

## Study on Photo-luminescence from $O_2^-$ molecules in Alkalihalide Crystals

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(Received December 27, 1991)

### Abstract

Luminescence from  $O_2^-$  molecules introduced into several alkalihalide crystals has been studied by means of time resolved spectroscopy. Decay times of two different components of a double-structure phonon sideband are found to be the same at low temperatures. This fact indicates that both components are caused by the transitions from the same initial level. The intensity and decay time of the luminescence remain almost unchanged up to about 180 K, above which they show steep decrease with further increase in temperature. The temperature dependence of the luminescence is interpreted in terms of the competition between radiative decay and thermally activated non-radiative decay from the excited state  ${}^2\Pi_u$  of the  $O_2^-$  molecule. Obtained values of the activation energy are of the order of 200 meV. Radiative decay times are of the order of 100 ns for the  $O_2^-$  molecules in K- and Rb-halides, while they are 9 and 19 ns in NaCl and NaBr. Spectral profiles of the phonon sidebands, decay times and quantum yields of the luminescence in various host crystals are discussed in relation to the orientations of the  $O_2^-$  molecules in the crystals.

### §1. Introduction

It is well known that  $O_2^-$  molecules introduced into alkalihalide crystals show luminescence spectra which consist of a series of sharp zero-phonon lines accompanied by phonon sidebands at low temperatures.<sup>1)</sup> Electronic properties of the  $O_2^-$  molecules in various alkalihalides were studied in detail by Känzig and co-workers,<sup>2-5)</sup> by Rolfe and co-workers<sup>6-9)</sup> and by L. A. Rebane and co-workers<sup>10-12)</sup> in 1960's ~ 70's. They shows that 1) the  $O_2^-$  molecule substitutes a halogen ion in the host crystal and its molecular axis lies along a  $\langle 110 \rangle$  direction in the ground state  ${}^2\Pi_g$ .<sup>2,4)</sup> 2) *uv* absorption around 5 eV and sharp luminescence lines in the visible region are caused by the electronic transitions  ${}^2\Pi_g \rightleftharpoons {}^2\Pi_u$  in the molecule.<sup>4,6)</sup> 3) The transition dipole moment, which is parallel to the molecular axis, of the luminescence lies along a  $\langle 110 \rangle$  direction in KCl, RbCl, RbBr and RbI, while it lies along a  $\langle 111 \rangle$  direction in NaCl, KBr and KI.<sup>9)</sup> 4) In KBr, a small

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fraction of the  $O_2^-$  molecules lie along  $\langle 110 \rangle$  directions and those molecules are designated as "extra" ones.<sup>8,9)</sup> 5) Profiles of the phonon sidebands accompanying the zero-phonon lines are classified into two groups,<sup>7)</sup> one is the "single-structure sideband" observed for the  $O_2^-$  molecules in NaCl, NaBr KBr and KI, and the other the "double-structure sideband" observed in KCl, RbCl, RbBr and RbI. The sidebands of the former group have been studied in detail, while the origin of the latter is not understood unambiguously.

In 1980's new progress has been made in the study on dynamics of optically excited states of the  $O_2^-$  molecules in alkali halides by the application of short pulse laser technique. Schmid and co-workers<sup>13-15)</sup> discovered superfluorescence in KCl:  $O_2^-$  and attracted new attention.<sup>16,17)</sup> Teegarden and his co-workers observed laser action in KCl:  $O_2^-$ .<sup>18)</sup> They also investigated the vibrational relaxation of the excited states in KBr:  $O_2^-$  and RbI:  $O_2^-$  by the measurement of transient behavior of hot luminescence.<sup>19)</sup> It has been reported that the superfluorescence is detectable only below  $\sim 25$  K.<sup>14,15)</sup> Around 25 K, reorientation of the  $O_2^-$  molecule becomes rapid and turns into nearly free rotation.<sup>3)</sup> Schmid and co-workers suggested that the rapid rotation of the  $O_2^-$  molecule is one of the significant factors which repress the superfluorescence.

In this article, we give a brief review and comments on the preceding works and report some results of the study on excited states of the  $O_2^-$  molecules in various alkali halide crystals. We investigate firstly, in the present work, the origin of the double-structure phonon sidebands of the  $O_2^-$  luminescence by measuring the decay times of the two different components of the sidebands and give an interpretation consistent with the two different orientations of the  $O_2^-$  axes determined from the EPR<sup>4)</sup> and luminescence<sup>9)</sup> studies. Secondly, we investigate the mechanism of thermal quenching of the luminescence in various host crystals by the measurement of decay times and yields of the luminescence and discuss their dependence on the host crystals, particularly their difference in Na-halides and K- and Rb-halides. Preliminary results of the present work were reported at ICL'90 held in Lisbon.<sup>20)</sup>

## §2. Experiment

### 2.1 Sample preparation

Luminescence from the  $O_2^-$  molecules in eight alkali halide crystals, NaCl, NaBr, KCl, KBr, KI, RbCl, RbBr and RbI are investigated in the present work. Crystals containing the  $O_2^-$  molecules were prepared in the following ways: 1) Crystals of KCl:  $O_2^-$ , KBr:  $O_2^-$  and KI:  $O_2^-$  were grown by Kyropoulos method from melts doped with about 1 mole % of  $KO_2$  in an oxygen atmosphere. 2) Crystals of NaCl:  $O_2^-$  and NaBr:  $O_2^-$  were grown from melt doped with about 1 mole % of  $Na_2O_2$ . 3) The  $O_2^-$  molecules were introduced into RbCl, RbBr and RbI crystals by keeping pure crystal pieces of  $10 \times 10 \times 15$  mm<sup>3</sup> about 30°C below respective melting points in an oxygen stream for several hours. Care was taken to prevent the crystals from contamination with  $OH^-$  impurity. The dopants  $Na_2O_2$  and  $KO_2$  are very hygroscopic and had already contained some amount of moisture. Then the

crystals grown from melt contained a trace of  $OH^-$  molecules. Some effect of the contamination was observed on the luminescence in  $KI: O_2^-$  and  $RbI: O_2^-$ , but not in other crystals. The effect is described briefly in 3.4.

### 2.2 Measurement of luminescence spectra

Luminescence spectra were measured in the temperature range of 2 ~ 600 K using a Spex double monochromator and a photon counting system. Samples were excited with light from a 500 W high pressure mercury lamp passed through a *uv* glass filter (Toshiba UV-D33S) and a cell filled with aqua-solution of  $NiSO_4$ . This assembly gives the excitation light in the range of 280 ~ 350 nm. The luminescence was collected at a right angle to the excitation light and was led to the monochromator through a glass filter UV-39 which cut the light below 390 nm. For the measurement in the range of 2 ~ 150 K, an immersion-type liquid helium cryostat was used, while in 80 ~ 600 K range a conduction-type liquid nitrogen cryostat was used.

### 2.3 Decay time measurement

Decay times of the luminescence were measured in the following two ways: 1) For the measurement at low temperatures where the decay times are longer than ~ 30 ns, samples were excited with 248 nm light pulses from a KrF excimer laser. The luminescence was passed through the monochromator and was detected with a rapid response photomultiplier (Hamamatsu R 1294 U) and its decay was recorded with a digitizing oscilloscope. Width of the light pulse from the laser was about 20 ns. Measurements were carried out in 2 ~ 150 K range. 2) For the measurement at high temperatures where the decay time becomes shorter than ~ 30 ns and the intensity becomes weaker, samples were excited with light pulses of synchrotron radiation from UVSOR under the single-bunch-operation installed in Institute for Molecular Science at Okazaki and the luminescence decay was recorded using a time correlated single photon counting system. The pulse width was about 500 ps and a separation between pulses was 177.6 ns. Measurements were carried out in 80 ~ 600 K range.

### 2.4 Measurement of luminescence yield

Ratios of quantum yields of the luminescence in  $NaCl: O_2^-$ ,  $NaBr: O_2^-$  and  $KBr: O_2^-$  to that in  $KCl: O_2^-$  were obtained at 80 K. In this procedure, following measurements on each sample were made in the same configuration as those on  $KCl: O_2^-$ . 1) Absorbed intensity of the *uv* excitation light was measured. 2) Intensity of the undispersed light of luminescence radiated into a definite solid angle was measured at a right angle to the excitation light through a *uv* cut-off filter. Then, the ratio of the photon number emitted from each sample to that from  $KCl: O_2^-$  was derived by applying corrections for the spectral response of the detecting system and for the spectral distribution of the luminescence.

### §3. Results and Discussion

#### 3.1 Profiles of phonon sidebands and origin of double-structure sideband

As mentioned in §1, the luminescence spectra of the  $O_2^-$  molecules in alkali-halide crystals at low temperatures consist of a series of zero-phonon lines accompanied by phonon sidebands.<sup>1-7,8)</sup> Samples are classified into two groups according to the profiles of the phonon sidebands, the group (A) which shows the

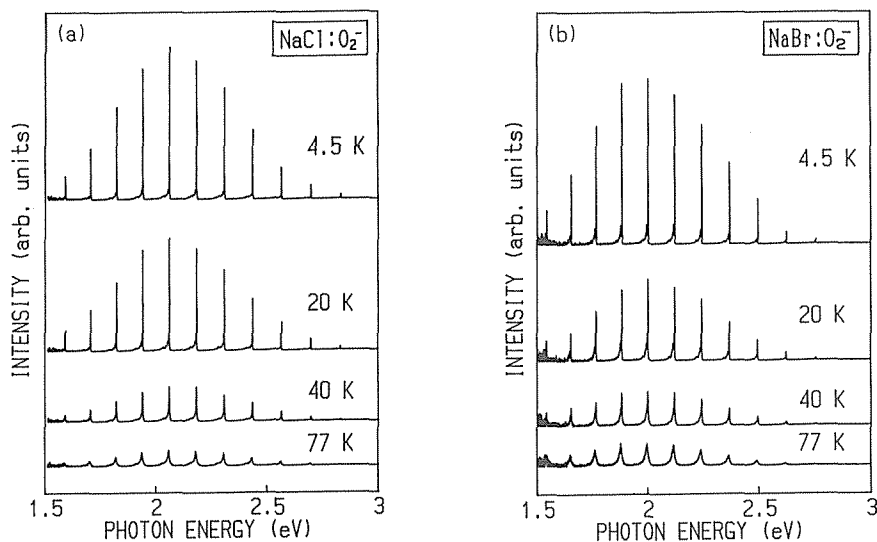


Fig. 1. Luminescence spectra of (a)  $NaCl:O_2^-$  and (b)  $NaBr:O_2^-$  at various temperatures. The spectra show "single-structure" phonon sidebands.

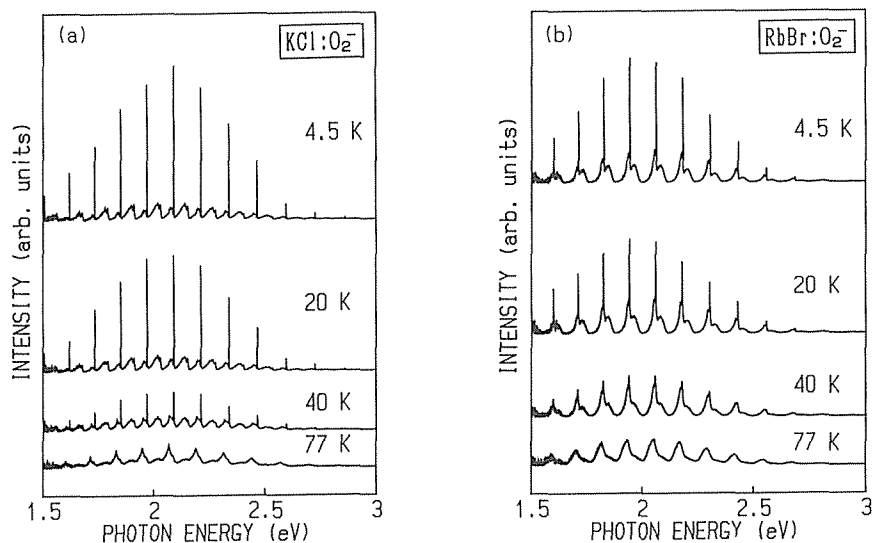


Fig. 2. Luminescence spectra of (a)  $KCl:O_2^-$  and (b)  $RbBr:O_2^-$  at various temperatures. The spectra show "double-structure" phonon sidebands.

“single-structure” sidebands and the group (B) the “double-structure” sidebands.  $NaCl:O_2^-$ ,  $NaBr:O_2^-$ ,  $KBr:O_2^-$  and  $KI:O_2^-$  belong to the former, while  $KCl:O_2^-$ ,  $RbCl:O_2^-$ ,  $RbBr:O_2^-$  and  $RbI:O_2^-$  belong to the latter. Typical luminescence spectra of two groups measured in the present experiment are shown in Figs. 1 and 2. Up to about 40 K, sharp zero-phonon lines are noticeable for each crystal. They become broad and weak with increase in temperature and merge into phonon sidebands above  $\sim 50$  K. Temperature dependence of the profiles of the zero-phonon lines and the phonon sidebands of  $NaCl:O_2^-$  and  $KCl:O_2^-$  are shown in Fig. 3 on an expanded scale. As will be discussed in 3.3 the luminescence intensity of each crystal integrated over its spectrum remains almost unchanged up to about 180 K irrespective of the drastic change in the spectral profile.

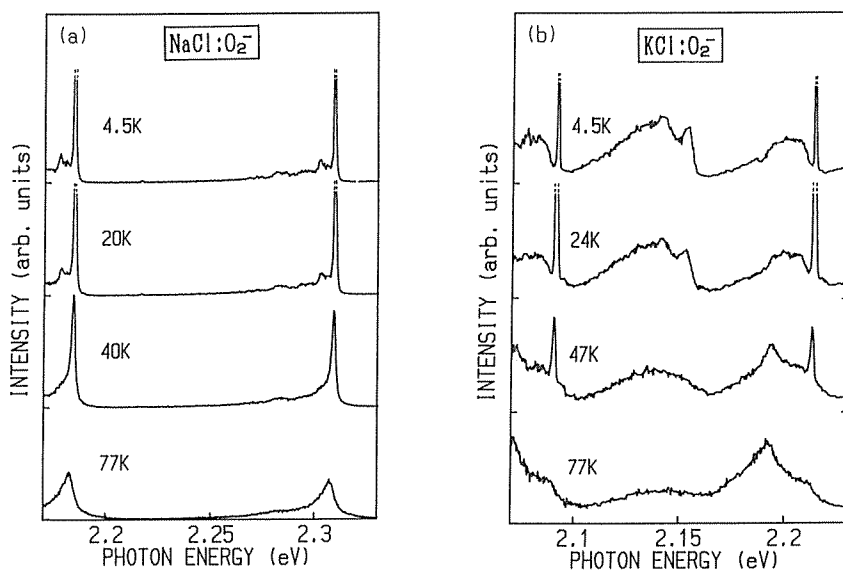


Fig. 3. Temperature dependence of the profiles of zero-phonon lines and phonon sidebands in (a)  $NaCl:O_2^-$  and (b)  $KCl:O_2^-$ .

As reported by Ikezawa and Rolfe,<sup>9)</sup> the axes of  $O_2^-$  molecules lie along  $\langle 110 \rangle$  directions in the crystals of the group (B), and lie along  $\langle 111 \rangle$  directions in the group (A). They interpreted the two types of the phonon sidebands as follows: The  $O_2^-$  molecules in the crystals of the group (B) are situated in the crystal field of  $D_{2h}$  symmetry. The doubly degenerate ground and excited states of the  $O_2^-$  molecule split in the field as follows;

$$\text{the ground state : } ^2\Pi_g \rightarrow ^2B_{2g} + ^2B_{3g},$$

$$\text{the excited state : } ^2\Pi_u \rightarrow ^2B_{2u} + ^2B_{3u}.$$

From the EPR measurements,<sup>2,4)</sup> it was concluded that the  $O_2^-$  molecule in the ground state is situated in the  $D_{2h}$  crystal field in any host crystal. The  $^2B_{3g}$  level is located below  $^2B_{2g}$  in K- and Rb-halides, while  $^2B_{2g}$  is located below  $^2B_{3g}$  in Na-

halides. Rolfe *et al.*<sup>8)</sup> speculated that each component of the double-structure sideband is caused by a transition from the same initial level, maybe from the lowest vibrational level of the  ${}^2B_{2u}$  state. The level scheme and the transitions are shown on the left part of Fig. 4 along with schematic profiles of the sidebands. The allowed transition  ${}^2B_{2u} \rightarrow {}^2B_{3g}$  gives a series of strong zero-phonon lines accompanied by usual phonon sidebands, while the forbidden (or weakly allowed) transition  ${}^2B_{2u} \rightarrow {}^2B_{2g}$  gives another series of phonon sidebands without zero-phonon lines.\* They also discussed a variety of the double-structure sidebands, in other words, the difference among those of  $\text{KCl}:\text{O}_2^-$ ,  $\text{RbCl}:\text{O}_2^-$ ,  $\text{RbBr}:\text{O}_2^-$  and  $\text{RbI}:\text{O}_2^-$ , and ascribed it to the difference in the magnitude of the crystal field splitting of the ground state  ${}^2\Pi_g$ .<sup>8)</sup> The  $\text{O}_2^-$  molecules in the crystals of the group (A) are located in the crystal field of  $D_{3d}$  symmetry and the single-structure sidebands observed in those crystals are simply interpreted by the level scheme and transitions shown on the right part of Fig. 4.

In order to confirm the above interpretation and to investigate the origin of the

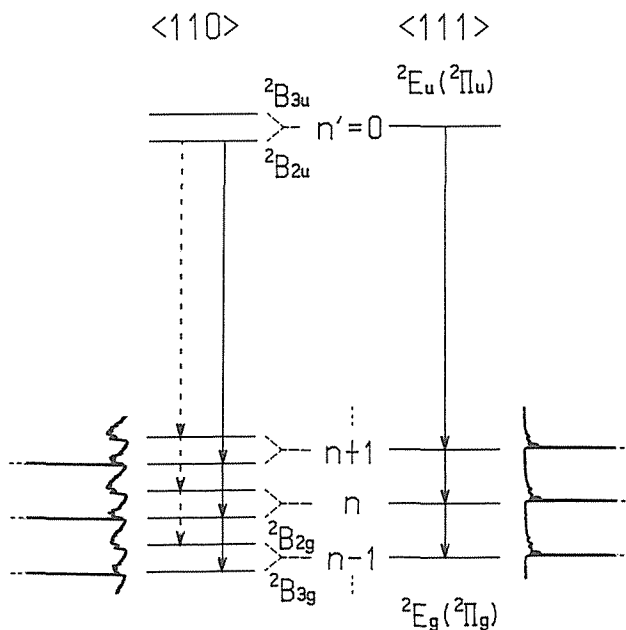


Fig. 4. Level scheme and optical transitions of  $\text{O}_2^-$  molecules in alkali halide crystals with their axes along  $\langle 110 \rangle$  directions (on the right) and along  $\langle 111 \rangle$  directions (on the left).

\* In  $\text{KCl}:\text{O}_2^-$ , weak and broad lines associate to the forbidden transitions are detectable. Rolfe *et al.*<sup>8)</sup> speculated that the vibrational relaxation of the  $\text{O}_2^-$  molecule in the  ${}^2B_{2g}$  state is very rapid and the weakly allowed zero-phonon lines become broad and weak in KCl. They also speculated that the relaxation may be more rapid in Rb-halides and the weakly allowed zero-phonon lines are much broader and merge into the sidebands of which profiles are more smooth and round. The speculation, however, seems less persuasive, because the vibrational relaxation in the ground state is not so rapid, maybe slower than 50 ps.<sup>15)</sup>

double-structure sideband, we have measured the decay times of the two different components of the sideband in each crystal. Typical results are shown in Figs. 5 and 6 for  $KCl:O_2^-$  and  $RbBr:O_2^-$ , respectively. The decay time measured at the position (a) corresponds to that of the sideband associated to the zero-phonon line, while that at (b) to the sideband not associated to the zero-phonon line. Both components (a) and (b) of the sideband show the same decay time each other at 4.5 K, as seen in the figures. They show the same decay time too at 40 K where the rotation of the  $O_2^-$  molecule becomes rapid and the zero-phonon line becomes broader and weaker. These results support the speculation that the double-structure sideband is caused by the transitions from the same initial level, that is the lowest vibrational level of the  ${}^2B_{2u}$  state, unless the magnitudes of the decay times at (a) and (b) coincide accidentally. Since the symmetry of the transition dipole moment is  $B_{1u}$ , the component (a) of the double-structure sideband is interpreted as the sideband associated with the allowed transition  ${}^2B_{2u} \rightarrow {}^2B_{3g}$  and reflects the density of states of  $A_g$  mode phonons originating from  $A_{1g}$  and  $E_g$  modes in  $O_h$  symmetry, while the component (b) with the forbidden transition  ${}^2B_{2u} \rightarrow {}^2B_{2g}$  reflecting the density of states of  $B_{1g}$  mode phonons originating from  $T_{1g}$  and  $T_{2g}$  modes in  $O_h$  symmetry.

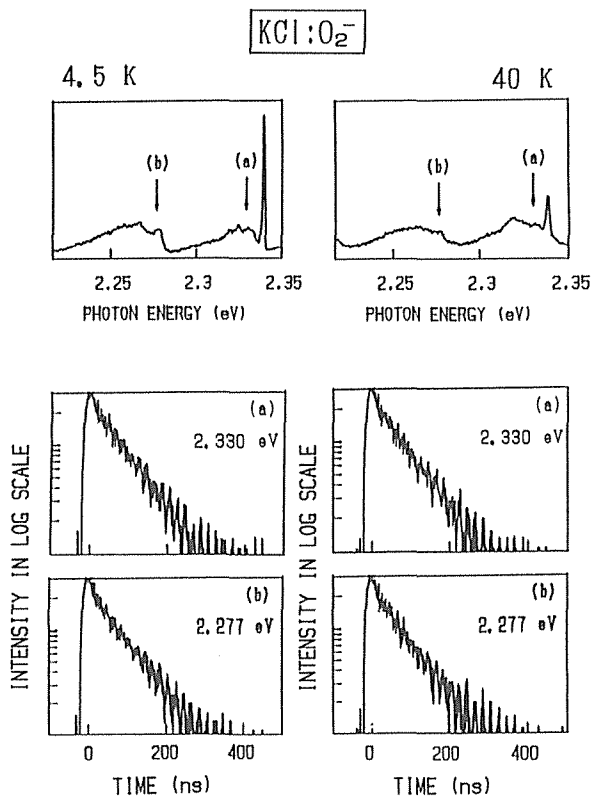


Fig. 5. Time response of the double-structure phonon sideband of the  $O_2^-$  luminescence in  $KCl:O_2^-$  at 4.5 and 40K; (a) the component associated with the zero-phonon line, (b) the component not associated with the zero-phonon line.

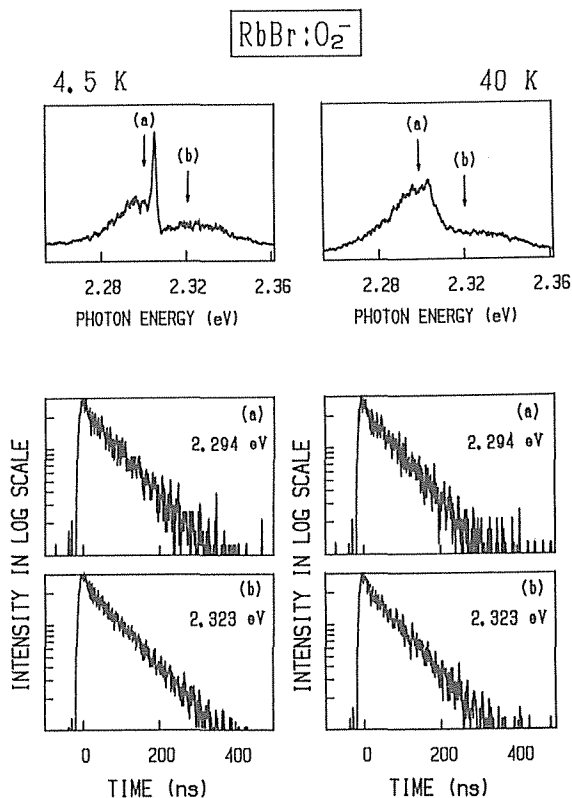


Fig. 6. Time response of the double-structure phonon sideband of the  $O_2^-$  luminescence in  $RbBr:O_2^-$  at 4.5 and 40 K; (a) the component associated with the zero-phonon line, (b) the component not associated with the zero-phonon line.

### 3.2 Reorientation of the molecular axis during an optical cycle

As mentioned in 3.1, Känzig *et al.* showed in their EPR study that the  $O_2^-$  molecules lie along  $\langle 110 \rangle$  directions in all host crystals.<sup>2,4)</sup> On the other hand, Ikezawa and Rolfe<sup>9)</sup> concluded that the  $O_2^-$  molecules lie along  $\langle 110 \rangle$  directions in KCl, RbCl, RbBr and RbI and show the double-structure sidebands, while they lie along  $\langle 111 \rangle$  directions in NaCl, KBr and KI and show the single-structure sidebands. Based on the discussion in the previous section, the latter conclusion is extended to  $NaBr:O_2^-$  which shows the clear single-structure sidebands. At first sight, the results of EPR and luminescence studies seem to conflict each other for NaCl, KBr, KI and NaBr. The discrepancy between them will be resolved by the following arguments: 1) In NaCl, NaBr, KBr and KI, the  $O_2^-$  axes lie along  $\langle 110 \rangle$  directions in the ground state, which is  ${}^2B_{2g}$  in NaCl and NaBr and is  ${}^2B_{3g}$  in KBr and KI. 2) By the absorption of *uv* light, the  $O_2^-$  molecules are excited into the  ${}^2B_{3u}$  state in the former and into the  ${}^2B_{2u}$  state in the latter, respectively. 3) During the vibrational relaxation in the excited state and/or at the bottom of the excited state, the  $O_2^-$  molecules turn their axes to  $\langle 111 \rangle$  directions in the crystals. The site



symmetry of the excited  $O_2^-$  molecule changes from  $D_{2h}$  to  $D_{3d}$ , in which the crystal field splitting is removed and the excited state of the  $O_2^-$  molecule changes to  ${}^2E_u$ . 4) The excited molecules make transitions from the lowest vibrational level of  ${}^2E_u$  to the vibrational levels of the ground state  ${}^2E_g$  keeping  $D_{3d}$  symmetry and give rise to a series of the zero-phonon lines accompanied by the single-structure phonon sidebands. 5) After the transition to the ground state, the  $O_2^-$  molecules reorient from  $\langle 111 \rangle$  to  $\langle 110 \rangle$  directions during their vibrational relaxation in the ground state and an optical cycle is closed. Schematic illustration of the reorientation during the optical cycle is shown in Fig. 7.

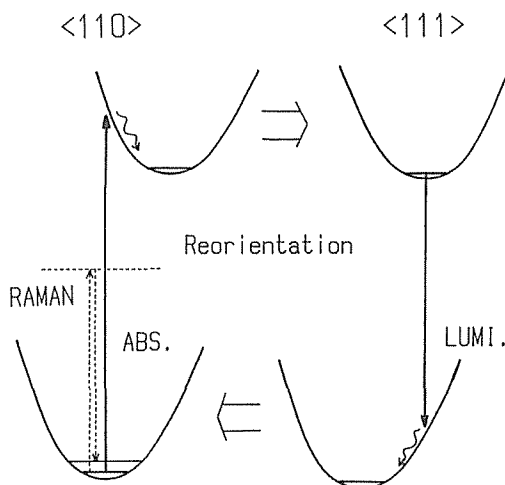


Fig. 7. Schematic illustration of the reorientation of the  $O_2^-$  molecule in the crystals of group (A) during an optical cycle.

The recent study on polarized Raman spectra of the  $O_2^-$  molecules in KCl, KBr and NaCl by Schoemaker and co-workers<sup>21)</sup> has shown that the site symmetry of the  $O_2^-$  molecule is  $D_{2h}$  in KCl and KBr, in agreement with the result of EPR study, while the site symmetry is  $D_{3d}$  or  $D_{2h}$  in NaCl. According to them, the result for NaCl is probably caused by the accidental degeneracy resulting from their "Behavior-Type analysis".<sup>22)</sup> Then, we can not deny the site symmetry of the  $O_2^-$  molecule in NaCl to be  $D_{2h}$ . Since non-resonant Raman scattering is an optical process *via* intermediate states, which are not really excited, the  $O_2^-$  molecules do not change their orientation during the Raman scattering process. Hence, the Raman scattering study gives the site symmetry of the  $O_2^-$  molecule in the ground state, that is,  $D_{2h}$  in the present case. The fact that the site symmetry of the  $O_2^-$  molecule in KBr, and probably in NaCl, determined by the Raman scattering is  $D_{2h}$ , in contrast to  $D_{3d}$  determined by the luminescence study,<sup>9)</sup> will be another support for the reorientation of the  $O_2^-$  molecules during the relaxation in the excited state. The optical transition corresponding to the Raman scattering is also shown in Fig. 7 by broken arrows.

### 3.3 Thermal quenching of the luminescence

In 2.1, it is noted that the luminescence intensity integrated over the spectrum remains unchanged up to about 180 K irrespective of the remarkable change in its spectral profile. It shows steep decrease for further increase in temperature. Time response of the luminescence in any crystal studied here showed a single exponential decay,  $I(t) \propto I(0) \cdot \exp[-t/\tau(T)]$ . The decay time  $\tau(T)$  shows a similar temperature dependence as the intensity does. Typical examples of the temperature dependence are shown in Fig. 8(a) ~ (d) for  $\text{NaCl}:\text{O}_2^-$ ,  $\text{NaBr}:\text{O}_2^-$ ,  $\text{KCl}:\text{O}_2^-$  and  $\text{RbBr}:\text{O}_2^-$ , respectively. This type of temperature dependence is interpreted in terms of the competition between a radiative decay and a thermally activated non-radiative decay

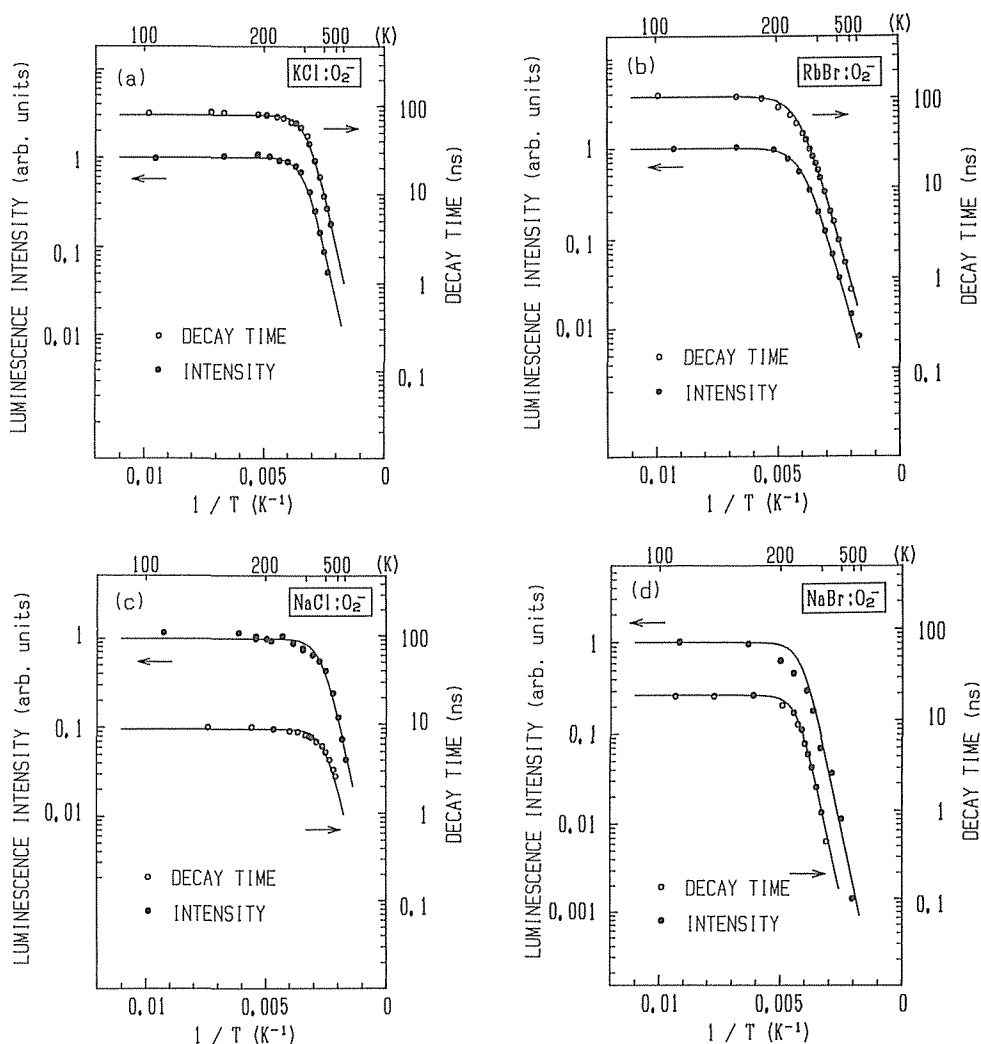


Fig. 8. Temperature dependence of the intensities (●) and decay times (○) of the  $\text{O}_2^-$  luminescence in (a) KCl, (b) RbBr, (c) NaCl, and (d) NaBr. Solid curves show the calculated ones fitted to the observed points using the equations (1) and (2) in the text, respectively.

from the same excited state. Schematic illustration for the decay processes is shown in Fig. 9 by referring to the adiabatic potential curves calculated for the free  $O_2^-$

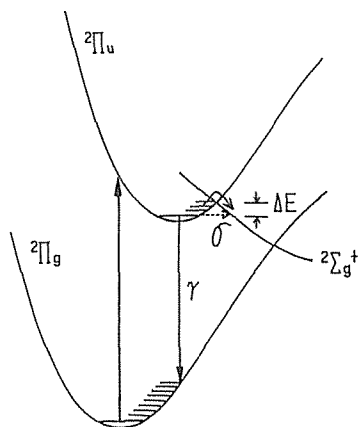


Fig. 9. Schematic illustration of the adiabatic potential curves of the  $O_2^-$  molecule, showing the transitions due to the radiative, non-radiative and tunneling processes.

molecule.<sup>23)</sup> The intensity and decay time of the luminescence are described as a function of  $T$  by the following formulae,

$$\tau(T)^{-1} = \tau_R^{-1} + \nu \exp(-\Delta E/kT) \dots \dots (1)$$

$$I(T)/I(0) = \tau_R^{-1} / \tau(T)^{-1}, \quad \dots \dots (2)$$

where  $\tau_R$  is a radiative decay time,  $\Delta E$  is an activation energy for the non-radiative decay process and  $\nu$  is a frequency factor. Solid curves in Fig. 8 show the calculated temperature dependence. They agree well with the observed points. Values of  $\tau_R$ ,  $\nu$  and  $\Delta E$ , which are derived from curve fitting analyses, are listed in Table 1 along with the orientations of the molecular axes. Values of  $\Delta E$  for all samples are of the order of 200 meV. Values of  $\tau_R$  are of the order of 100 ns, except those for NaCl:  $O_2^-$  and NaBr:  $O_2^-$ . It should be noted that  $\tau_R$  of the  $O_2^-$  molecule in Na-halides is roughly one order of magnitude smaller than those in K- and Rb-halides. The frequency factor  $\nu$  for NaBr:  $O_2^-$  is extraordinary larger than those for other crystals. The reason is not clear.

Table 1. Summary of  $\tau_R$ ,  $\nu$ ,  $\Delta E$  and the orientation of  $O_2^-$  molecules in alkali-halide crystals.

	$\tau_R$ (ns)	$\nu$ ( $10^{11} \text{ sec}^{-1}$ )	$\Delta E$ ( $10^2 \text{ meV}$ )	Orientation <sup>a</sup>	Orientation <sup>b</sup>
KCl: $O_2^-$	80±3	1.3	2.5	<110>	} (ground state)
KBr: $O_2^-$	93±3	3.3	2.4	<111> & <110>	
KI: $O_2^-$	92±3	-	-	<111>	} <110> B <sub>3g</sub> (Π <sub>g</sub> <sup>+</sup> )
RbCl: $O_2^-$	80±3	0.45	1.9	<110>	
RbBr: $O_2^-$	100±3	0.99	2.0	<110>	
NaCl: $O_2^-$	9±2	1.5	2.5	<111>	} <110> B <sub>2g</sub> (Π <sub>g</sub> <sup>+</sup> )
NaBr: $O_2^-$	19±2	180	2.6	<111>	

<sup>a</sup> Determined by the luminescence measurement. (ref. 8 and 9)

<sup>b</sup> Determined by the EPR experiment. (ref. 2 and 4)

The luminescence in Na-halides is empirically known to be relatively weak. In order to investigate the relation between the weak luminescence intensity and the short  $\tau_R$  in Na-halides as compared with those in K- and Rb-halides, we have measured relative quantum yields of the luminescence in NaCl:  $O_2^-$ , NaBr:  $O_2^-$  and KBr:  $O_2^-$  to that in KCl:  $O_2^-$ . Since the integrated intensity of the luminescence does not change up to about 180 K, we regarded the luminescence yields measured at about 90 K as the yields at 0 K. The results are shown in Table 2. The yields in

Table 2. Ratios of the radiative decay times and relative quantum yields of  $O_2^-$  luminescence.

X	$\tau_R$ (ns)	$\tau_X(0)/\tau_{KCl}(0)$	Relative Yield
KCl: $O_2^-$	80±3	1	1
KBr: $O_2^-$	93±3	1.1 <sub>6</sub>	0.8±0.1
NaCl: $O_2^-$	9±2	0.1 <sub>1</sub>	0.26±0.05
NaBr: $O_2^-$	19±2	0.2 <sub>4</sub>	0.25±0.05

NaCl:  $O_2^-$  and NaBr:  $O_2^-$  are smaller than that in KCl:  $O_2^-$  by a factor of about 4. This may be due to another non-radiative decay which does not depend on temperature. If we introduce a non-radiative decay *via* a tunneling process, the decay time  $\tau(T)$  is, then, described as follows;

$$\tau(T)^{-1} = \gamma + \sigma + \nu \exp(-\Delta E/kT). \quad \dots\dots (3)$$

The radiative decay rate  $\tau_R^{-1}$  in eq. (1) is replaced by  $\gamma + \sigma$  here, and  $\gamma$  is the intrinsic radiative decay rate of the  $O_2^-$  molecule and  $\sigma$  is the decay rate *via* the tunneling process. It is supposed that  $\gamma$  does not depend strongly on the kind of host crystal, while  $\sigma$  depends on the host crystal but does not on temperature. The quantum yield at low temperatures is then expressed by,

$$\eta(0) = \gamma/(\gamma + \sigma) = \tau(0) \cdot \gamma. \quad \dots\dots (4)$$

The relative quantum yield is given by,

$$\eta_x(0)/\eta_{KCl}(0) = \tau_x(0) \cdot \gamma_x / [\tau_{KCl}(0) \cdot \gamma_{KCl}], \dots\dots (5)$$

where x specifies the kind of host crystal. If we regard the intrinsic decay rate  $\gamma_x$  to be independent of x, then we get

$$\eta_x(0)/\eta_{KCl}(0) = \tau_x(0)/\tau_{KCl}(0). \quad \dots\dots (6)$$

The right hand side of eq. (6) is the ratio of the observed decay times at 0 K, practically the decay times below 100 K. As seen in Table 2, the relation (6) seems to hold for NaBr:  $O_2^-$  vs. KCl:  $O_2^-$ , but does not for NaCl:  $O_2^-$  and KBr:  $O_2^-$  vs. KCl:  $O_2^-$ . The relative yield in NaCl:  $O_2^-$  is about 2.5 times larger than that expected from the ratio of the decay times. For KBr:  $O_2^-$ , the relative yield deviates from that expected from the ratio of the decay times in the opposite direction. These facts suggest that we cannot adopt the same  $\gamma$  for the  $O_2^-$  molecules in various host crystals, but have to use different  $\gamma_x$  for respective host

crystals. However, we may say, the relatively short decay times and weak intensity of the  $O_2^-$  luminescence in Na-halides are partly due to the faster decay *via* the tunneling process from the excited state than that in K- and Rb-halides. Since the transition dipole moments of the  $O_2^-$  molecules in KBr and KI lie along  $\langle 111 \rangle$  directions as in NaCl and NaBr, we can not simply ascribe the shorter decay times in Na-halides to  $\langle 111 \rangle$  orientations of the dipole moments in the crystals. Probably we have to take into account the difference in the interaction of the  $p\pi$ -orbitals of the  $O_2^-$  molecule with neighbouring alkali ions. As discussed by Känzig *et al.*,<sup>2,4)</sup> an unpaired  $p\pi$ -electron of the ground state  $O_2^-$  molecule in Na-halides occupies a  $\pi_x$  orbital which lies along a  $\langle 001 \rangle$  direction, while the unpaired electron in K- and Rb-halides occupies a  $\pi_y$  orbital which lies along a  $\langle 1\bar{1}0 \rangle$  direction. These are due to the difference in the interaction of the  $p\pi$ -orbitals of the  $O_2^-$  molecule with the neighbouring alkali ions *via* covalent bonding,<sup>4,5,24)</sup> and this difference may cause the difference in  $\gamma_x$ .

There remains another question why the tunneling rate  $\sigma$  is larger in Na-halides than in K-halides, irrespective of nearly the same values of the activation energy  $\Delta E$  for all crystals. In Fig. 9, the tunneling process is depicted by the broken arrow. If the tunneling occurs only near the bottom of the excited state, we may expect nearly the same value of  $\sigma$  for all crystals studied here. It is speculated that there exists some dynamical non-radiative process which might be related to the reorientation of the  $O_2^-$  molecules in the excited state in Na-halides. More detailed study is required to answer the question.

In the above argument, we have regarded  $\tau(T)$  to be constant with increase in temperature from 2 to about 180 K. In this temperature range, however, some of the samples showed gradual decrease in  $\tau(T)$  and the decrement amounted to several %, as reported by Schwan *et al.* for KCl:  $O_2^-$ .<sup>15)</sup> This fact suggests that there exists another slow decay channel, which might be related to the rotation of the  $O_2^-$  molecules in host crystals.

### 3.4 Photo-induced degradation of $O_2^-$ luminescence in iodide crystals

It was found that the  $O_2^-$  luminescence in KI:  $O_2^-$  and RbI:  $O_2^-$  shows a drastic change in its spectrum by irradiation with *uv* light even at 2 K. A typical example is shown in Fig. 10. The sample was irradiated with light from the mercury lamp described in § 2. At the initial stage (a), the sample showed the pure  $O_2^-$  luminescence. After  $\sim 0.5$  hour irradiation (b), the intensity of the luminescence decreased remarkably and broad red luminescence grew up in 2.1  $\sim$  1.6 eV range. With irradiation for  $\sim 0.5$  hour more (c), the intensity of the  $O_2^-$  luminescence became about 1/10 of that at the initial stage and the red luminescence built up further. The cause of the spectral change is not clear at present. It is supposed that the photo-induced disintegration and migration of the  $O_2^-$  molecules and/or other impurity such as  $OH^-$  molecules in the host crystal may occur and finally cause the destruction of the isolated  $O_2^-$  molecules in the crystal.

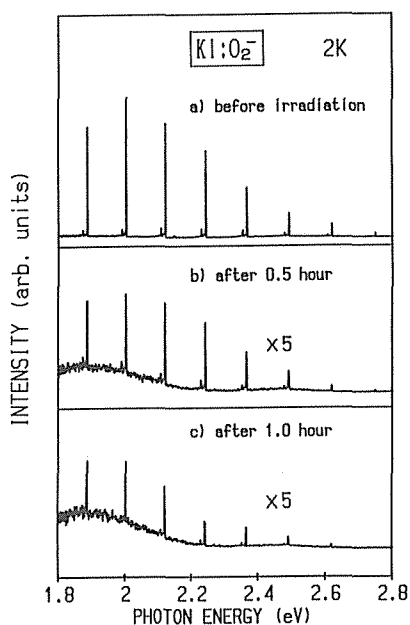


Fig. 10. Change in the luminescence spectrum of  $\text{KI}:\text{O}_2^-$  induced by  $uv$  irradiation.

#### §4 Summary

1) The origin of the double-structure phonon sidebands of the  $\text{O}_2^-$  luminescence in K- and Rb-halides has been investigated. The decay times of the two different components of the sidebands are found to be the same, showing that both components are caused by the optical transitions from the same initial level. The result supports the interpretation given by Rolfe and co-workers. 2) An interpretation has been given for the origin of the difference in the orientations of the  $\text{O}_2^-$  molecules in NaCl, NaBr, KBr and KI crystals determined by the EPR and luminescence studies, by taking account of reorientation of the molecule during an optical cycle. 3) The thermal quenching of the  $\text{O}_2^-$  luminescence above  $\sim 200$  K has been found in all crystals. It is interpreted in terms of the thermally activated non-radiative decay of the excited state. Shorter radiative decay times and lower quantum yields of the  $\text{O}_2^-$  luminescence in Na-halides than those in K- and Rb-halides are ascribed to the non-radiative decay *via* some tunneling process. 4) The  $\text{O}_2^-$  luminescence in iodide crystals has been found to show drastic change caused by irradiation with  $uv$  light even at 2 K.

#### Acknowledgements

The authors are indebted to Prof. M. Watanabe and other members of UVSOR laboratory in Institute for Molecular Science at Okazaki for their support to the decay time measurement using synchrotron radiation. This work was supported in part by the grant-in-aid from Nippon Sheet Glass Foundation for Materials Science.

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