PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON CRYSTAL LATTICE DEFECTS, 1962, CONFERENCE
JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 18, SUPPLEMENT II, 1963

F'-Type New Absorption Bands in KCl and KBr Crystals

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New absorption bands in KCl and KBr crystals were observed in near infrared region. It is considered that they arise from F' type centers which consist of R_1, R_2 or M center and one more electron. F' type bands appear during the process of $F \rightarrow F'$ conversion in the crystal containing complex centers, and they are located at 1.60 μ, 1.72 μ, 2.14 μ and 1.49 μ, 1.60 μ, 1.94 μ in KBr and KCl crystals, respectively. F' type centers are thermally unstable than F' center. These centers are called R_1', R_2' and M'.

§1. Introduction

As is well known, when the alkali halide crystals containing F centers are illuminated at a low temperature with F light, electrons are ionized from some F centers and trapped by other F centers. Thus, F' centers are produced, each consisting of an F center and an electron. By analogy with this phenomenon, if crystals containing complex centers such as M, R_1, R_2, N_1 and N_2 are illuminated at a low temperature with F light, we might expect these complex centers to also capture one more electron and generate F' type centers. In fact, we have discovered new absorption bands which are considered to have arisen from these F' type centers.

§2. Experimental Procedure

In this experiment all absorption measurements were carried out at liquid air temperature by using a Hitachi EPS-2 Recording Spectrophotometer. KCl crystals grown by the Kylopoulos method with chemically purified powder and Harshaw KCl and KBr crystals were additively colored. The F center concentration in each crystal was about 8×10^{17}/cc.

§3. Experimental Results

1) New absorption bands in near infrared region

When KCl and KBr crystals containing F and complex centers are illuminated, respectively, at $-110°$C and $-130°$C with F light to make $F \rightarrow F'$ conversion; in addition to the well known F' band, new absorption bands are found to appear at 1.49 μ, 1.60 μ, 1.94 μ in KCl and 1.60 μ, 1.72 μ, 2.14 μ in KBr, respectively, at liquid air temperature. These three bands are termed R_1', R_2' and M' centers, respectively. These F' type bands appear at the expense of R_1, R_2 and M bands and are never found in the crystals containing no complex centers.

After the formation of F' band and F' type bands, if the crystal is illuminated with white light at liquid air temperature or warmed up to room temperature, the absorption curve of the crystal return to the initial state before the formation of F' band and F' type bands.

2) Thermal stability of F' type centers

R' bands and M' band in KCl or KBr crystal are thermally unstable at temperature above $-150°$C, $-160°$C or $-150°$C, $-170°$C, respectively. When the crystal showing F' type bands is gradually warmed up from liquid air temperature to room temperature, F' type bands begin to disappear at temperatures mentioned above. However, they again appear at temperature where F' center become thermally unstable. This will be explained by considering that the electrons ionized thermally from F' centers are re-trapped by complex centers thus temporarily generating F' type centers again.

3) Dichroism of F' type bands

A KCl crystal containing F and complex centers was illuminated at room temperature by M (800 mμ) light polarized in the direction of [0$\bar{1}$1] to induce dichroism in M band. As is shown by curves (a) and (b) in Fig. 1 which were measured at liquid air temperature by [011] and [0$\bar{1}$1] light, respectively, M band showed large dichroism. After warming up the crystal to $-110°$C the crystal was illuminated with F light to make $F \rightarrow F'$ conversion. R' bands and M' band appeared, but in this case only M' bands showed the same dichroism as that of M band as shown by curves (c) and (d) in Fig. 1. Similarly, in the case of the crystal showing dichroism at only

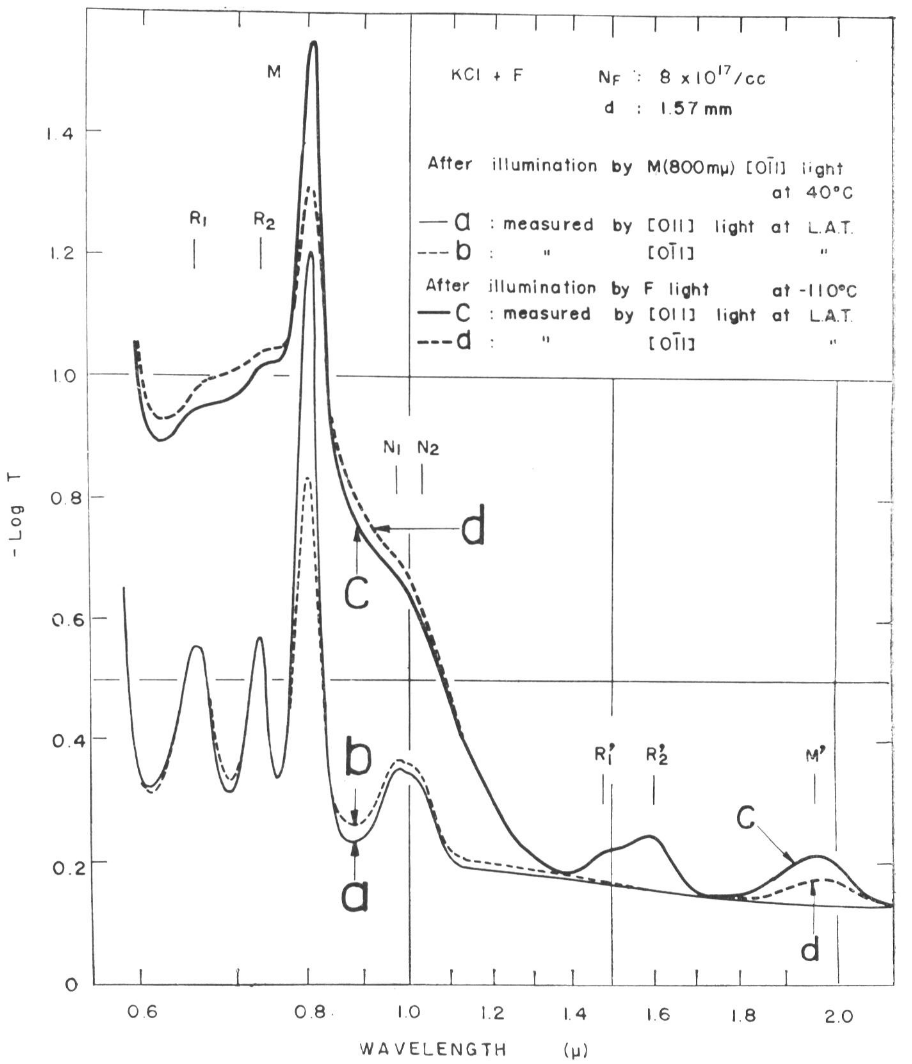

Fig. 1. Correspondence between dichroisms of M and M' bands.

R bands, by the treatment which induces F' type bands, only R' bands showed the same dichroism as that of R bands.

In contrast with above mentioned observation when the crystal showing R' bands and M' band was illuminated with polarized R_2' light at liquid air temperature, R' bands decreased in their height and showed the dichroism. While, R bands enhanced and showed the dichroism opposite to that of the R' bands. In this case the dichroism of M and M' bands were not observed. These results are explained clearly if we consider that R' center has the same symmetry to that of the R center and that the R' center decomposes to one electron and the original R center.

From the correspondence between the dichroisms of F' type bands and the R or M bands it was confirmed that these new bands can be attributed to the R_1', R_2' and M' centers.

§ 4. Conclusion

From these results it is considerably well established that complex centers such as R and M centers may capture an electron released from the F or F' center by optical or thermal ionization, and that they generate F' type centers.

The band widths of R_1', R_2' and M' bands in KBr are 0.06±0.005, 0.06±0.005 and 0.05±

0.005 eV, respectively. They are very narrow as compared with that of the F' band. In the case of KCl crystals they are also very narrow as are those in the KBr crystals. At the present stage of investigation, the reason for the narrow band width is not clear.

R_1 and R_2 bands always behave similarly in respect to dichroism and the increase or decrease in height. On the other hand, R_1' and R_2' bands also behaved in a similar fashion with each other. Thus, R_1 and R_2 bands as well as R_1' and R_2' bands may arise from two electronic transitions in the identical R and R' centers.

The F' type bands corresponding to N_1' and N_2' bands were not observed in the present experiment, because of the short life times of these centers.

The detail results on the F' type bands will be reported in J. Phys. Soc. Japan **17** (1962) No. 9.

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α Centers in Alkali Halide Crystals

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Optical studies are made concerning α centers in KI, KBr, KCl, NaCl and NaF. Position, half width and oscillator strength of α absorption bands, thermal stability of α centers and fluorescence by α light absorption and its quantum efficiency are investigated. The observed fluorescence suffers quite a large Stokes shift in all the crystals measured. The quantum efficiency of α fluorescence is determined on KCl by referring to that of 305 mμ emission excited by 246 mμ band in KCl:Tl phosphor. Temperature dependence of the emission spectrum of α fluorescence is found not remarkable and the quantum efficiency seems to be independent of method of coloration and concentration of α and F centers.

I. Introduction

Since the discovery of α band in additively colored KI[1], the band has been observed in RbI, RbBr, NaBr[2], KCl, NaCl and NaF[3]. When an alkali halide crystal is exposed to ionizing radiation at a low temperature or crystal that contains F centers is bleached with F light at an appropriate temperature, an absorption band due to negative ion vacancies appears in the vicinity of the fundamental absorption. From several experimental evidences it is now believed that this band, α band, is due to an absorption that forms excitons around a negative ion vacancy. The negative ion vacancy is then called α center.

In the present study, position, half width and oscillator strength of this absorption band, thermal stability of the center, and fluorescence by α light absorption and its quantum efficiency were investigated on KI, KBr, KCl, NaCl and NaF single crystals. The results together with brief account of already published work will be summarized in this report.

II. Material and Equipment

Most of crystals of KBr, KCl, NaCl and NaF used were obtained from Harshaw Chemical Company. Some NaCl samples were cleaved out from an old rock salt prism, and KI crystals were grown in our laboratory. All alkali halides investigated except NaF were able to be colored both additively and by X-irradiation. A KCl:Tl crystal grown by Dr. Aoyagi was used as a standard phosphor for determining the quantum efficiency of α fluorescence.

Vacuum spectrophotometer used has been reported separately[4]. In the study of α fluorescence, emission from sample was obtained through a devised side window of the