

COLOR CENTERS IN POTASSIUM CHLORIDE CRYSTAL CONTAINING BARIUM IONS

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Introduction

In the additively colored crystals of alkali halide containing the divalent positive ions, new absorption bands were discovered in the wavelength range between the F and M bands by Pick¹⁾. These bands, termed Z bands, have been studied extensively by Heiland and Kelting²⁾ and by the Italian investigators³⁾. On the other hand, Hummel⁴⁾ and Etzel⁵⁾ have found that the addition of divalent positive ions to alkali halides enhances the colorability of these salts at room temperature and it has been suggested that the F band enhancement might be due to the trapping of holes at the positive ion vacancies accompanying the divalent ions: the recombination of electrons and holes would be retarded and the F center formation would be promoted.

Now, the author, in connection with the previous investigations⁶⁾, has studied the thermal bleaching of the F centers and the formation of the colloid centers in the potassium chloride crystal colored by electrolysis and the effects of the impurity, barium ions, on these color centers and found that barium ions being introduced, the bleaching of the F centers is accelerated and the formation of the colloid centers is disturbed.

Experimentals

Preparation of single crystal The KCl crystal and the KCl (Ba) crystals (initial concentration of Ba ions = 2×10^{-2} , 5×10^{-2} mole %) were prepared by Kyropoulos' method. The rate of growth of the crystals was 5 mm/hour. After crystallization, the crystals were annealed at 600°C for 12 hours and then cooled gradually to room temperature. In the KCl (Ba) crystals, the crystal of the low initial concentration of Ba ions was transparent, but the crystal of the high initial concentration of Ba ions was milky.

Determination of concentration of Ba ions in the crystal The concentration of Ba ions in the crystals was determined by the gravimetry of BaSO₄, namely, the length between the top and the bottom of the cylindrical crystal was divided into three or four equal parts and the crystal of about thirty grams was cleaved from each part. Each crystal was dissolved into water

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1) H. Pick, *Ann. Physik*, **35**, 73 (1937); *Z. Physik*, **114**, 127 (1939)

2) G. Heiland and H. Kelting, *Z. Physik*, **126**, 689 (1949)

3) G. Chiarotti, F. G. Fumi and L. Giulotto, *Report of The Conference on Defects in Crystalline Solids*, p. 317, The Physical Society, London (1954)

4) H. Hummel, *thesis*, Göttingen University (1950)

5) H. W. Etzel, *Phys. Rev.*, **87**, 906 (1952)

6) K. Shimizu, *This Journal*, **26**, 48 (1956)

and acidified with hydrochloric acid, and then Ba ions were precipitated as BaSO₄ by adding an ammonium sulfate solution. After drying, the precipitates of BaSO₄ were weighed. The results are shown in Table 1. The concentration of Ba ions increased with increasing the distance from the top of the cylindrical crystal. This may be ascribed to the constant rate of growth. Therefore, the constancy of the concentration of Ba ions in the crystal will be kept within certain limits, if the rate of growth is diminished gradually as the crystal grows.

Table 1 Concentration of Ba ions in KCl (Ba) crystal 10⁻³ mole %

Initial conc. of Ba ²⁺ 10 ⁻² mole %	2	5
	h ₁	
h ₁ (top)	3.0	8.4
h ₂	3.2	9.6
h ₃	3.5	14.6
h ₄		19.2

As mentioned above, the crystal, whose initial concentration of Ba ions was 5 × 10⁻³ mole %, was milky. This crystal became transparent by heating above 450~490°C and it kept transparent at room temperature by being rapidly cooled from these temperatures, but by gradual cooling the crystal became again milky. The temperature at which the milky crystal became transparent was higher as the concentration of Ba ions in the crystal increased (Table 2).

Table 2

Concentration of Ba ²⁺ in KCl (Ba) crystal 10 ⁻³ mole %	Temperature °C
8.4~9.6	~450
14.6	470
19.2	490

Procedure The coloration of the crystals was performed by means of electrolysis with the pointed cathode of nichrome and the flat anode of graphite in the furnace of 600°C and then quenched rapidly in the air. The specimen for measurements of absorption spectra was cleaved from the inner region of the colored crystal.

For the purpose of studying the thermal bleaching of the F centers, the moderately colored specimens of the pure crystal and of the crystals containing Ba ions were wrapped in tin-foil and heated at 300~450°C for a definite time. After heating, each specimen was quenched in the air. As for the investigations of the formation of the colloid centers, the deep colored specimens were heated at 350°C and quenched in the same way as the above experiments. After quenching, the absorption spectra of these colored specimens were measured in the wavelength range from 400 to 1000mμ at room temperature by means of a Beckman model D U Spectrophotometer. For the confirmation of the band, after uniaxially compressing the colored specimen, the absorption spectra were measured with polarized light.

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Results

The absorption spectra of the specimens of the pure crystal and the crystals containing Ba ions colored by electrolysis are shown in Fig. 1. a, b and c. In each specimen, F and M bands were produced by electrolysis (curve 1). At the same time, in the wavelength range between the F and M bands, another band seemed to be produced in the specimens of the crystals containing Ba ions, though this band could not be observed in the colored specimen of the pure crystal. By heating these colored specimens of the crystals containing Ba ions above 300°C for a few minutes, the absorbance in this wavelength range was reduced down to the same degree as in the pure crystal and the height of the F band increased (curve 2). Therefore, for studying the thermal bleaching of the F centers, each colored specimen was preheated at each temperature and then the investigations were performed. The results are shown in Fig. 2. a, b and c. In the colored specimens of the pure crystal, the bleaching rate of the F centers increased as the temperature rose and decreased with the lapse of heating time at each temperature. In the colored specimens

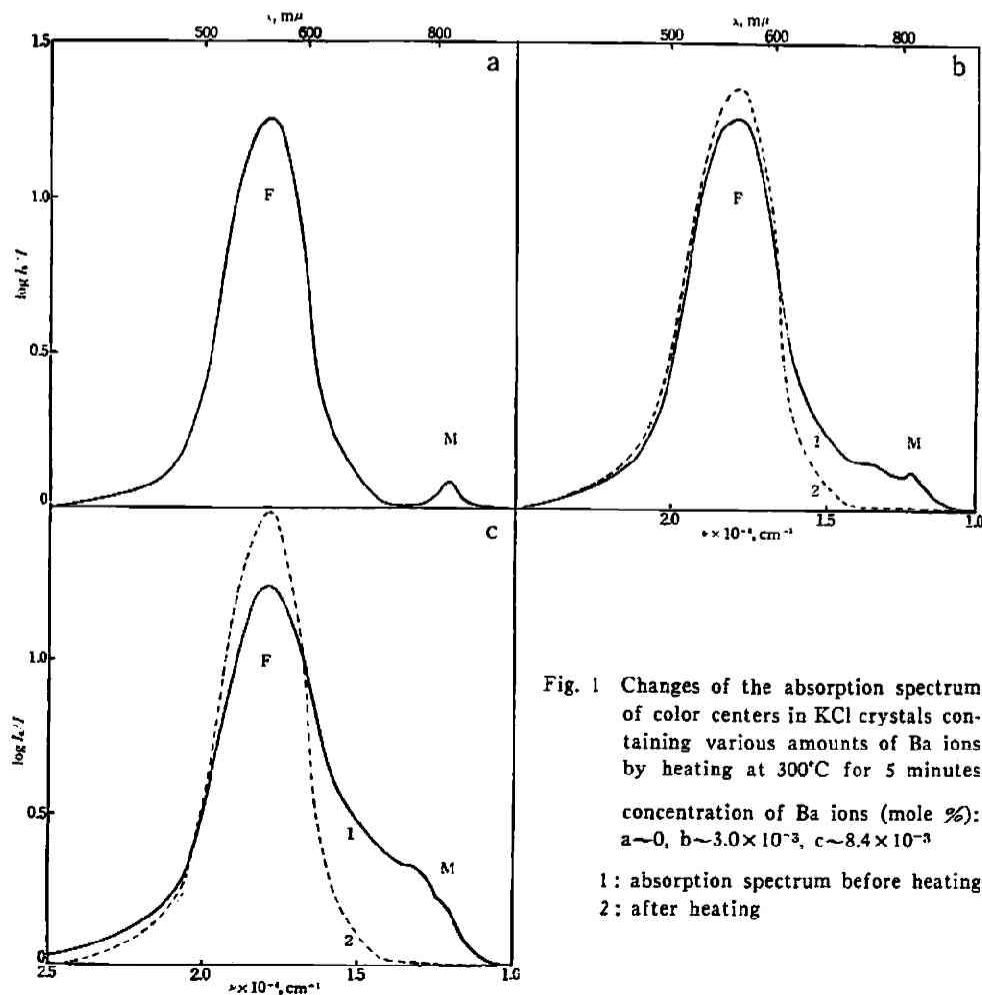


Fig. 1 Changes of the absorption spectrum of color centers in KCl crystals containing various amounts of Ba ions by heating at 300°C for 5 minutes
concentration of Ba ions (mole %):
a~0, b~ 3.0×10^{-3} , c~ 8.4×10^{-3}

1: absorption spectrum before heating
2: after heating

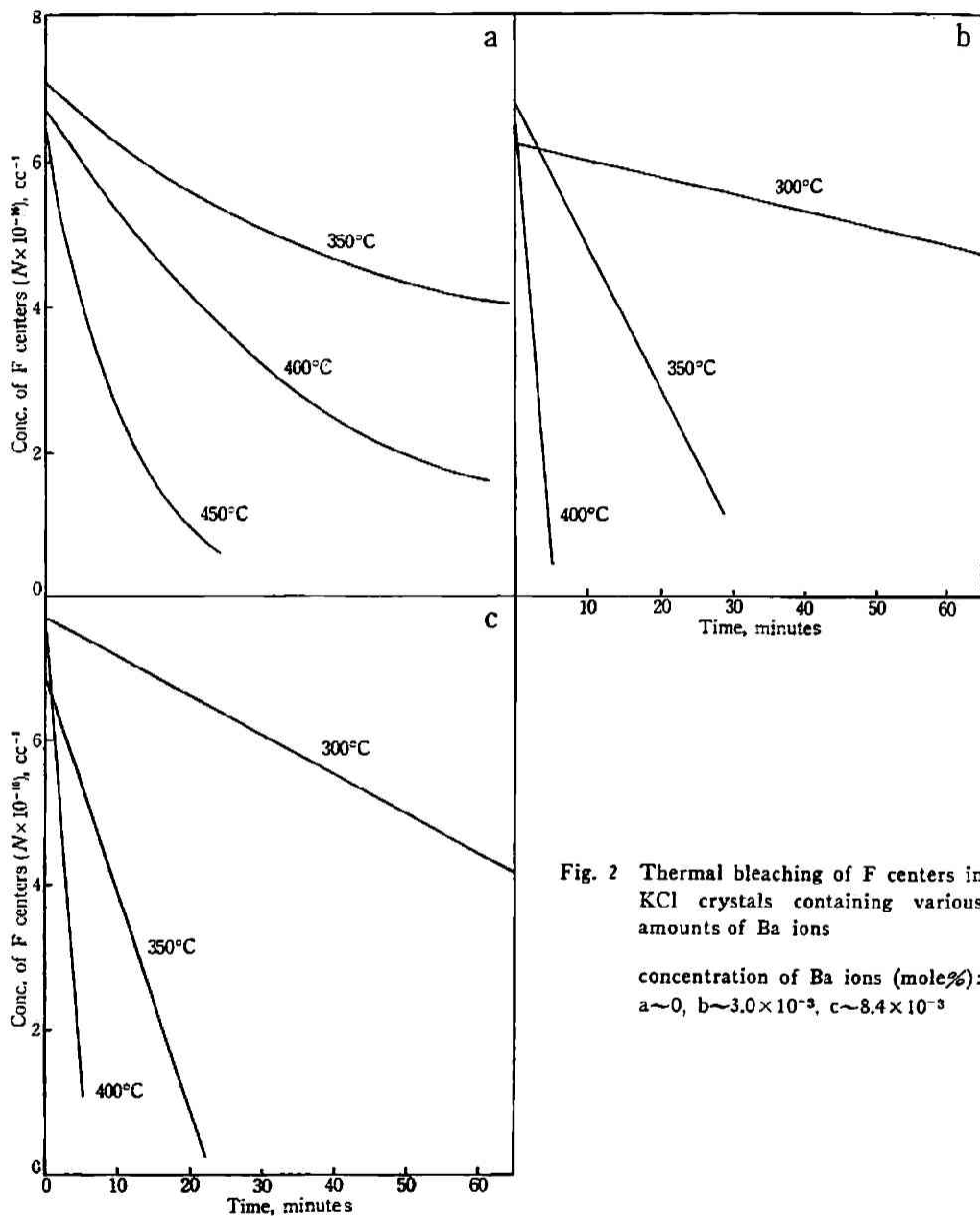


Fig. 2 Thermal bleaching of F centers in KCl crystals containing various amounts of Ba ions

concentration of Ba ions (mole%):
a ~ 0 , b $\sim 3.0 \times 10^{-3}$, c $\sim 8.4 \times 10^{-3}$

of the crystals containing Ba ions, the bleaching rate of the F centers was larger than that in the pure crystal at the corresponding temperature and increased as the concentration of Ba ions in the crystal increased, and in contrast with the colored specimens of the pure crystal, the bleaching rate at each temperature did not change with the lapse of heating time.

As for the formation of the colloid centers, the deep colored specimens were heated at 350°C. As shown in Fig. 3, by heating the colored specimen of the pure crystal for two hours, the height of the F band decreased and another band formed at 700 $\text{m}\mu$. This band corresponds to the colloid band²⁾ (curve 2). Both bands decreased after further one hour heating (curve 3). The results on

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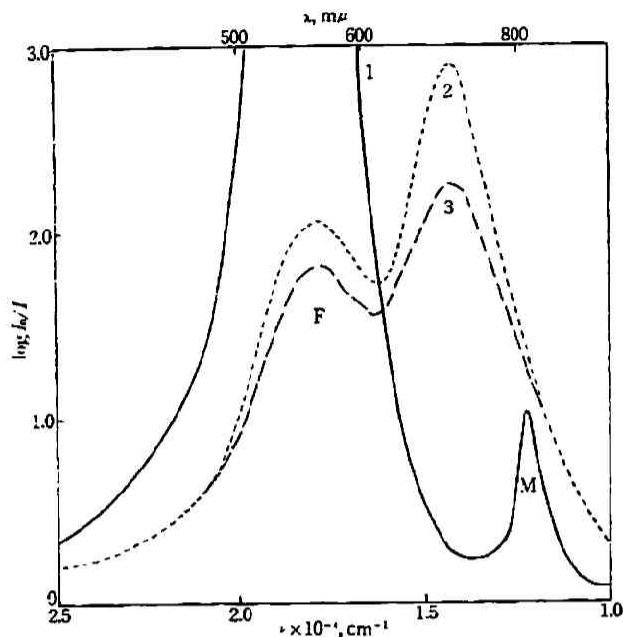


Fig. 3 Heating effect at 350°C on the absorption spectrum of color centers produced electrolytically at 600°C in KCl specimen

- 1: absorption spectrum before heating
 2: 2 hours heating
 3: 3 hours

the specimens of the crystals containing Ba ions are shown in Figs. 4 and 5. In the colored specimen of the crystal containing 3.0×10^{-3} mole % Ba ion, the height of the F band decreased gradually by 1.5 hours heating and the decrease of the band height was more rapid than that in the pure crystal (curve 3 in Fig. 3 and curve 4 in Fig. 4). On the other hand, the absorption in the long wavelength side of the F band was increasing after 30 minutes (curve 2 in Fig. 4) and, after one hour, increased still more than that after 30 minutes (curve 3), but after 1.5 hours, this

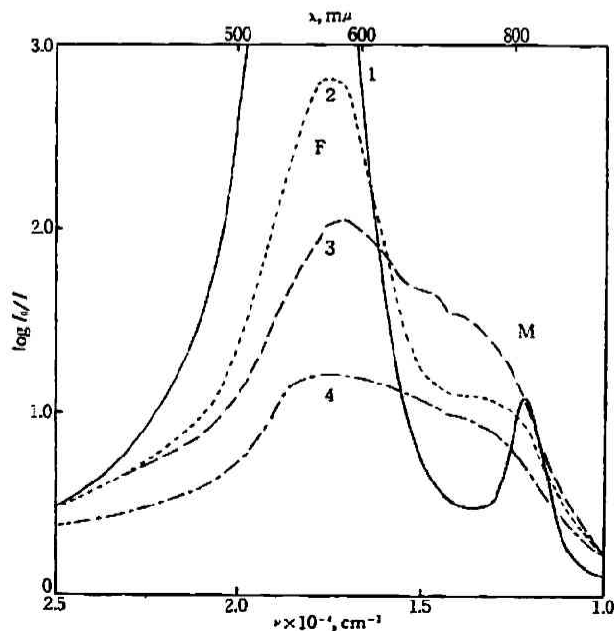


Fig. 4 Heating effect at 350°C on the absorption spectrum of color centers produced electrolytically at 600°C in KCl (Ba) specimen

concentration of Ba ions = 3.0×10^{-3} mole %

- 1: absorption spectrum before heating
 2: 30 minutes heating
 3: 1 hour
 4: 1.5 hours

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In the colored specimens containing Ba ions, the absorption band located in the wavelength range between the F and M bands was produced by electrolysis and enhanced by heating at 350°C. In order to confirm if this band is due to the same centers or not, the colored specimens were compressed uniaxially and the absorption spectra were measured with the polarized light normal and parallel to the direction of the compression. Before heating at 350°C, the deformation did not make the colored specimen dichroic, so that this band may be ascribed to the Z centers originating from Ba ions. On the other hand, in the colored specimen heated at 350°C, the dichroism was observed after compression as shown in Fig. 6, so that this band may be attributed to the colloid centers.

Considerations

In order to determine the order of the thermal bleaching of the F centers in the pure crystal, the logarithm of the concentration of the F centers is plotted against time. The straight lines are given as shown in Fig. 7, so the bleaching follows the first order kinetics. In case of the

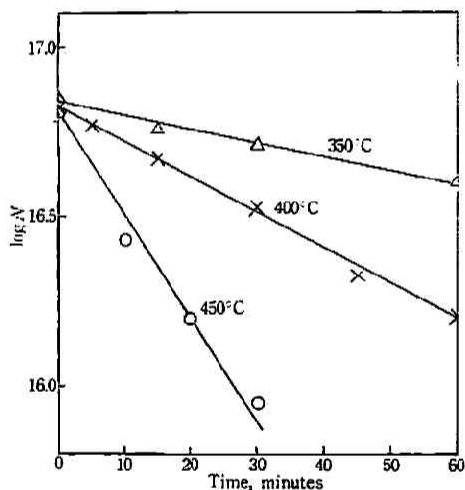


Fig. 7 Relations between $\log N$ (concentration of F centers) and heating time in the colored specimens of the pure crystal

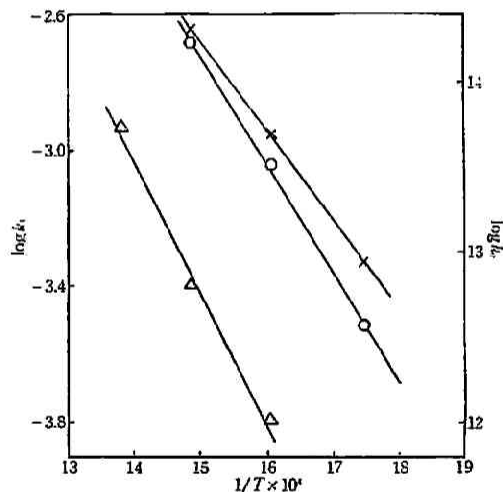


Fig. 8 Relation between $\log k$ and $1/T$ concentration of Ba ions (mole %): $\Delta \sim 0$, $\circ \sim 3.0 \times 10^{-3}$, $\times \sim 8.4 \times 10^{-3}$

crystals containing Ba ions, as shown in Fig. 2. b and c, it is apparent that the bleaching occurs with zero order. The rate constants of the bleaching are calculated from the slopes of these straight lines and the plots of $\log k$ against the reciprocal of the absolute temperature $1/T$ are shown in Fig. 8. Their slopes give the apparent activation energies that are 0.78 eV in the pure crystal, 1.3 eV in the crystal containing 3.0×10^{-3} mole % Ba ion and 1.0 eV in the crystal containing 8.4×10^{-3} mole % Ba ion respectively. The activation energy in the pure crystal is smaller than the energy required to ionize the F centers thermally, 1.98 eV, that was obtained by Mott and Gurney⁷⁾. The author proposes to explain the observed facts in the following way.

The vacancies are produced at the time of the coloration by electrolysis at high temperature.

7) N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystal*, p. 114, Oxford University Press, London (1940)

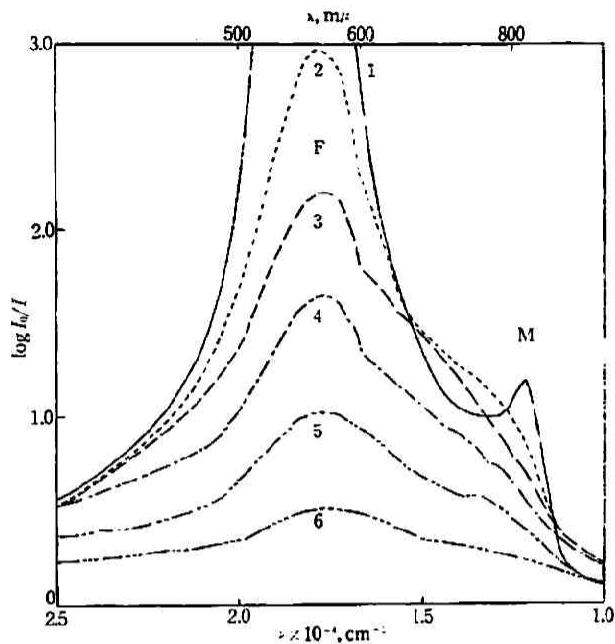


Fig. 5 Heating effect at 350°C on the absorption spectrum of color centers produced electrolytically at 600°C in KCl (Ba) specimen

concentration of Ba ions = 8.4×10^{-3} mole %

- 1: absorption spectrum before heating
- 2: 5 minutes heating
- 3: 15 minutes
- 4: 30 minutes
- 5: 1 hour
- 6: 1.5 hours

absorption was decreasing (curve 4). In the colored specimen of the crystal containing 8.4×10^{-3} mole % Ba ion, the height of the F band decreased more rapidly by 1.5 hours heating than that in the colored specimen of the crystal containing 3.0×10^{-3} mole % Ba ion (curve 4 in Fig. 4 and curve 6 in Fig. 5). The absorption in the long wavelength side of the F band increased by 5 minutes heating (curve 2 in Fig. 5). But, after 15 minutes, the absorption began to decrease (curve 3) and thereafter it was decreasing with the F band (curves 4 and 5). After 1.5 hours, this absorption decreased much more than that in the colored specimen of the crystal containing 3.0×10^{-3} mole % Ba ion (curve 4 in Fig. 4 and curve 6 in Fig. 5).

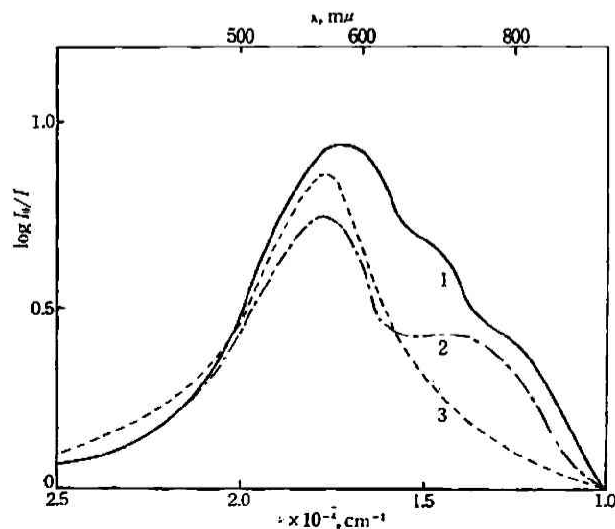


Fig. 6 Dichroism of colloid centers in the KCl crystal containing Ba ions after plastic deformation

- 1: absorption spectrum of the specimen measured before plastic deformation
- 2: measured with polarized light normal to the direction of compression
- 3: measured with polarized light parallel to the direction of compression

During the heating of the colored specimen at low temperature, there is a tendency for vacancies to decrease in number so as to recover the equilibrium concentration of vacancies. Then, the F centers coagulate, possibly with vacancies or vacancy pairs, forming the complex aggregates which are more mobile than the isolated F centers. These aggregates arrive at the surfaces after diffusing in the crystal and the vacancies disappear there. At these points, the electrons of the F centers are attached to K ions and K metal atoms evaporate from the surfaces.

In the pure crystal, the bleaching rate of the F centers is proportional to the concentration of the F centers, so the rate determining step would be the process of the migration of the F centers and the complex aggregates of the F centers from the inner regions to the surfaces of the crystal.

In the crystal containing Ba ions, Ba ion should introduce extra positive ion vacancies at the low temperatures (corresponding to the extrinsic range of the ionic conductivity) for the electrostatic balance. Therefore, this would decrease the concentration of the negative ion vacancies much more than that in the pure crystal according to the mass action law, as the concentration of Ba ion increases, and would promote the migration of the F centers to the surfaces of the crystal. As the result of this, the lattice sites at surfaces available for evaporation of K metal atom would be always saturated with the F centers migrated from the inner region, though the evaporation occurs successively, so that the bleaching follows the zero order kinetics.

The formation of the complex aggregates and their diffusion and the evaporation of the K metal atoms would be accelerated at higher temperature so that the bleaching rate is larger as the temperature rises.

The decrease of the apparent activation energy with the concentration of Ba ions may suggest that Ba ions introducing, the more active points for evaporation, such as the dislocation line, would be formed and increase in number with the concentration of Ba ions.

In case of the deep colored specimens, during heating at 350°C, the F centers are evaporating in the same way as mentioned above, but, the F centers are still contained in excess. So the complex aggregates of the F centers would migrate to the dislocation lines in the crystal, as dislocation lines are to be considered as sinks for vacancies. The vacancies would disappear there and the electrons of the F centers would be attached to K ions, namely, the formation of the colloid centers. The F centers in the crystal containing Ba ions evaporate from the surfaces more easily than that in the pure crystal and moreover the surplus Ba ions precipitate out, possibly at the dislocation lines³⁾, so that the formation of the colloid centers would be disturbed by Ba ions.

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³⁾ S. Amelinckx, W. Van der Vorst, R. Gevers and W. Dekeyser, *Phil. Mag.*, **46**, 450 (1955)