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On the K-center in KCl Crystal

By

Masayasu Ueta

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1. Introduction

Many interesting investigations on the color centers in alkali-halide crystals were made, both experimentally and theoretically, by Pohl(**1**), Mott and Gurney(**2**), Seitz(**3**), Muto(**4**) and others. Recently, new centers other than F, F′ and U bands have been discovered and called them V, M, R_1, R_2(**3**) and N(**5**) bands respectively. We have also discovered another new band in ultra-violet region in NaCl crystal which was colored by pushing electrons into from a pointed cathode, and have called it K-center(**6**). In our previous paper(**6**) it has been shown that several properties of K-center can be explained satisfactorily, if we make use of the model of F_2^+ which was already used by Seitz(**3**) for explaining Molnar's R_1, R_2 bands. Now that a center similar to K-center in NaCl crystal has been discovered in KCl crystal, the writer has investigated its properties, and to the description of the results of our investigations the present paper is mainly directed.

2. Production of K-center

When a single crystal of KCl ($10 \times 10 \times 20\ \mathrm{mm}^3$) is held between a flat anode of platinum (or carbon) and a pointed cathode of platinum (or iron) at temperature of about 430° C, and electrons are pushed into from cathode, the crystal gives rise to a new absorption band ranging from 250 mμ to 350 mμ and its maximum absorption wave-length lies at 295 mμ at room temperature. We call it K-center, since this center has properties similar to K-center in NaCl crystal previously reported, i. e., (1) By irradiation of light lying in the absorption band, the crystal shows luminescence accompanied by photo-conduction ; (2) By heating it above 500° C for ten minutes, both the luminescence ability and K-absorption disappear ; (3) With the continuation of illumination, the luminescence gradually decays, its effect being prominent especially at 200° C.

The curve a in Fig. 1 shows K-absorption spectrum in KCl crystal measured with a Beckman-type quartz monochromator, a quartz photocell and an electrometer, while the curve b shows the absorption curve of the crystal which had lost the luminescence ability.

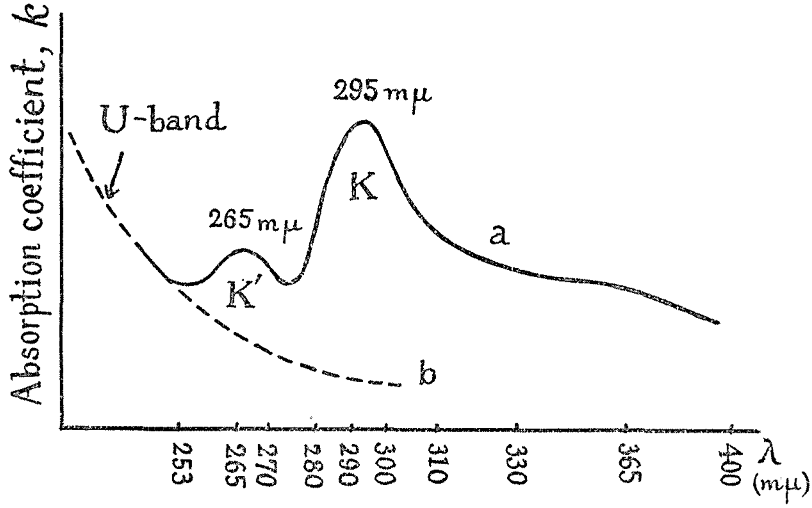

Fig. 1. Absorption spectra of K-center in KCl crystal.

3. Properties of K-center in KCl crystal

As mentioned above, the crystal having K-centers gives rise to photo-conduction when illuminated by the light lying in its absorption band. When the crystal containing K-centers is supported between two flat electrodes applied with an electric field of 1000 V/cm and is illuminated by the monochromatic light from a hydrogen discharge tube, through a powerful quartz spectrograph, then the photo-current flows, and it produces the potential drop across a high resistance ($10^9 \sim 10^{10}\,\Omega$) and causes a deflection of the electrometer. The relation between wave-length of exciting light and flowing photo-current is shown in Fig. 2. It will be seen that the wave-length corresponding to the maximum of the curve coincides with that of K-absorption maximum.

The wave-length region effective for exciting luminescence was photographed by the method of M. Hüniger and J. Rudolf (7). It was found that the maximum effective wave-length also coincides with that of K-absorption maximum.

K-centers are produced most prominently at 430° C and above this temperature the density of K-centers decreases, and F-centers begin to appear. Above 500° C, however, K-centers are not produced at all in spite of intense coloration of F-centers. It was found that when a clear KCl crystal was heated once at 700° C, which is below its melting point by 50° C, and was then cooled rapidly to 430° C, the density of K-centers was considerably smaller as compared with the case when the crystal was heated to 430° C from room temperature. Thus, it is found that the formation of K-centers in KCl crystal has an intimate connection with the combination of positive and negative ion vacancies.

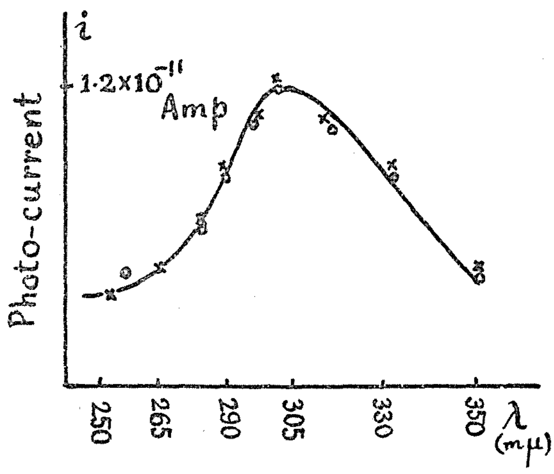

Fig. 2. The relation between photo-currents and wave lengths of excitation.

4. Displacement of K-center

It was previously mentioned that a crystal containing K-centers shows photo-conductivity just as a crystal containing F-center does. As is well known, the F-center moves towards the anode when an electric field is applied, and it is expected that the similar phenomenon would occur in the case of K-center.

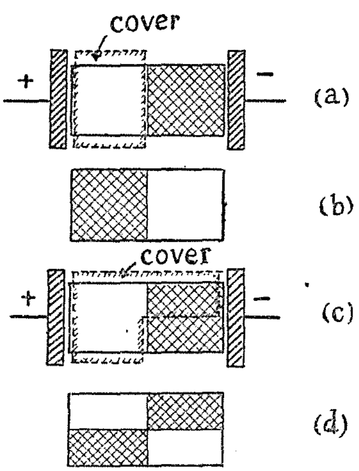

Fig. 3. Displacement of K-centers under the effect of illumination of light. Shadowed portion represents the existence of K-centers.

The crystal having K-centers in its one half was held between the two flat electrodes of carbon and was applied an electric field of 1000 V/cm. In Fig. 3 (a) the shadowed portion represents the existence of K-center. This crystal was heated at 300° C and illuminated by the light in K-absorption region for fifty minutes, on covering the other half of the crystal which does not contain any K-center.

After illumination, the crystal showed luminescence only in the covered portion, but not in the illuminated one (Fig. 3 (b)). The similar experiment was carried out in the case when only the lower half of K-containing portion was illuminated, and the remaining upper half of it as well as the half clear one of the crystal were covered (Fig. 3 (c)). After illumination, the K-containing portions became as shown in Fig. 3 (d). Thus, it has been found that K-centers move under the effect of illumination, but not due to the effect of an electric field only at this temperature.

5. Luminescence of K-center

Luminescence spectrum of K-center of KCl crystal was photographed with twenty minutes exposure and it was found that the spectral region extends from 600 mμ to 700 mμ, the maximum intensity being at 650 mμ. This luminescence does not decay so quickly during excitation at room temperature, but at 200° C, by the excitation of six hours the luminescence power decreases to half value of its initial intensity and at 250° C, K-centers disappear perfectly under this long excitation. At low temperatures, however, K-center does not decay so quickly, in spite of relatively strong emission. Thus, as for the mechanism of luminescence we must consider that electrons which had been raised to the excited state of K-center have to return ultimately to the ground state after emission. We consider that the model of K-center in KCl will be F_2^+ as in the case of NaCl, and since, according to Seitz, F_2^+ is analogous to H_2^+ molecule, the potential curve of F_2^+ (i. e., of K-center) may be as shown in Fig. 4. K-absorption occurs when electrons are raised from the ground state K to the upper excited state K* and then electrons transfer to the repulsion state on emitting the luminescence and ultimately return back to the original ground state.

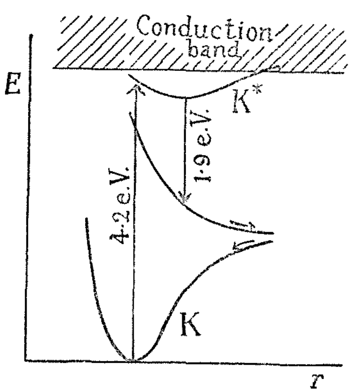

Fig. 4. Potential curve of F_2^+ molecule.

Considering in this way we can infer that the decay of K-center is not prominent at low temperatures, but at higher temperatures, on the other hand, electrons which are raised to the excited state K* move away into the conduction band by obtaining the lattice energy. When the K-center is thus ionized, the residual must be F_2^{++}, and these two negative ion vacancies flight away from each other under the mutual repulsive force, and consequently the K-center vanishes.

6. Absorption band of 265 mμ in KCl crystal

In KCl crystal in which electrons have been pushed into from a pointed cathode at 560° C ~ 580° C, there is formed the F discoloration with density of $10^{17} \sim 10^{18}/cm^3$, but no K-center is formed at all at these high temperatures. When this crystal is irradiated by the light of shorter wave-length than the K-absorption band and successively by the light in the K-absorption band region, it shows the luminescence due to the K-center. This fact indicates that there exists another absorption band on the shorter wave-length side of K-absorption band. We shall call this K′-center.

As mentioned just in the above, the formation of K′-centers is accompanied by the formation of F-center, but we can also obtain such a crystal that contains K′-center only, in the following way. After the cystal had been colored with F-centers at high temperatures, it is quenched to 430° C, and at this temperature F-centers are driven away under the influence of an electric field. Then, the colored crystal becomes to contain K′-centers only and its maximum absorption lies at about 265 mμ, as will be seen from its absorption spectrum shown by curve a in Fig. 5. When this crystal is irradiated by the light in its absorption region, the K′-absorption will disappear and the K-absorption will be formed (cf, curve b in Fig. 5). If this crystal is again illuminated by the light lying in the K-absorption, it emits luminescence, and by continuing illumination, luminescence and consequently the K-absorption band will ultimately disappear (cf, curve c in Fig. 5).

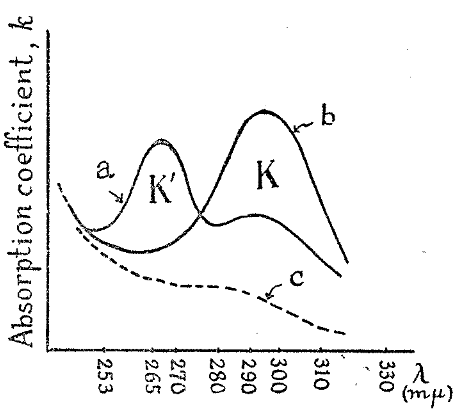

Fig. 5. Absorption spectra of K′-center.

When the crystal containing K′-centers together with F-ceners is irradiated, K′-centers disappear and there remain F-centers only in the crystal, but, by heating the crystal to 430° C, these F-centers are driven away perfectly under the influence of an electric field and the crystal becomes again to contain K′-centers. Thus, it can be inferred thatK′-centers are formed in the process of migration of F-centers.

Since several properties of K-centers in KCl crystal as well as in NaCl crystal can be explained satisfactorily by assuming the model of K-center to be F_2^+, it may be considered that K′-center has a model of F_2 from the K′→K light transformation.

On the other hand, Seitz has given F_2^+ model to Molnar's R_1 and R_2 centers in alkali-halide crystals colored by X-ray. If this model for R_1 and R_2 centers were correct, it may be expected that the same R_1 and R_2 bands should be formed in KCl crystal when it is F-colored additively. Thus, the writer has carried out experiments for the purpose of finding out the effect of visible light on F-centers in KCl crystal which had been colored additively and by electron bombardment or otherwise. But, the expected R_1 and R_2 centers could not be obtained except for one big band whose maximum wave-length is 710 mμ. This band may be considered to be due to the colloids.

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Institute of Physics,
Faculty of Science,
University of Kyoto.