PHYSICAL REVIEW B VOLUME 21, NUMBER 12 15 JUNE 1980

Trapping of electrons in electrolytically colored NaCl:Cu^+ crystals

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(Received 10 December 1979)

The optical-absorption spectra of crystals of NaCl containing Cu^+ ions were examined after the crystals had been electrolytically colored using a pointed cathode. It is shown that the Cu^- center which was formed by the coloration releases the electron by optical excitation to form the Cu^0 center. The released electron is then trapped by a negative-ion vacancy to form the F center. Moreover, by optical or thermal excitation, the F center releases the trapped electron which is subsequently trapped by the Cu^0 center to reform the Cu^- center. A study of the photochemistry of the colored NaCl:Cu^+ crystals reveals that the *K* band previously named by Uchida, Ueta, and Nakai is due to the Cu^- center.

I. INTRODUCTION

Three decades ago, Uchida *et al.*[1-3] found a new absorption band peaking at 4.20 eV at room temperature (RT) in electrolytically colored NaCl crystals, which was named the *K* band.[4] They suggested that the *K* band arises from an electron-trapped center, i.e., $F_2{}^+$. Later, however, Schneider and Rabin[5] found that (i) the absorption band due to $F_2{}^+$ appears at 1.20 eV in NaCl, (ii) the formation of the $F_2{}^+$ center is accompanied by the decay of the hole-trapped centers, V_k and *H*, which were formed at liquid-helium temperature, and (iii) the $F_2{}^+$ decays on warming to liquid-nitrogen temperature, i.e., the $F_2{}^+$ center is thermally unstable at RT. This indicates that the *K* band does not arise from $F_2{}^+$. The origin of the *K* band has been unknown for a long time.

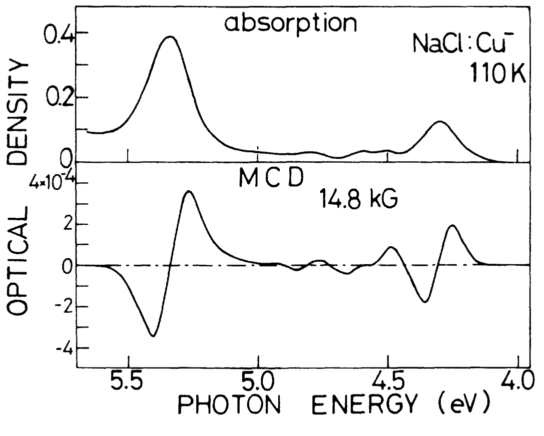

FIG. 1. Optical-absorption spectrum of the Cu^- bands in an NaCl crystal at 110 K (shown in the upper part) and the magnetic circular dichroism spectrum measured at the same temperature in a magnetic field of 14.8 kG (shown in the lower part). The dichroism is given by the difference between the optical densities for the left and right circularly polarized components of light.

Recently we studied the optical properties of Cu^+-doped alkali halides which were electrolytically colored using a pointed cathode as Uchida *et al.* Several absorption bands appear in the ultraviolet and vacuum ultraviolet region in the colored crystals.[6] These bands have been attributed to Cu^- ion[6-10] which, unlike Cu^+ ion, replaces a halide of the lattice just as the case of Ag^- ion.[8,11-13] The optical properties of the Cu^- bands, especially absorption, emission, lifetime, uniaxial-stress effect and crystal-field effect, have been studied by Kleemann,[8] Kleemann *et al.*,[9] and Tsuboi.[6,10] In addition to these optical studies, we studied the magnetic-field effect and found that circular dichroism appears in the Cu^- bands of NaCl as shown in Fig. 1.[14] These studies (including the magnetic circular dichroism study) confirm the presence of the Cu^- center in NaCl crystals. Of the Cu^- bands observed in NaCl, a relatively strong absorption band peaking at 4.24 eV at RT[6] [4.30 eV at 77 K (see also Fig. 1)] is located at almost the same position as the *K* band. Therefore, taking into account that the 4.24-eV band appears in the electrolytically colored NaCl crystals, we have a suggestion that the 4.24-eV band may be identical with the *K* band although, according to Uchida *et al.*,[1,2] the *K* band has a peak at 4.20 eV. In this paper, in order to make sure the suggestion, we investigate the behavior of the Cu^- bands by the optical or thermal excitation and compare it with the case of the *K* band. At the same time, we will be concerned with the whereabouts of the electron which is optically or thermally released in the colored NaCl:Cu^+ crystals.

II. EXPERIMENTAL PROCEDURE

Single crystals of NaCl containing 0.001–0.1 mole% CuCl in the melt were grown by the Kyropoulos method. These crystals were colored using a pointed cathode applied voltage of 450–470 V in a furnace at a temperature of 350–500 °C. A flat plate was used as an anode. When a voltage was applied, a cloud of color (pale brown) entered from the pointed cathode and moved toward the anode. It was observed in a dark room that a faint luminescence is emitted from the cloud and moves with the cloud. When the luminous cloud reached the anode, a spark came out from the anode. After coloration, the crystals were rapidly removed from the furnace for quenching. The dimension of the crystal used for the coloration was about $10 \times 10 \times 20$ mm^3. Absorption spectra were measured with a Shimadzu spectrophotometer MPS-50L. A 500-W Xe lamp was used for the excitation of the crystal.

III. RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra of electrolytically colored NaCl:Cu$^+$ crystals. When an NaCl:Cu$^+$ crystal is colored at 450 or 500 °C, the F band (peaking at about 2.70 eV at RT) is produced in addition to the Cu$^-$ bands (curve a). However, when colored at a lower temperature like 400 °C, a broad band peaking at about 2.88 eV is produced in the visible region (curve 1). Irradiation with light into the 4.24-eV band (or the 5.34-eV band[6]) of Cu$^-$ causes a reduction in intensity of all the Cu$^-$ bands and a growth of the F band. The increase of the F band is proportional to the decrease of the Cu$^-$ bands. At the same time, the irradiation causes a growth of a band peaking at about 3.76 eV as shown in curve 2. It was not found, after the irradiation, that other electron-trapped centers such as F$^-$ center,[15] which gives rise to an absorption band at 2.43 eV, are produced. The experimental result may be interpreted as follows: (i) The Cu$^-$ center is optically excited and releases an electron into the conduction band, resulting in the formation of Cu^0 center,[13,14] and (ii) the electron is subsequently trapped at a negative-ion vacancy to form the F center. The 3.76-eV band appeared in curve 2 is suggested to be attributable to Cu^0. Indeed, the Cu^0 center in NaCl is known to give rise to two absorption bands in the vicinities of 3.76 and 3.26 eV.[16] The 3.26-eV Cu^0 band, which is rather smaller than the 3.76-eV Cu^0 band,[16] is believed to be hidden under the strong F and 3.76-eV bands.

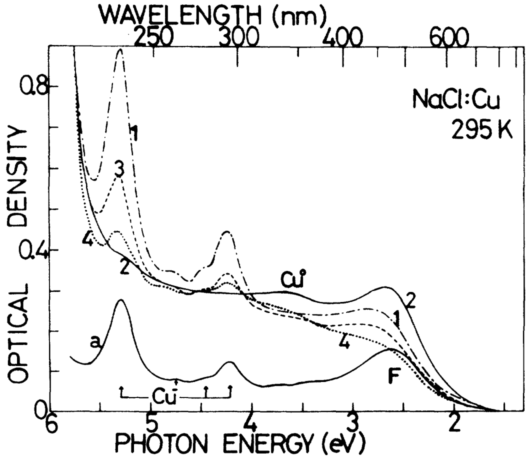

FIG. 2. Absorption spectra, measured at RT, of two electrolytically colored NaCl:Cu$^+$ crystals. Curve a shows the spectrum of a crystal which was colored in the furnace at 500 °C, whereas curve 1 the spectrum of another crystal which was colored in the furnace at 400 °C. Curve 2 was obtained after the irradiation with 4.28-eV light for 60 min at RT. Curve 3 was obtained after warming the crystal of curve 2 to 200 °C for 75 min at RT. Curve 4 was obatined after warming the crystal of curve 3 to 350 °C for 10 min at RT.

When the crystal of curve 2 is warmed to 200 °C, the F and Cu^0 bands are annihilated whereas the Cu$^-$ bands are grown as shown in curve 3. On the other hand, when the crystal of curve 2 or of curve a was irradiated with the F-band light, it was also found that the F band is reduced whereas the Cu$^-$ bands are grown. These results indicate that, when the F center becomes thermally or optically unstable, the trapped electron is released and then retrapped by Cu^0 to form Cu$^-$.

Such a correlation between the Cu$^-$ and F bands is quite similar to that between the K and F bands which was observed by Uchida *et al.*[1] Regarding the luminescence of the Cu$^-$ center, we observed that an emission band peaking at 2.88 eV is produced at RT by the optical excitation of the 4.24-eV Cu$^-$ band,[6] and, moreover, the blue emission fades out with the exposure to light of 4.24-eV wavelength. The same result was also obtained in the case of the *K*-band excitation.[1] Therefore, it is concluded that the 4.24-eV band of the Cu$^-$ is identical with the *K* band. This conclusion is consistent with the earlier observation[1] of electrical conductivity induced by irradiation with *K*-band light; i.e., it is likely that the electron is released from Cu$^-$ by the optical stimulation into the conduction band, giving rise to the photocurrent. Thus, it is suggested that Cu$^+$ impurity ions were accidentally contained in the NaCl crystals used by Uchida *et al.*[1] for the electrolytical coloration.

As mentioned above, the Cu$^-$ band is regrown by the thermal excitation. However, it has never regrown to its original intensity even after the complete annihilation of the produced F center as shown in curve 3 or Fig. 2. From this, it seems likely that the Cu$^-$ center is thermally unstable at such a high temperature and, therefore, a fraction of the Cu$^-$ centers are annihilated with raising the temperature. The thermal instability of the Cu$^-$ center is confirmed by warming the crystal to a temperature more than 200 °C. Certainly the decrease of the Cu$^-$ band is observed in curve 4 which was taken after warming up

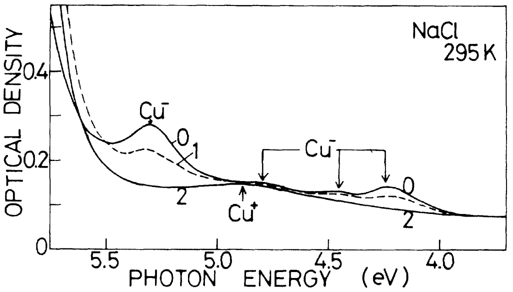

FIG. 3. Absorption spectra, measured at RT, of an electrolytically colored NaCl:Cu^+ crystal which was thermally excited. Curve 0 shows the spectrum measured immediately after the coloration. Curve 1 was obtained after warming the crystal of curve 0 to 430 °C for 15 min and then rapidly quenching to RT. Curve 2 was obatined after warming the crystal of curve 1 to 500 °C for 60 min and then rapidly quenching to RT.

to 350 °C or in curve 1 of Fig. 3 which was taken after warming up to 430 °C. When the crystal is warmed up to 500 °C, the Cu^- bands are completely annihilated whereas a band peaking at about 4.88 eV is produced as shown in curve 2 of Fig. 3.

The 4.88-eV band is attributable to the Cu^+ center.[6] In fact, curve 2 of Fig. 3 is the same as a spectrum which was taken before the coloration of Cu^+-doped NaCl crystal. The above experimental result indicates that the Cu^- ion is converted to the original Cu^+ ion by warming the colored crystal up to a very high temperature near the melting point. This seems to be consistent with that the Cu^- ion has a position at an anion site in NaCl lattice whereas the Cu^+ ion at a cation site, namely, a very high temperature is needed so that appreciable ionic motion occurs in NaCl lattice.

Finally, we shall investigate how far the electrons which were released from the Cu^-, Cu^0, or F centers can migrate in the NaCl crystal. In order to investigate it, a crystal in which two zones of the colored and uncolored coexist was used. Such a crystal was obtained by controlling the applied voltage and furnace temperature during the electrolytical coloration. It was confirmed, from the absorption spectra, that the colored zone contains the Cu^- and F centers but not the Cu^+ center whereas the uncolored zone only the original Cu^+ center. We found that, when the crystal is optically excited, the electron transfer between the F and Cu^- centers occurs uniformly within the colored zone, but the electrons released in the colored zone never enter the uncolored zone to produce the F, Cu^-, or Cu^0 center. From this, we may suggest that either a high potential barrier is built for the released electrons at the boundary between the colored and uncolored zones, or that the cross section for trapping electrons by the Cu^+ ions is quite small at RT when compared with the cases of trapping by the Cu^0 and negative-ion vacancy. The former suggestion seems more reasonable than the latter one. This can be seen from the following experiment. When the colored zone which is in contact with a cathode plate was illuminated by the K-band (i.e., Cu^--band) light in a furnace of 300 °C and, at the same time, when an electric field is applied, the K centers (i.e., Cu^- centers) were found to be produced in the uncolored zone which is in contact with an anode plate.[2] This experimental result can be interpreted as follows; the electrons are released from the Cu^- centers by the illumination and moved into the uncolored zone by the electric field and then trapped by Cu^+ ions, resulting in the formation of the Cu^- centers. That is to say, the experiment indicates that, when the electric field is applied, the released electrons can easily get over the potential barrier and enter the uncolored zone.

In summary, we have demonstrated that, first, the previous K band arises from the Cu^- center, second, an electron is released from a Cu^- ion by the optical excitation and then trapped by a negative-ion vacancy, resulting in a formation of the F and Cu^0 centers, third, the electron is released from the F center and then trapped by the Cu^0 center, resulting in a formation of the Cu^- center, and finally, the Cu^- center becomes unstable with raising the temperature and is converted to the Cu^+ center at about 500 °C.

ACKNOWLEDGMENT

This work was supported in part by the Grants-in-Aid from the Ministry of Education in Japan.

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