Color Centers in Cu-doped NaCl and KCl Crystals

Kuniya FUKUDA*
Department of Physics, Faculty of Science, Kyoto University
and
Toshiko NAKAGAWA**
Department of Physics, Faculty of Science, Nara Women's University

(*Received Decenber 15, 1960*)

Cu-doped NaCl and KCl crystals, when irradiated by γ-rays from Co^{60} at room or dry ice temperature, showed optical absorption bands of color centers associated with neutral Cu atom and divalent Cu ion, while F-coloration was desensitized and V-type bands such as V_2 or V_3 were completely suppressed by the existence of Cu ions in these crystals.

INTRODUCTION

Cu^+ ion has the electron configuration similar to that of Ag^+ ion, that is, $3d^{10}$ for Cu^+ and $4d^{10}$ for Ag^+, and so it may be expected that Cu^+ ion acts as an electron trap in colored alkali halide crystals just like Ag^+ ion. On the other hand, since Cu ion has another stable form of $Cu^{++}(3d)^9$ for chlorides, it may be also supposed that Cu^+ ion acts as a hole trap on coloration of the crystals by ionizing radiation to form any stable center associated with Cu^{++} ion. Concerning the behaviors of Cu ions in colored alkali halide crystals, few works so far have been made, though there are many researches on the coloration of Ag doped crystals1). This seems to be mainly because Cu ions are apt to form complex or coaguration states in both uncolored and colored alkali halide crystals. In this work, these aggregation states of Cu ions were first examined by measuring the changes of absorptions of Cu-doped NaCl and KCl crystals for heat-treatments and then color centers associated with Cu ions were investigated by observing the optical absorption bands of the crystals colored by ionizing radiations (X- or γ-rays) or by pointed cathode and the transformation behaviors of the bands under optical and thermal bleachings.

EXPERIMENTAL PROCEDURES

Four sorts of Cu-doped alkali halide single crystals, NaCl-CuCl, NaCl-$CuCl_2$, KCl-CuCl and KCl-$CuCl_2$, were grown by Kyropoulos method from the melts containing 0.01～1 mole % of cuprous or cupric chlorides. The absorptions of these crystals and their changes by heat-treatments or with the concentration of Cu ions were examined and then ionizing radiations were irradiated at room or dry ice temperature on the samples which showed no absoption due to complex or coaguration state of Cu ions. Ionizing radiations were γ-rays from Co^{60} (2.3×10^5 r/hr) and X-

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** 中 川 淑 子

rays from 30 KV-20 mA X-ray tube. The absorption bands of the crystals colored by ionizing radiations were compared with those of the crystals electrolytically colored by pointed cathode and, further, the optical bleaching experiments were made at room temperature on the X- or γ-ray irradiated crystals.

Optical absorption measurements were carried out by using Beackman DU and Hitachi EPS-2 spectrophotometer in longer wavelengths than 190 mμ and by using a vacuum ultraviolet spectrophotometer[2)] in shorter wavelenhths than 200 mμ.

EXPERIMENTAL RESULTS

(a) Optical Absorption of Crystals before Coloration

The absorption bands caused by doping of NaCl and KCl with CuCl or $CuCl_2$ are listed in Table 1. In NaCl-CuCl and $CuCl_2$ crystals, absorption bands appeared at 340 and 255 mμ and absorption rapidly increased below 210 mμ. The 340 mμ band appeared somewhat strongly for the crystals of higher Cu concentration, but it was hardly appreciable for those containing 0.01 mole % Cu. Further, this band vanished after the crystals were heated at about 500°C for an hour. The 255 mμ band, which remained after heat-treatment, is considered to correspond to the transition $3d^{10}$ ($^1S_0$)$-3d^9 4s$ (^3D, ^1D) of free Cu^+ ion, the prohibition of which is broken in crystal by the interaction with lattice vibrations[3)]. No band characteristic to Cu^{++} ion was observed in NaCl-$CuCl_2$ crystals, whereas Boesman and Dekeyser found it at 220 mμ[4)].

In KCl-CuCl crystals appeared a weak band at 370 mμ and a strong one at about 270 mμ with a shoulder at about 300 mμ and absorption rapidly increased below 210 mμ. After the crystals were heated at about 300°C for half an hour, the 370 mμ band easily vanished and a definite band appeared at 260 mμ without shoulder on its longer wavelength side. At the same time, a weak and broad band remained at 340 mμ, but this band vanished after heat-treatment at about 500°C for an hour. Further, after this heat-treatment, a band at 186 mμ with a small hump at about

Table 1. Absorption bands of Cu-doped NaCl and KCl crystals at room temperature (λ in mμ).

	Cu^{++}	Cu^+			
NaCl-CuCl		255 4.96 ev HW : 0.55 ev		(340)	
NaCl-$CuCl_2$	220* 5.61 ev	255		(340)	
KCl-CuCl	186~200 6.7 ev	260 4.81 ev HW : 0.6 ev	(~300)	(340)	(370) f. s. at liq. air temp.
CuCl film**	~195		~300		372 f. s. at liq. N_2 or He temp.***
KCl-$CuCl_2$	225 5.48 ev	260		(340)	

The bands in bracket vanish after heat-treatment. HW : Half-width ;
* by Boesman[4)] ; ** by Fesefeld[5)] ; *** by Nikitine[7)].

200 mμ was definitely observed on the tail of characteristic absorption of KCl crystals. Being compared with the absorption of CuCl film at room temperature[5], the bands at 370 and about 300 mμ, which were easily removed by heat-treatment at lower temperature, are probably due to CuCl coagurations in KCl crystal. This is, further, certified by the fact that at liquid air temperature the 370 mμ band showed the fine structure[6] quite similar to that of the exciton band observed by Nikitine on CuCl film at liquid nitrogen or helium temperature[7]. The 260 mμ band, the peak position and half width of which somewhat differ from those previously observed[8], is considered to correspond to the 255 mμ band of NaCl-CuCl, that is, $3d^{10}-3d^9 4s$ transition of free Cu^+ ion. As for the 186 mμ band, it can not be decided in the present stage of our experiments whether this band is caused by the transition $3d^{10}\,(^1S_0)-3d^9 4p\,(^3P, {}^1P, \text{etc.})$[9] of Cu^+ ion in KCl crystal or by the exciton localized near a site of Cu^+ ion.

In KCl-$CuCl_2$ crystals, absorption bands appeared at 340, 260 and 225 mμ and absorption below 210 mμ was considerably smaller than that of KCl-CuCl crystals. After heat-treament, the 340 mμ band vanished but the bands at 260 and 225 mμ suffered no change. The appearance of the 225 mμ band in KCl-$CuCl_2$ crystals seems to depend on the conditions of crystal growth, espescially on the existence of atomospheric vapor or oxygen, as Boesman suggested on the 220 mμ band of NaCl-$CuCl_2$ crystals[4]. It may be allowed to assign tentatively the 225 mμ band to the absorption associated with Cu^{++} ion as in the case of the 220mμ band of NaCl-$CuCl_2$.

(b) Absorption Bands of Crystals after Coloration

NaCl-CuCl, KCl-CuCl and KCl-$CuCl_2$ crystals were colored by ionizing radiations (γ- or X-rays) at room or dry ice temperature as well as by pointed cathode. The absorption measurements of colored crystals were carried out at room temperature. The absorption bands which appeared in colored crystals are listed and designated by alphabetic letters in Table 2. These designations of absorption bands, of course, does not always correspond to those of colored alkali halide crystals containing Ag ions[1].

In NaCl-CuCl crystals, A-, B-, C- and D-bands appeared besides F-band after γ- or X-ray irradiation at room temperature (Table 2 and curve-a in Fig. 1). In this case, the 255 mμ band of Cu^+ ion in uncolored crystals seemed to decrease or to vanish after coloration, depending on Cu-concentration in crystals and irradiation

Table 2. Absorption bands of colored NaCl and KCl crystals doped with Cu ions (λ in mμ).

Crystals		A (Cu^{++})	B	C	D	E	F	
NaCl-CuCl		220	235	290	340		470	γ- or X-ray irrad. at room temp.
KCl-CuCl		225	245	305	340	460?	560	
		225	245		340		560	: γ- or X-ray irrad. at dry ice temp.
	215		245	305	355	460?	560	: pointed cathode
KCl-$CuCl_2$		225	245	305	340	460?	560	: γ- or X-ray irrad. at room temp.
		225			340		560	: γ- or X-ray irrad. at dry ice temp.

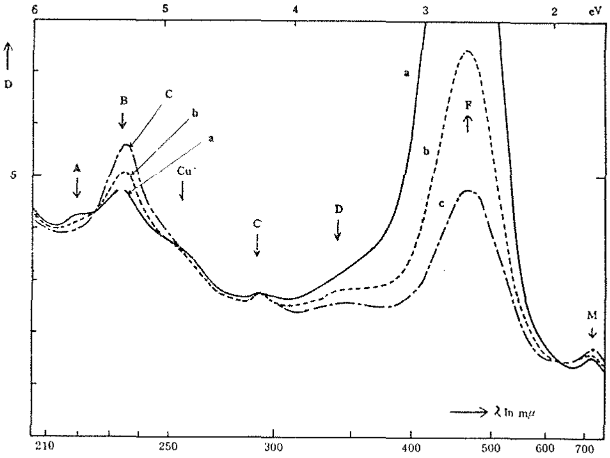

Fig. 1 Absorption curves of NaCl-CuCl (0.02 mole %) crystal after γ-ray irradiation at room temperature and after optical bleaching at room temperature (crystal thickness : 1.2mm).

a : after 4 hrs γ-ray irradiation ; b : after 15 min F-light irradiation ;
c : after further 1 hr F-light irradiation.

period of ionizing radiation. A-band at 220 mμ coincides in its peak position with Cu^{++} band observed by Boesman in uncolored NaCl-CuCl$_2$ crystals. By F-light bleaching at room temperature, A- and F-bands decreased but B-band increased (curves-b and c in Fig. 1). Further, when the colored crystals were kept in dark at room temperature, A- and F-bands also decreased but B-band remained nearly unchanged. From the above facts, it may be allowed to consider that A-band is associated with Cu^{++} ion formed by hole trap at Cu^{+} ion and B-band with Cu neutral atom formed by electron trap at Cu^{+} ion. The models of A- and B-centers will be further discussed in the following section.

In KCl-CuCl crystals, A-, B-, C-, D- and E-bands appeared besides F-band after γ- or X-ray irradiation at room temperature (Table 2 and curve-a in Fig. 2). In this case, the 260 mμ band of Cu^{+} ion observed before coloration also seemed to decrease or to vanish depending on Cu-concentration and γ- or X-ray irradiation period ; and A-band also coincide in its peak position with the 225 mμ band of Cu^{++} ion in uncolored KCl-CuCl$_2$ crystals just as in the case of NaCl. When the colored crystal was bleached with F-light at room temperature (curve-b in Fig. 2) or when it was kept in dark at room temperature, A- and F-bands decreased but B-band hardly changed. On electrolytic coloration of KCl-CuCl crystal by pointed cathode, B-, C-, D-, E- and F-bands appeared together with a weak band at about 215 mμ (curves-a and b in Fig. 4) and, when the sign of applied voltage was reversed after coloration with pointed cathode, F-centers could be easily pulled out from the crystal and B-, C- and D-bands and the 215 mμ band remained on a flat background absorption below 500 mμ (curve-c in Fig. 4). The flat absorption below 500 mμ may be considered to be due to colloid of Cu atoms[10] and it seems likely that the existence of E-band is virtual and caused by the shoulder of this flat absorption. From the comparison of the absorption of electrolytically colored crystal with that of γ- or

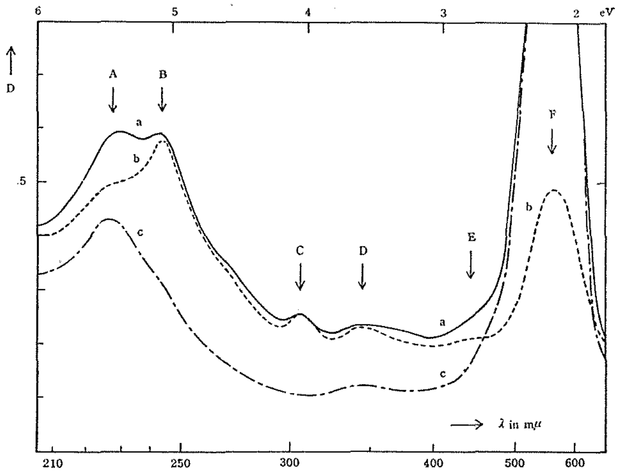

Fig. 2 Absorption curves of KCl-CuCl (0.1 mole %) crystals after γ-ray irradiation and after optical bleaching at room temperature.

a and b : after 4 hrs γ-ray irradiation at room temperature and after 1 hr F-light bleaching, respectively (crystal thickness : 1.15 mm) ; c : immediately after 3 hrs γ-ray irradiation at dry ice temperature (crystal thickness : 1.0 mm ; measurements : at room temperatre).

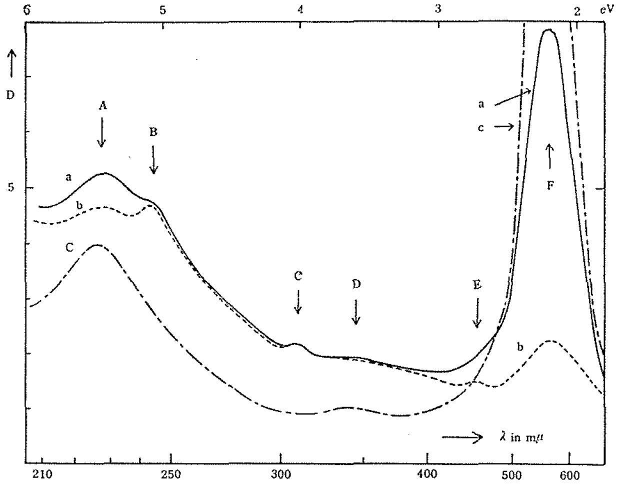

Fig. 3 Absorption curves of KCl-$CuCl_2$ (0.1 mole %) crystals after γ-ray irradiation and after optical bleaching at room temperature.

a and b : after 3 hrs X-ray irradiation at room temperature and after 1 hr F-light irrdiation, respectively (crystal thickness: 2.0 mm) ; c : immediately after 3 hrs γ-ray irradiation at dry ice temperature (crystal thickness : 1.15 mm ; measurements : at room temperature).

X-ray irradiated one, it is certain that A-band relates to a hole-type center and B-band to an electron-type center. Further, the behaviors of F-light bleaching of γ-ray irradiated crystal supports that A-band may be associated with Cu^{++} ion and B-band with Cu neutral atom in KCl-CuCl crystals just as in the case of NaCl-CuCl. When

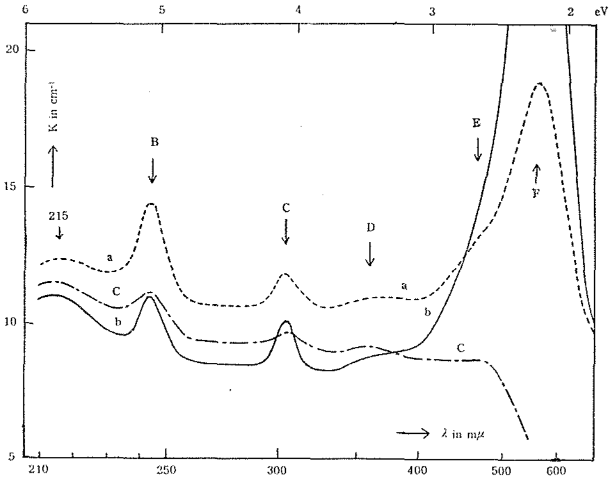

Fig. 4 Absorption curves of KCl-CuCl (0.1 mole %) crystals colored by pointed cathode. a and b : after coloration at 550°C and 700°C, respectively ; c : after drawing-out of F-centers from the crystal electrolytically colored at 650°C.

KCl-CuCl crystals were irradiated with γ-rays at dry ice temperature, A-band more strongly and B-band only weakly appeared in comparison with the coloration of the crystals at room temperature and at the same time, C- and E-bands were not found at all (Table 2 and Curve-C in Fig. 2). Further, the desensitization of F-coloration, which occured to considerable extent for γ-ray irradiation at room temperature, was hardly observable for the irradiation at dry ice temperature.

In KCl-$CuCl_2$ crystals appeared the same absorption bands as those of KCl-CuCl after γ- or X-ray irradiation at room temperature; and in this case A-absorption appeared more strongly than B-absorption contrary to the case of KCl-CuCl coloration at room temperature (Table 2 and curve-a in Fig. 3) and, further, F-coloration was much more desensitized than in the case of KCl-CuCl coloration. The behaviors of A- and B-bands under F-light bleaching were similar to those of both bands in KCl-CuCl (curve-b in Fig. 3). When KCl-$CuCl_2$ crystals were irradiated with γ- or X-rays at dry ice temperature, only A-, D- and F-bands appeared, while B-, C- and E-bands were not detected at all (Table 2 and curve-c in Fig 3). In this case, the desensitization of F-coloration was not observed in spite of strong desensitization at room temperature.

The above results concerning γ- or X-ray coloration of KCl-CuCl and $CuCl_2$ crystals at room or dry ice temperature seem to lead to the following conclusions: Cu^+ ion has larger capture cross section for electron at room temperature and for hole at dry ice temperature. In other words, Cu^+ ion tends to act more strongly as an electron trap at higher temperature and to do as a hole trap at lower temperature. As for Cu^{++} ion, it is a strong electron trap at room temperature, but it has a small cross section of electron at dry ice temperature.

C-band, which always appears except for the case of γ- or X-ray irradiation at dry ice temperature, may be tentatively assigned to pair or more complex of Cu neutral atoms which probably contains some negative ion vacancies. D-band at about 340 mμ is observed in all sorts of colored crystals and its peak position nearly coincides with that of the band which appears in the uncolored crystals containing higher concentration of Cu^+ ions. So it might be considered that this band is due to pair or more complex of Cu^+ ions. E-band of γ- or X-ray irradiated crystals seems to correspond to the shoulder of colloid band in electrolytically colored crystal as mentioned above. If it is the case, it may be considered that a very small amount of colloid is formed by ionizing radiations at room temperature. This consideration might be supported by the speculation that E-band does not appear for γ- or X-ray irradiation at dry ice temperature and, hence, colloid formation does not occur at lower temperature.

DISCUSSION

The electron spin resonance of Cu^{++} in alkali halide crystals doped with Cu^{++} ions was measured by Abe et al at room temperature(11), but only a weak and very broad line was observed. On the other hand, Tucker obtained the fine results of electron spin resonance of Cu^{++} ion at the temperature range from room to liquid nitrogen temperature on AgCl-CuCl crystal heated in Cl_2 gas and concluded that a center of Cu^{++} ion plus one positive ion vacancy was dominantly formed in this crystal(12). It may be plausible that A-center of our crystals consist of Cu^{++} ion and a positive ion vacancy, but the electron spin resonance measurements were unsuccessful at room temperature on both uncolored and colored $KCl\text{-}CuCl_2$ crystals. As for B-center in the colored Cu-doped crystals, it is likely that this center corresponds to B-center of colored alkali halide crystals containing Ag^+ ions. B-center of Ag-doped crystals may be approximated by a model of Ag neutral atom plus one negative ion vacancy rather than by that of Ag^+ ion plus an F-center from the experiments of electron spin resonance(13). If B-center in our crystals has a model similar to that of the center of same letter in colored alkali halide-Ag crystals, it will show a much larger hyperfine constant and a more complex spectrum than B-center due to Ag because of large magnetic dipole- and electric quadrupole-moment of Cu atom. The electron spin resonance measurements were made without success at room temperature on the crystals containing B-centers. The spin resonance measurements of A- and B-centers will be tried at lower temperature in near future.

Further experiments will be necessary to get detailed informations of the coloration mechanism of Cu-doped alkali halide crystals, espescially of the roles of Cu^+ and Cu^{++} ions in coloration.

ACKNOWLEDGEMENT

The authors express their thanks for the help of Mr. Y. Nakayama in γ-ray irradiation.

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