay of M centers above 120°C. His value of ionization energy is presumably for the M_H centers.

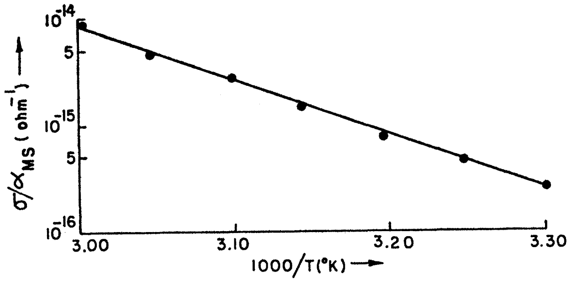

FIG. 5. Plot of $\ln_{10}(\sigma_e/\alpha_{MS})$ as a function of reciprocal of the absolute temperature T for an additively colored highly pure H KCl crystal ($n_F = 1.5 \times 10^{18}$ cm^{-3}) exposed to visible light for 15 min at room temperature prior to conductivity measurements in dark. The σ_c/σ_n-versus-temperature plot for this crystal is shown by curve 3 in Fig. 4.

The M_H centers may be expected to contribute to the excess conductivity at higher temperatures. However, ionic conductivity decreases by the aggregation process (see next section) between 100 and 250°C. Further, in crystals not exposed to light, M concentration remains small at all temperatures. In crystals exposed to light, M centers change to X centers in highly pure crystals and to Scott R' centers in "pure" crystals near 120°C.

5. Excess Conductivity due to R and N Centers

It was shown in the previous section that the 60°C peak in σ_c/σ_n-versus-temperature plots cannot be due to R centers. Curves 4, 5, and 6 in Fig. 4 show increasingly large values of σ_c/σ_n near 30°C. In fact, it is apparent that there would be a peak in σ_c/σ_n-versus-temperature plot at lower temperatures in curve 6. Obviously, this excess conductivity below 40°C must be attributed to the presence of R or N centers. Further work is necessary to separate out the effects of R and N centers on the conductivity of crystals heavily bleached with white light. It would be interesting to extend this work to lower temperatures in detail.

C. Second Region, 100 to 300°C

1. Effect of Light and Divalent Impurity

On heating the $B2$ crystal in light, σ_c becomes less than σ_n in the temperature range 100 to 300°C (curve 3, Fig. 1). A large decrease in σ_c/σ_n in this temperature range is obtained in $D1$ crystals doped with Ba even in dark (not shown in Fig. 1). The effect becomes more pronounced when $D2$ crystal is heated in light (curve 4 of Fig. 1); the ratio σ_c/σ_n now decreases to 0.02 between 200 and 300°C. Optical-absorption results discussed in I show that this decrease is accompanied by the decrease in F concentration and formation of the broad absorption band similar to the Scott R' band observed by Scott and Bupp.[15]

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[14] T. Tomiki, J. Phys. Soc. Japan 15, 488 (1960).

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

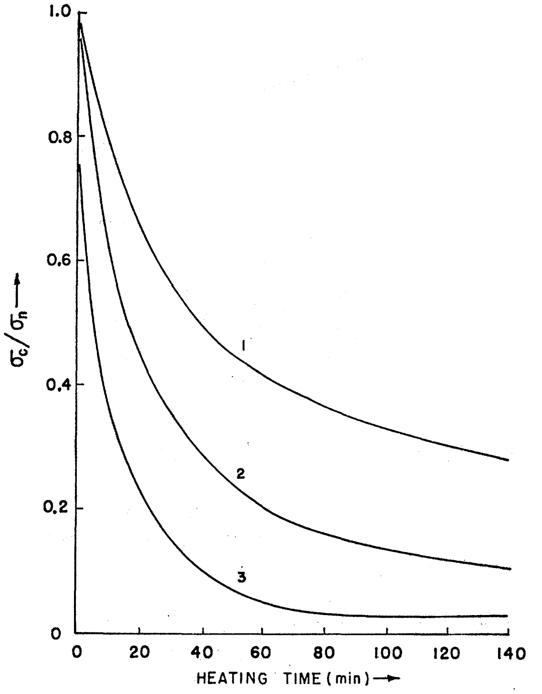

FIG. 6. Isothermal plots of σ_c/σ_n as a function of time at (1) 175, (2) 200, and (3) 230°C in visible light for a B crystal containing 7.0×10^{17} cm^{-3} F centers.

To understand the mechanism of decrease of conductivity and F concentration, the crystals were heated to different temperatures in visible light in the range 130 to 230°C and the decrease of σ_c with time at constant temperatures in this range was studied. The experiment was repeated for different initial concentrations of F centers. The typical results at 175, 200, and 230°C for a B crystal containing 7.0×10^{17} cm^{-3} F centers are shown in Fig. 6 by curves 1, 2, and 3, respectively. The general features of these curves are similar to those obtained by Ingham and Smoluchowski[16] for γ-irradiated NaCl crystals. The rate of decrease of F centers at different constant temperatures in optically bleached crystals was also studied. In agreement with Theisen and Scott,[17] the rate of decrease of F centers is bimolecular, with an activation energy of 0.4 eV, and is much faster than the rate of decrease of conductivity shown in Fig. 6.

The above results show that on heating the colored and optically bleached crystals containing divalent impurity, the decrease in F-center concentration and that in conductivity take place in two steps. In the first step, F concentration decreases and presumably an R' band is formed. Since the conductivity does not decrease in the first step, we suggest that in the first reaction, F centers and impurity-vacancy pairs combine to form Scott R' centers.[15] It is possible that another defect is also a part of Scott R' center, or Scott R' centers consist of various stages of aggregation of F centers and impurity-vacancy pairs, as suggested by the highly composite nature of R' centers. The reaction is accelerated in the presence of light, presumably because of the increase in the F-center mobility by visible light.[5] As the impurity-vacancy pairs are used up in this reaction, the equilibrium between the pairs and the free cation vacancies is disturbed and some more free cation vacancies and divalent impurity cations combine to form pairs. It is during this second reaction that conductivity decreases.

The differential equation for the second reaction can be written as

$$dC/dt=-kC^2, \qquad (1)$$

where C is the concentration of free cation vacancies or of the free divalent cation impurity ions at time t. The initial condition is

$$C=C_i \quad \text{at} \quad t=0 \qquad (2)$$

and $k=e^{-E'/kT}$, where E' is the activation energy for the second reaction. Remembering that

$$\sigma_n=(AC/T)e^{-E/kT},$$

where A is a constant, the solution of Eq. (1) can be written in the form

$$(\sigma_n/\sigma_c-1)=\sigma_n bTte^{-(E'-E)/kT}, \qquad (3)$$

where E is the energy of activation for the migration of a cation vacancy in a KCl crystal.

The approach to equilibrium will be influenced by the back reaction not included in Eq. (1), and Eqs. (1) and (3) will not be applicable for large values of time.

Plots of $(1/T)(\sigma_n/\sigma_c-1)$ as a function of t for different constant temperatures are found to be straight lines for small values of time t, confirming the bimolecular nature of the reaction. For larger values of time t the plots deviate from the straight line, indicating the presence of back reaction and approach to equilibrium. The slopes S of the straight-line plots are measured and $\ln_{10}(S/\sigma_n)$ versus $1/T$ is plotted in Fig. 7. It is seen that the plot is a straight line parallel to the $1/T$ axis, the slope being equal to $(E'-E)/k=0$ and $E=E'$ within the experimental accuracy. This suggests that the second reaction in which conductivity decays is controlled by the migration of cation vacancies,

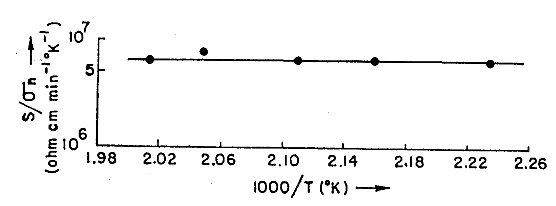

FIG. 7. Plot of $\ln_{10}(S/\sigma_n)$ as a function of reciprocal of absolute temperature, S being the slope of the straight-line plots $(1/T)\times(\sigma_n/\sigma_c-1)$ as a function of time (not shown in the figure).

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[16] H. S. Ingham and R. Smoluchowski, Phys. Rev. **117**, 1207 (1960).

[17] F. E. Theisen and A. B. Scott, J. Chem. Phys. **20**, 529 (1952).

in agreement with the result of Ingham and Smoluchowski[16] on γ-irradiated NaCl crystals.

Thus, at temperatures greater than 100°C, F centers move to combine with pairs of divalent impurity and cation vacancy and form stable aggregates. Fresh pairs of cation vacancies and divalent impurities are formed by the migration of cation vacancies to restore equilibrium between the pairs and free impurity ions and vacancies.

Efforts were made to find alternative interpretations of the decrease in conductivity. Conversion of M^{2+} ion into M^{+} ion or precipitation of the impurity as a separate phase and consequent elimination of cation vacancies by diffusing out of the crystal are the possible alternative explanations. However, the observed results cannot be explained so elegantly on these models.

2. *Highly Pure Crystals*

If the F-center concentration is smaller than 5×10^{17} cm^{-3}, then σ_c/σ_n becomes somewhat less than unity even when the H crystal is heated in dark to 150°C. The effect is more pronounced in B crystals. This suggests that some aggregation of cation vacancies with impurity ions and F centers takes place even when the crystals are highly pure and are heated in dark. In crystals containing large concentrations of F centers, there is perhaps some increase of conductivity due to ionized electrons from F or F-aggregate centers which compensates the small decrease due to aggregation of cation vacancies with F centers and impurity ions in dark, and σ_c/σ_n remains unity within experimental errors.

In H crystals exposed to light before or during the heating process, X centers are formed in the temperature range[2,4] 120–280°C. Curve 2 in Fig. 1 shows that σ_c/σ_n remains close to unity in this temperature range in the $H4$ crystal. It seems that the cation-vacancy concentration is not disturbed appreciably by the presence of X centers.

D. Comparisons with Results of Other Workers

(1) Electrical conductivity of additively colored alkali-halide crystals was measured in the intrinsic range in Pohl's laboratory.[18,19] A large increase in conductivity was observed due to ionized F centers at high temperatures. In the impurity range, the contribution to electrical conductivity by the F centers would be much smaller than that by M or R centers because of the much higher value (1.98 eV) of the thermal ionization energy for F centers[19,20] as compared with the values for M and R centers.[5] The number of ionized electrons will be further reduced if the number of negative-ion vacancies is large.[4] Recent work on thermoluminescence and growth of F centers has shown that there are more than 10^{17} cm^{-3} negative-ion vacancies present in the crystal at room temperature.[21] Using the earlier results on excess conductivity due to F centers in the intrinsic range[18,19] and taking this value of anion vacancy concentration, it can be shown that the excess conductivity due to F centers will be negligible below 300°C, which is consistent with the present experimental results.

(2) Krasnopevtsev,[22] Maycock,[23] and Jain[24] have measured the conductivity of additively colored KBr crystals. Results obtained with KBr crystals of different purity and heated in light or dark[24] support the interpretation given in this paper to the observed conductivity of colored KCl crystals.

(3) Ingham and Smoluchowski[16] found that the conductivity of an NaCl crystal irradiated by γ rays decreases at any constant temperature in the range 60 to 120°C. The decrease was bimolecular and the energy of activation was close to that needed for the motion of a cation vacancy. These results are similar to those obtained by us with additively colored KCl crystals containing background impurity and heated in light.

Extensive measurements of electrical conductivity of LiF crystals irradiated by neutrons or γ rays have been made by Berge and co-workers.[25] The authors found that in crystals irradiated by γ rays or by low doses of neutrons, the conductivity is suppressed by a factor of up to 100 in the impurity range. This effect was considerably more pronounced in relatively impure crystals. An aggregation process similar to that discussed in this paper seems to be responsible also for the decrease in conductivity observed by Ingham and Smoluchowski[16] in NaCl crystals and by Berge and co-workers[25] in LiF crystals. It would be interesting to repeat the experiments of Ingham and Smoluchowski with highly pure crystals and in dark.

(4) The slight excess conductivity observed by Chirsty *et al.*[26] in x-irradiated KCl and NaCl crystals is due to the release of electrons from F centers at lower temperatures in the irradiated crystals and will be discussed in a separate paper. It is known that thermal energy of ionization of F center is much less in irradiated crystals as compared with that in additively colored crystals.[20] Parashar[27] has made careful experiments on highly pure x-irradiated KCl crystals in dark and found a correlation in the thermoluminescence peaks obtained by Jain and Mehendru[21] and the peaks in σ_c/σ_n obtained by him with the irradiated crystals.

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