PHYSICAL REVIEW B VOLUME 13, NUMBER 4 15 FEBRUARY 1976

Effects of the Na^+ impurity on the relaxation of an exciton in KBr at low temperatures

K. Tanimura and T. Okada
Department of Nuclear Engineering, Osaka University, Yamada-Kami, Suita 565, Japan

(Received 19 May 1975; revised manuscript received 14 October 1975)

Studies on defect formation in Na^+-doped KBr at low temperatures, where primary interstitials are stable, have been performed by means of optical-absorption and luminescence measurements. It is found that the Na^+ impurity suppresses the colorability, enhances the 2.90-eV emission band, but does not affect the intensity of intrinsic luminescence. The origin of the 2.90-eV emission band is identified to be radiative decay of the $(V_{KA}+e^-)^*$. The suppression of the defect formation is ascribed to the trapping of the exciton state which is responsible for the creation of the pair of F and H centers by the Na^+ impurity: The trapping gives rise to the formation of the $(V_{KA}+e^-)^*$. A model for the relaxation of an exciton is discussed based on these results.

I. INTRODUCTION

The role of monovalent cation impurity such as Na^+ or Li^+ for defect formation in alkali halides has been mainly investigated in terms of the secondary reaction of halogen interstitials or their interaction with the impurity. It has been established[1–3] that the impurities stabilize interstitial halogen atoms and ions to form the H_A and I_A centers, respectively, and result in the enhancement of the production of F and α centers at liquid-nitrogen temperature (LNT). On the other hand, this type of impurities causes characteristic emission bands under x-ray or uv light excitation at low temperatures.[4,5] For example, KBr containing Na^+ ions shows the 2.90-eV emission band together with singlet (4.42 eV) and triplet (2.27 eV) emissions. Nakai *et al.*[5] have proposed that the emission should have the origin in the $(V_{KA}+e^-)^*$ system (* denotes the excited state), but the clear identification has not been done yet. We have identified the origin of the 2.90-eV emission band to be radiative decay of the $(V_{KA}+e^-)^*$, i.e., the exciton trapped by a nearest-neighbor Na^+ ion. This means that the impurity-ion affects the relaxation of the hot exciton[6] to cause other products apart from "normal" relaxed exciton and lattice defects.

It is generally accepted that color-center formation is taking place during the relaxation of the exciton. One should, therefore, reconsider the role of the monovalent cation impurity for defect-formation process from a more general approach involving not only interaction process of created interstitials, but also dissociation of an exciton. From such a point of view, we studied defect formation of KBr:Na system at 6 K, paying main attention to the correlation between colorability and luminescence by x-ray irradiation. Results obtained in this study have revealed that the Na^+ impurity-ion affects defect formation at low temperature to suppress the colorability, and that the suppression is probably responsible to the selective interaction of exciton state which leads to the defect formation with a Na^+ ion to form the $(V_{KA}+e^-)^*$, and the 2.90-eV emission.

II. EXPERIMENTALS

Doped crystals used in this study were grown in dry nitrogen atmosphere by the Kyropoulos method from KBr melts to which various amounts of NaBr were added. Crystals doped with KNO_2 were also used. The concentration of Na^+ impurity ion (C_{Na}) was determined by the semiquantitative spectrographic analysis with ±10% error. It was found that most specimens used in this study contained Na^+ ion up to 0.61 mol%. Within such an extent of impurity concentration, the number of impurity pairs may be so small, assuming random distribution of impurity ions, that we need not consider any effects of pairs. Specimens with thickness of 0.55 ± 0.02 mm were placed in a cryostat cooled by thermal conduction, and were irradiated by x rays generated with a Toshiba x-ray tube operated at 50 kV 40 mA through a KBr filter with a thickness of 0.2 mm to promote uniform coloration of the crystal. Temperature was calibrated by Au:Co-Cu and/or Au:Fe-Chromel thermocouples and by Allen-Bradley carbon resistor. Optical absorption was measured by a Shimazu-SV50A spectrophotometer. EPR was measured by a JEOL-JM-PE-3. A xenon ark lamp (Ushio UXL-500D in UL-501C) with appropriate filters was used as an exciting light source. Luminescence was detected by a liquid-nitrogen-cooled HTV R292 photomultiplier which was placed behind the exit slit of a grating monochromator. All emission spectra were corrected for monochromator dispersion and photomultiplier response.

III. EXPERIMENTAL RESULTS

A. Effect of Na^+ ion on colorability and luminescence

Figure 1 shows the radiation-induced absorption spectra of KBr containing Na^+ ion of different con-

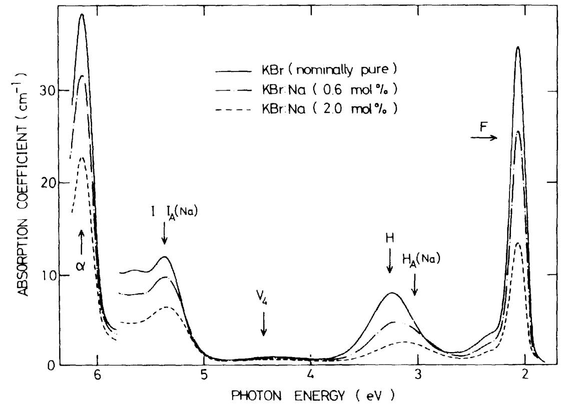

FIG. 1. Optical-absorption spectra induced by the 30-min x-ray irradiation at 6 K. The irradiation time was shortened to 8 min for measurements of the α band.

centrations. The heights of both F and H bands decrease with increasing C_{Na}. In the H-band region, the shift of peak position toward low-energy side is noticeable. The heights of α band and of the band due to the interstitial bromine ion (I and I_A bands) also decrease. The Na$^+$ ion, which enhances the formation of F and α centers at LNT, suppresses the colorability at low temperature where primary interstitials are stable.

Figure 2 shows the emission spectra of KBr crystals excited by x rays at 6 K. The impurity causes the characteristic emission band situated at 2.90 eV besides intrinsic emission bands. The 2.90-eV emission band grows with increasing C_{Na}, whereas the singlet and triplet emission bands do not change the intensity.

In order to obtain the correlation between the formation yields of F and α centers and the luminescence intensity, measurements were made of the changes of both quantities as a function of the Na$^+$ concentration. The results are shown in Fig. 3. One can see that the yields of both F and α centers decrease linearly with increasing C_{Na}, though the rates are not equal. The intensity of 2.90-eV band increases in proportion to C_{Na}, within the present range of the impurity concentration. One could notice the following two characteristic features; the complementary behavior between the decrease of colorability and the enhancement of intensity of the 2.90-eV emission band, and the constancy of the intensities of singlet and triplet emissions irrespective of the Na$^+$ concentration. Therefore, it is clear that the existence of the 2.90-eV emission band plays an important role in the suppression of the colorability at 6 K.

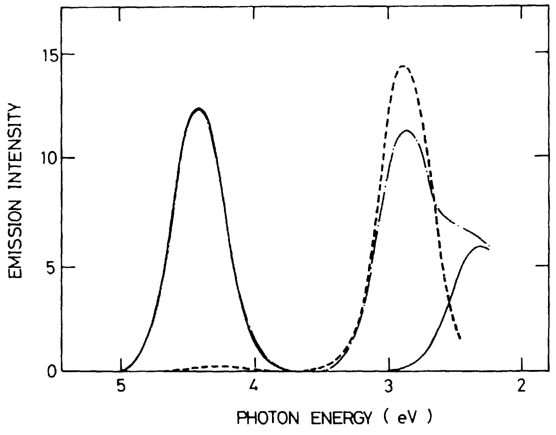

FIG. 2. Emission spectra of KBr crystals at 6 K. The solid line and the dash-dot line are the spectra of the nominally pure and of KBr:Na(0.61 mol %), respectively, which were generated by the x-ray excitation. The broken line is the spectrum introduced by the F-light illumination at 6 K of KBr:NO$_2$:Na which was previously annealed at 170 K after x-ray irradiation at LNT.

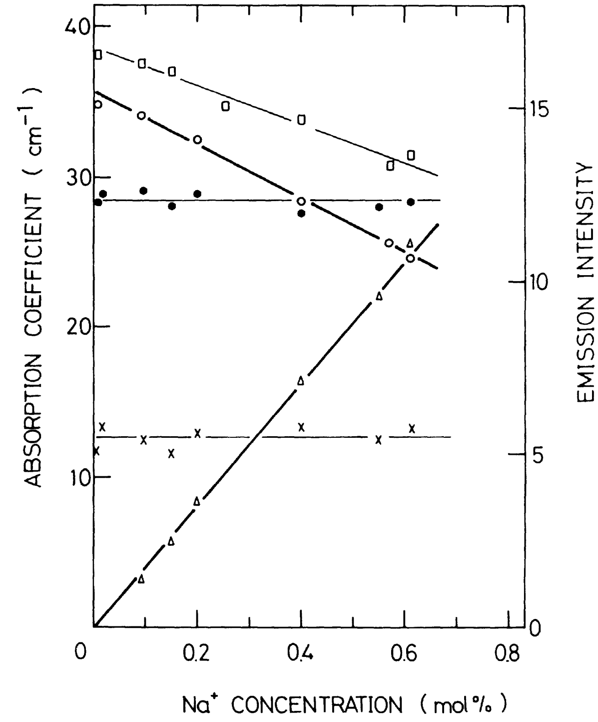

FIG. 3. Na$^+$ concentration dependence of the yields of the F center (○) and α center, and (b) of the intensities of singlet (●), triplet (×), and 2.90-eV (△) emissions, respectively.

B. Origin of 2.90-eV emission band

It is important to make clear the origin of the 2.90-eV emission, for further understanding of the mechanism of the suppression of the F-center formation by the Na$^+$ ion.

In order to check the Nakai's model,[5] it may be decisive to measure directly the emission spec-

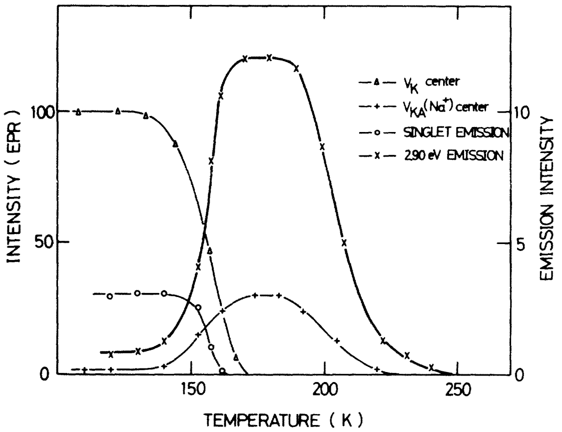

FIG. 4. Annealing curves of V_K and V_{KA} centers in KBr:NO_2 and in KBr:NO_2:Na crystals, respectively. The relative intensities of the centers are given in arbitrary units. The figure also shows the annealing temperature dependence of intensities of singlet and 2.90-eV emission bands in a KBr:NO_2:Na crystal, induced by the release of electron at LNT.

trum caused by the recombination of a V_{KA} center and an electron. Figure 4 shows the result of isochronal pulse annealing experiments on the EPR signal for V_K and V_{KA} (Na⁺) centers in KBr doped with NO_2^- and/or Na⁺. Samples were irradiated by Co-60 γ rays at LNT. EPR was measured at 80 K after warming an irradiated sample at a given temperature for 5.0 min. It is seen that the V_K center decays thermally around 155 K and that the V_{KA} (Na⁺) center, which grows as the V_K center decays, annihilates at 200 K. By conducting a proper treatment based on these results, we can obtain a sample which contains V_{KA} centers and F centers, but no V_K centers. The broken line in Fig. 2 is the emission spectrum introduced by F-light illumination at 6 K of KBr:NO_2:Na, which was previously annealed at 170 K after x-ray irradiation at LNT. It is clear from Fig. 4 that such a sample does not contain V_K centers. The spectrum consists of the main peak situated at 2.90 eV, accompanied by a very weak band at 4.25 eV.[7] In Fig. 2, the 2.90-eV band for this sample is compared with that generated by the x-ray excitation of KBr:Na crystals at the same temperature, and it is seen that these are essentially the same.

Further support for the assignment that the 2.90-eV emission is caused by $(V_{KA}+e^-)^*$ is obtained from the following experiments. In Fig. 4, the change of the intensity of 2.90-eV emission band which was introduced by the F-light illumination at LNT is also shown. In this experiment, the sample was first irradiated with x rays at LNT, then the sample was annealed at a given temperature for 5.0 min and cooled down to LNT, and immediately the luminescence under F-light illumination was measured. The intensity of the 2.90-eV emission increases between 150 and 160 K where the V_K center (and the singlet emission) diminishes, and decreases between 190 and 200 K with thermal decay of the V_{KA} center. Since the luminescence is measured at LNT, the intensity of the emission is proportional to the number of luminescence centers. Since the F center is hardly bleached by F-light illumination after thermal treatment, the number of released electrons may be substantially identical in each measurement. Thus the main cause of the change in the number of luminescence center is due to the change of the number of hole centers, the V_K or V_{KA} (Na⁺) centers.

The results above described lead us to the conclusion that the 2.90-eV emission has the origin in the radiative decay of the $(V_{KA}+e^-)^*$ system, or the exciton trapped by a nearest-neighbor Na⁺ ion in KBr, as proposed by Nakai *et al.*[5] It is interesting to note that the emission spectrum of the $(V_{KA}+e^-)^*$ consists of only one dominant band, whereas that due to the $(V_K+e^-)^*$ involves two bands.[8] Polarization experiments, which were carried out using a KBr:NO_2:Na containing arranged V_{KA} centers, revealed that the 2.90-eV band is π polarized. We will hereafter call, therefore, the 2.90-eV emission "π_A emission." Details of the electronic structure of the $(V_{KA}+e^-)^*$ will be discussed elsewhere, and here we only emphasize that the 2.90-eV emission has its origin in the $(V_{KA}+e^-)^*$ as discussed below.

IV. DISCUSSIONS

A. Secondary reactions of defects and suppression of colorability

In discussing the suppression of defect formation in the present case, we can consider the following sequence of defect-formation processes[9]; one is the dissociation of an exciton, and the other is the secondary reactions of created defects. First, we shall discuss several possible secondary reactions which might cause the suppression.

1. Interaction of replacement sequence with Na⁺ ion

Kondo *et al.*[10] have shown that the primary defect created by ionizing radiation is a pair of an F center and an H center. Dynamic behaviors of the energetic H center in alkali halides have been extensively studied by Saidoh, Itoh, and their coworkers. At temperatures as low as 6 K the thermal migration of the H center is not active,[11] and the main mode of motions may be adiabatic replacement sequence. Saidoh *et al.*[12,13] have shown that the replacement sequence attractively interacts with a Na⁺ ion to form an H_A center. Therefore, the Na⁺ ion may not act for the replacement sequence as does the I^- ion in KBr, which is considered to reflect back the moving interstitial atom as shown by Hirai.[14] Thus, the interaction of the replacement sequence with Na^+ ions may not be responsible for the suppression of the F-center formation. Kondo *et al.*[10] have also shown, from their study by electron pulse irradiation, that only $\frac{1}{50}$ of the initial F centers remains stable, and they attributed the bleaching to the recombination of a pair with short distance. It may be, therefore, also impossible to attribute the suppression of the colorability by the Na^+ ion to this transient bleaching effect, on the basis of the results of attractive interaction between the H center and a Na^+ ion.

2. *Conversion from the neutral Frenkel pair into charged pair*

Next, it is necessary to consider the conversion reaction of a F-H pair into an I-α pair: Such a reaction could exist, since the primary product is shown to be the former, though the details of the reaction are not known. One possible type of such reactions may be capture of an electron from the F center by the H and/or H_A center during irradiation.[15] The ratio of the formation yield of the H_A center to that of the H center increases with increasing C_{Na}, since the probability of finding a Na^+ ion along the interstitial collision sequence increases. This is, probably, the cause of the shift of peak position of the H-band region shown in Fig. 1.[12,13] The conversion reaction can be a cause of the decrease of the yield of the F center only when the $H_A(Na^+)$ center captures an electron more effectively than the H center: Effective conversion of the pair in the form of F–H_A center might result in the further decrease of the F center corresponding to the increase of C_{Na}. But this is impossible: (i) Saidoh and Itoh[16] have shown that the $H_A(Na^+)$ center cannot be converted into $I_A(Na^+)$ center by capturing an electron from the F center, although the $H_A(Li^+)$ center can, and (ii), in fact, the yield of the I- and α-center production also decreases with increasing C_{Na} as shown in Figs. 1 and 3. Thus the conversion reaction also cannot be the main cause of the decrease of the yield of the F center.

3. *Optical bleaching by π_A emission*

Another possibility should also be considered, which is the optical bleaching effects by the luminescence during irradiation.[17,18] The intensity of the π_A emission increases with increasing C_{Na}, and the π_A emission band appreciably overlaps with the H and H_A absorption bands, as shown in Figs. 1 and 2. The decrease of the yield of defect formation by Na^+ ion might be due to the reabsorption of the emission by H and/or H_A centers, which results in the excitation of the centers and the succeeding recombination with F centers. This optical bleaching effect can be, however, also disregarded in view of the following experimental results: An optical illumination with the similar band shape and intensity as that of the π_A emission during or after x-ray irradiation was made on a nominally pure KBr. The illumination caused little change in the yield of each color center. The light even with the intensity, two orders of magnitude larger than that of the π_A emission of KBr:Na (0.61 mol%), bleached at most a few percent of the H and F centers produced by irradiation, and no appreciable decrease was observed in the heights of α and I bands. On the contrary, the suppression of the colorability by Na^+ impurity correlated with the considerable decrease in the yield of the α-center production as shown in Fig. 1. Therefore, the main origin of the suppression in the present case cannot be ascribed to the optical bleaching by the π_A emission.

Thus, we can conclude that the secondary processes of the created color centers are not responsible for the suppression of the F-center formation. Thus our attention should be focused on the dissociation process of an exciton, or relaxation of the hot exciton.

B. Relaxation of exciton in KBr : Na system

As shown in Fig. 3, the suppression of defect formation strongly correlates with the formation of the $(V_{KA}+e^-)^*$ state. Two types of reactions may be possible for the formation of the $(V_{KA}+e^-)^*$; (i) one is the interaction between an exciton and a Na^+ ion, and (ii) the other is the interaction of a hole with a Na^+ ion followed by the subsequent electron trapping. If the $(V_{KA}+e^-)^*$ is formed mainly through the latter reaction, the intensity of the intrinsic luminescence should be also suppressed corresponding to the increase of the π_A emission intensity, since the increment of the formation probability of the V_{KA} center with increasing C_{Na} may result in the decrease of the number of V_K center to form the exciton state. Kondo and Hirai[19] have shown that a small amount of Ag impurity suppresses the formation of H and F centers in KCl at 10 K. They attributed the suppression to the trapping of an electron by the impurity, which may result in the decrease of the probability of electron-hole recombination to form the exciton state. In such a case, intensity of intrinsic luminescence should also be suppressed. As shown in Fig. 3, the Na^+ ion has no effect on the intrinsic luminescence, at least within the present range of the impurity concentration. This result rules out the possibility that the formation of the $(V_{KA}+e^-)^*$ would take place mainly through the interaction of a hole with a Na^+ ion. The present results strongly indicate that the Na^+ ion interacts "selectively" with the state of the exciton which is responsible for the F-center formation.

In the earliest excitonic-formation mechanism model,[20,21] the same state is responsible for the defect formation and intrinsic luminescence. These models cannot explain the present results. According to the very recent model proposed by Toyozawa,[22] the adiabatic instability at the $2p_z$ state of the electron trapped by the V_K center is responsible for the F-center formation and the 1s state for the intrinsic luminescence. And the origin of the occurrence of two channels (defect formation and intrinsic luminescence) are whether the relaxation follows the adiabatic potential or the transition to the 1s state occurs. Apparently this model cannot explain the result that only the exciton state which results in the defect formation is affected by Na^+ ions.

Karasawa and Hirai[23] have measured the yield of the F center and the intrinsic luminescence of KCl and KBr below 4 K, and found that the yield of the F center decreases with decreasing temperature with an activation energy of a few meV, while the intensity of intrinsic luminescence is almost constant. Their results that the behavior of the F-center formation and of the intrinsic luminescence are independent of each other may suggest that the exciton state responsible for each phenomenon is essentially different. The results and discussions above described lead us to suggest the following model of the relaxation of an exciton: The exciton splits, with a fixed ratio which might depend only on the salt, into different two states: one is responsible for defect formation, and the other for intrinsic luminescence, and a "turning point" between two channels lies just after a hot exciton is formed. In the light of this model, the features of the present results are well described in the following reaction: After the splitting, the exciton state which leads to defect formation interacts selectively with a Na^+ ion to form the $(V_{KA}+e^-)^*$ which release energy in terms of the π_A emission.

Here, it is worth considering the model proposed by Itoh and Saidoh.[9] In their model, the cause of the splitting into two channels lies in the relaxation of the hole in an exciton; the exciton with a V_K center in a Π_g state (Π_g exciton) is responsible for the F-center formation, and that in a Σ_u state (Σ_u exciton) for the intrinsic luminescence, respectively. The relaxation of the hole into Π_g or Σ_u state is considered, presumably, to take place with a given ratio. Since the V_K center in a Π_g state is energetically higher than that in a Σ_u, the Σ_u exciton may be more deeply self-trapped. Thus the perturbation of the Π_g exciton by a Na^+ ion may be more serious, and the Π_g exciton would be selectively attracted by the Na^+ ion. This model can also explain the characteristic features of the relaxation of an exciton as revealed above. In their model, however, one question remains unsolved. Kellor and Patten[24] have shown that the H center can be formed by the recombination of an electron with the V_K center in KCl crystal. In their study, the V_K center must be in the state of Σ_u. This result is not consistent with Itoh's model. Thus, more detailed experimental and theoretical studies are necessary for clear understanding of the defect-formation mechanism in alkali halides.

ACKNOWLEDGMENTS

The authors acknowledge Professor N. Itoh and Dr. M. Saidoh for critical discussions and useful suggestions during this work, and acknowledge Professor S. Imoto for his kind reading of the manuscript. They thank Dr. Y. Itoh of the National University's Laboratory for the common use of JEARI facilities for EPR measurements of the samples. Thanks are also given to Mr. M. Fujiwara of our laboratory and Dr. J. Yamamoto, Mr. Y. Tsuji, Mr. Y. Wakisaka, and Mr. H. Makiyama of Low Temperature Center of Osaka University for their valuable help in low-temperature experiments using liquid helium.

---

[1] N. Itoh, Cryst. Lattice Defects 3, 115 (1972).

[2] C. T. Delbecq, E. Hutchinson, D. Schoemaker, E. U. Yasaitis, and P. H. Yuster, Phys. Rev. 187, 1103 (1969); and F. W. Patten and F. J. Keller, *ibid.* 187, 1120 (1969).

[3] G. Giuliani, Solid State Commun. 7, 79 (1969); and Phys. Rev. B 2, 464 (1970).

[4] Ya. A. Valbis, Opt. Spectrosc. 21, 106 (1966).

[5] Y. Nakai, T. Toyoda, M. Itoh, and K. Nakamura, Proceedings of the International Conference on Color Centers in Ionic Crystals, Sendai, 1974, Abstract No. C20 (unpublished).

[6] M. Hirai, Oyo Buturi 41, 666 (1972).

[7] As shown in Fig. 2, the 4.25-eV emission band can be observed when the sample involving the V_{KA} center is illuminated with the F light. However, the weak intensity of the band prevented us for knowing the detailed properties of this band. Further description about the emission band is not given here.

[8] M. N. Kabler, Phys. Rev. 136, A1296 (1964).

[9] N. Itoh and M. Saidoh, J. Phys. (Paris) C 34-9, 101 (1973).

[10] Y. Kondo, M. Hirai and M. Ueta, J. Phys. Soc. Jpn. 33, 151 (1972).

[11] E. Sonder and M. Sibley, *Point Defects in Solids*, edited by J. H. Crawford and L. M. Slifkin (Plenum, New York, 1972), Vol. 1, p. 201.

[12] N. Itoh and M. Saidoh, Phys. Status Solidi 33, 649 (1969).

[13] M. Saidoh, J. Hoshi, and N. Itoh, Solid State Commun.

13, 431 (1973).

[14]M. Hirai, Solid State Commun. 10, 493 (1972).

[15]R. Smoluchowski, O. W. Lazareth, R. D. Hatcher, and G. J. Dienes, Phys. Rev. Lett. 27, 1288 (1971).

[16]M. Saidoh and N. Itoh, J. Phys. Soc. Jpn. 27, 1551 (1969).

[17]E. Sonder and W. A. Sibley, Phys. Rev. 129, 1578 (1963).

[18]M. N. Kabler, International Symposium on Color Centers in Solids, Urbana, Illinois, 1965, Abstract No. 100 (unpublished).

[19]Y. Kondo and M. Hirai, J. Phys. Soc. Jpn. 30, 1765 (1971).

[20]H. N. Hersch, Phys. Rev. 148, 928 (1966).

[21]D. Pooley, Proc. Phys. Soc. Lond. 87, 245, (1966); 87, 257 (1966).

[22]Y. Toyozawa, Proceedings of the International Conference on Color Centers in Ionic Crystals, Sendai, 1974, Abstract No. D43 (unpublished).

[23]T. Karasawa and M. Hirai, Proceedings of the International Conference on Color Centers in Ionic Crystals, Sendai, 1974, Abstract No. 79 (unpublished).

[24]F. J. Keller and F. W. Patten, Solid State Commun. 7, 1603 (1969).