Luminescence Study of O_2^- Centers in Alkali Halide Crystals

By
Osamu Morikawa
Department of Physics, Faculty of Science Kyoto University, Sakyo, 606-01, Japan

Part.I. –Luminescence from O_2^- center in KBr under uniaxial stress

Abstract

Photoluminescence from O_2^- centers in KBr crystal under application of uniaxial stress has been studied in the temperature range of 2~40 K. At 2K, the intensities of the weak extra lines are strongly enhanced by application of the stress, while the strong ordinary lines become weaker. The enhanced extra lines are found to be accompanied by double-structure phonon sidebands. The decay times of the extra lines and the ordinary lines are 96±1 ns and 92±1 ns, respectively. The extra and ordinary lines are confirmed to originate from different centers, that is, the former from <110> and the latter from <111> centers. It is concluded that the double structure sidebands are caused by the crystal field splitting of the ground state of the O_2^- centers which have D_{2h} symmetry. The enhanced extra lines are found to decrease with an increase in temperature, while the ordinary lines recover their intensities. The temperature dependence of the intensities of the ordinary and extra lines is discussed by taking into account of reorientation of the O_2^- centers between <111> and <110> orientations. Orientational degeneracy of <110> center is lifted by application of <001> stress. The energy separation between <110>$_{90°}$ and <110>$_{45°}$ centers is found to be the same for excited and ground states. This result is consistent with the fact that the extra lines in KBr:O_2^- show no splitting regardless of application of the stress.

Key words: O_2^- centers, zero-phonon lines, phonon sidebands, orientation, crystal field splitting, alkali halide, uniaxial stress.

§ 1. Introduction

It is well known that luminescence from O_2^- centers in alkali halide crystals shows a series of zero-phonon lines accompanied by phonon sidebands at low temperatures under UV excitation.[1] The luminescence has attracted new attention since the discovery of superfluorescence by Florian et al. in 1982[2] and laser activity by Wilk et al. in 1983.[3] Electronic and optical properties of the O_2^- centers in various alkali halides were studied by several authors in 1960's and 70's.[4-10] Followings have been confirmed: 1) An O_2^- molecule substitutes for a halogen ion in a host crystal and forms an O_2^- center. 2) A series of sharp luminescence lines are caused by transitions from the lowest vibrational level of the excited state $^2\Pi_u$ to vibrational levels of the ground state $^2\Pi_g$ of O_2^- molecules. 3) The transition dipole moments of the luminescence are parallel to the molecular axis, which lies along either <110> or <111> direction of the host crystal in the relaxed excited state depending on the kind of the host crystal. 4) The axis of an O_2^- molecule in the ground

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state lies along a <110> direction in all host crystals studied so far except in Cs-halides. 5) The luminescence spectra are classified into two groups; (a) spectra which consist of a series of zero-phonon lines accompanied by "single-structure phonon sidebands", and (b) spectra which consist of a series of zero-phonon lines accompanied by "double-structure phonon sidebands". Typical spectra of both groups are shown in Fig.1.
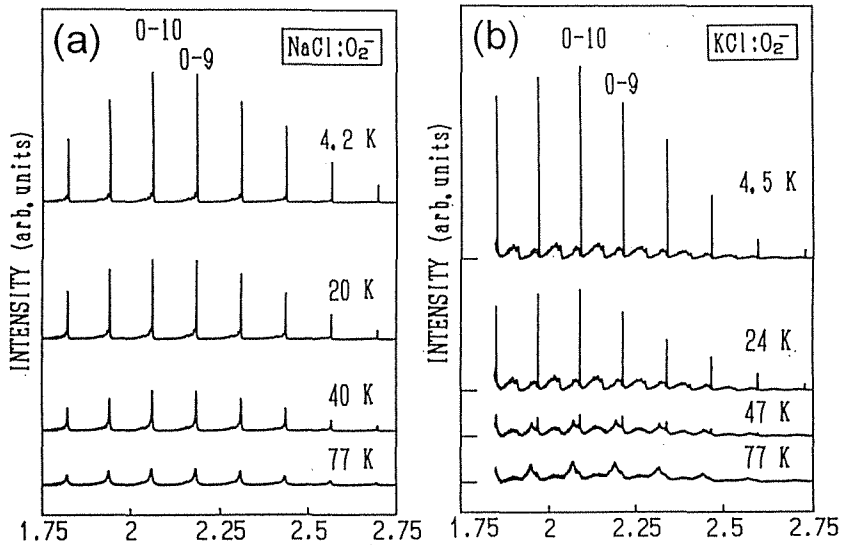

Fig. 1 : Typical spectra of O_2^- luminescence: (a) spectra of $NaCl:O_2^-$ which show a series of zero-phonon lines accompanied by single-structure sidebands, (b) those of $KCl:O_2^-$ which consist of a series of zero-phonon lines accompanied by double-structure side bands.
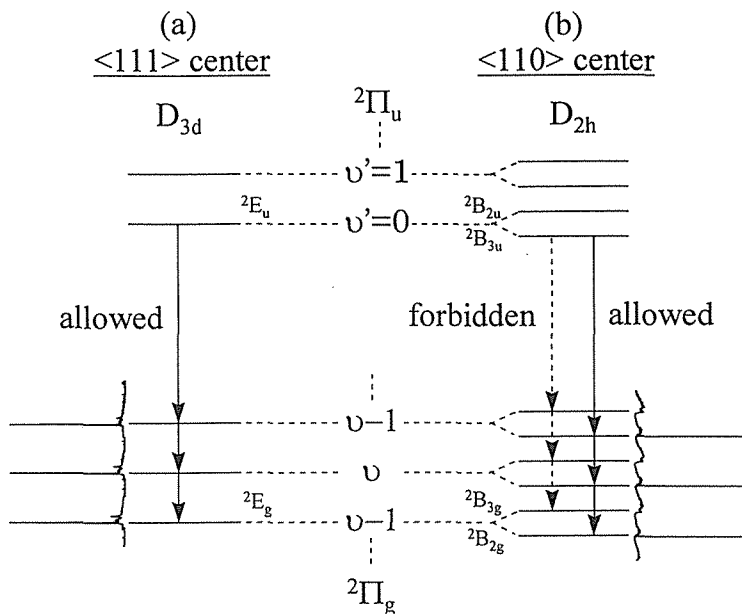

Fig. 2 : Energy level diagrams and optical transitions in O_2^- centers: (a) <111> and (b) <110> orientations.

Spectra of type (a) appear in NaCl, NaBr, KI and KBr. The O_2^- centers in these crystals have <111> orientations in the relaxed excited state, and their spectra are well understood by the level scheme and the transitions shown in Fig.2a. Spectra of type (b) appear in KCl and Rb-halides, and the O_2^- centers have <110> orientations in the relaxed excited state. The profiles of the phonon sidebands of type (a) spectra have been interpreted by Rolfe et al.[9] However, the origin of the double structure sidebands of type (b) spectra is not clear. Hongo et al. found that two parts of the double structure sidebands in KCl and RbBr have the same luminescence decay time and confirmed that both parts are caused by transitions from the same initial level.[11] The spectra of type (b) were tentatively interpreted by the level diagram shown in Fig.2, which is depicted by taking into account the above experimental result and the model already proposed by Rolfe et al.[9]

As seen in Fig.2b each vibrational level in the ground states $^2\Pi_g$ (the excited state $^2\Pi_u$) of the O_2^- molecule in group (b) crystals splits into two levels $^2B_{2g}$ and $^2B_{3g}$ ($^2B_{2u}$ and $^2B_{3u}$) in a crystal field with D_{2h} symmetry. In the ground states the $^2B_{2g}$ level is situated below $^2B_{3g}$ in K-halide and Rb-halides,[6] while in the excited state the $^2B_{3u}$ level is supposed to be situated below $^2B_{2u}$.[12] When O_2^- centers in these crystals are excited, they relax into the lowest vibrational level of $^2B_{3u}$ and make optical transitions to the vibrational levels of the ground states $^2B_{2g}$ and $^2B_{3g}$. The transitions $^2B_{3u} \rightarrow {}^2B_{2g}$ are allowed and give rise to sharp zero-phonon lines accompanied by phonon sidebands. The transitions $^2B_{3u} \rightarrow {}^2B_{3g}$ are forbidden (or weakly allowed) and give rise to no zero-phonon lines but only phonon sidebands (or sidebands associated with weak zero-phonon lines). Both phonon sidebands form the double structure sidebands.

The O_2^- centers in KBr are known to have a peculiar property.[8] Namely their spectra contain a series of weak zero-phonon lines in addition to the spectra of type (a): the former is called the "extra series" and the latter the "ordinary series". Ikezawa and Rolfe ascribed the luminescence of the ordinary series to <111> centers by measurements of the polarized spectra of the zero-phonon lines under uniaxial stress.[8] They also found that the zero-phonon lines of the extra series were strongly enhanced by the application of the uniaxial stress along <001> direction of the host crystal. The enhancement was accompanied by a decrease in the intensity of the ordinary series. The zero-phonon lines of the extra series, which are called "extra lines" hereafter, are polarized perpendicular to the stress. Ikezawa and Rolfe suggested that the extra lines are probably caused by <110> centers.

If the extra lines are really due to <110> centers and the model shown in Fig.2b is right, one may expect that the enhanced extra lines under uniaxial stress are accompanied by double structure sidebands. In order to clarify the origin of the extra series in KBr and to confirm the origin of the double structure sideband, the author has measured the luminescence spectra of O_2^- centers in KBr under <001> stress at low temperature, paying particular attention to the change in the profile of the phonon sidebands. The luminescence decay times of the ordinary and extra lines have been also measured to confirm whether each line originates from a different center or not. Temperature dependence of the intensities of the ordinary and extra lines is also measured to investigated the reorientation of the O_2^- centers in the crystal.

Experimental results are discussed by referring to the level diagrams shown in Figs. 2a and 2b. Discussion is also given on the relationship between the magnitude of the crystal

field splitting Δ of the $^2\Pi_g$ state in various host crystals, as determined from the present luminescence spectra, and λ/Δ from an EPR study,[6] where λ is the spin-orbit coupling constant of the O_2^- molecule in the host crystal. Discussion is made on the reorientation of the O_2^- molecules in KBr, adopting an adiabatic potential curve which is depicted based on the temperature dependence of the intensity ratios of the ordinary and extra lines, measured in 2~40 K range. Splitting of the orientational degeneracy of <110> center under <001> stress is discussed, as well, based on the analysis of the temperature dependence of polarized spectra.

§ 2. Experimental

2.1 Samples

Reagent grade powder of KBr was dried in vacuum at 200-400°C for a few days and was admixed with about 1 mol% of KO_2. Crystals were grown using Kyropoulos method from the melt in an argon atmosphere or in air. The crystals showed weak infrared absorption bands around 3600, 1430, and 880cm^{-1}; the first one is due to OH$^-$ and the last two to CO_3^{2-} impurities. The effect of those impurities was not observed in the luminescence spectra. However, the intensity of the luminescence in the crystals showed a gradual decease under prolonged UV irradiation during the measurements. The latter effect may be caused by the impurities.

Samples of about $5 \times 5 \times 12$ mm^3 were cleaved out of as-grown crystal blocks. A sample was mounted on a sample holder of a stress apparatus and immersed in liquid helium in a cryostat. Stress was applied to the sample through a stainless steel rod of 10 mm in diameter driven by an oil pump attached at the top of the apparatus. Figure 3 shows the stress apparatus schematically.
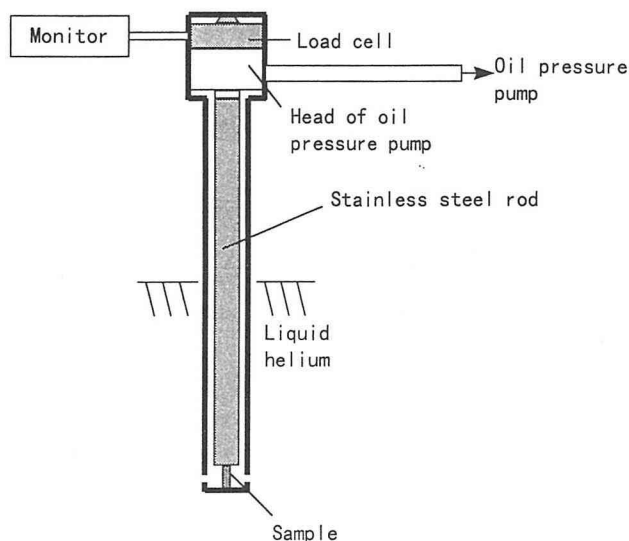

Fig. 3 : Stress aparatus

2.2 Measurement of luminescence spectra

Samples were excited with a 500W high pressure mercury lamp through a glass filter Toshiba UV-D33S and a quartz cell filled with an aqueous solution of $NiSO_4$. This assembly produces light in the range of 2800-3500A. The luminescence was collected at a right angle to the incident light and was led to a double monochromater SPEX 1402 through a glass filter HOYA L-42, which cuts off light shorter than 4100A. The output light from the monochromater was detected with a cooled photomultiplier R1396, and luminescence spectra were recorded by a microcomputer through a digital electrometer.

2.3 Decay time measurement

For the decay time measurements samples were excited with 260 nm light pulses of 3ω of Ti:Saphire laser with a pulse width of about 2 ps. The luminescence was led to the monochromater and was detected with a rapid response photomultiplier and analysed by TAC system through a pre-amplifier. The decay times of the luminescence were determined within an accuracy of about 1 ns by applying convolution analysis.

§ 3. Results and discussion

3.1.luminescence spectra and decay time.

Figure 4 shows the spectral changes of the O_2^- luminescence in KBr upon the application of <001> stress at 2K. All the spectra in the figure were obtained by measurements without a polarizer. As seen in Fig.4, the spectrum (a) under no stress shows the ordinary zero-phonon lines accompanied by single-structure phonon sidebands. In the expanded spectrum (a') in Fig.4 , a weak zero-phonon line is discernible at 2.3 eV on the high energy side of the ordinary zero-phonon line. Another weak line is discernible on the high energy tail of the ordinary line and is likely to be caused by some impurity. The intensity of the weak extra line is about 1/100 of that of the corresponding ordinary line but this ratio differs from sample to sample. The intensity of the extra line under no stress at 2K presumably depends on internal strain or on some impurities in the crystal.
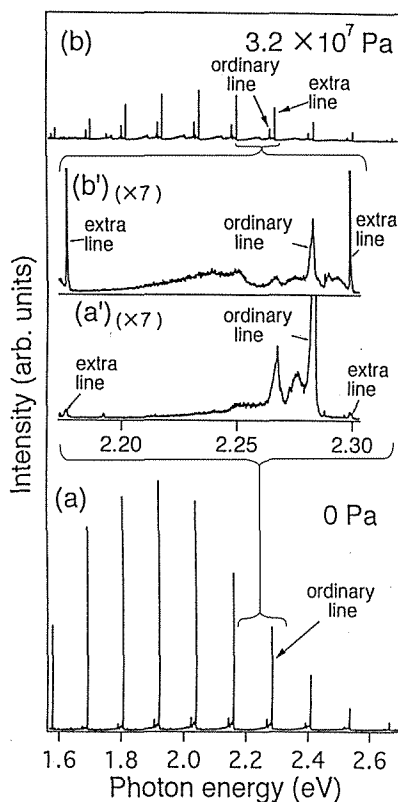

Fig. 4 : Spectral change of the O_2^- luminescence in KBr upon the application of <001> stress at 2 K; (a) spectrum before the application of the stress, (b) spectrum under the stress of 3.2× 10^7Pa. (a') and (b') show parts of spectra of (a) and (b), respectively, on an expanded scale.

As seen in the spectra (b) and (b') in Fig.4, the intensities of extra lines are remarkably enhanced upon the application of the stress, while those of ordinary lines show a drastic decrease. In addition, new sidebands become evident on the low energy tails of the extra lines and in the middle regions between adjacent extra lines. The ordinary and extra lines show no appreciable shift , but the former show a little broadening for the increase in the stress. Their intensities change monotonically with the increase in the stress, however, the total intensity of the luminescence is nearly conserved. The original spectrum, that is, the one before the application of the stress is recovered when the stress is removed.
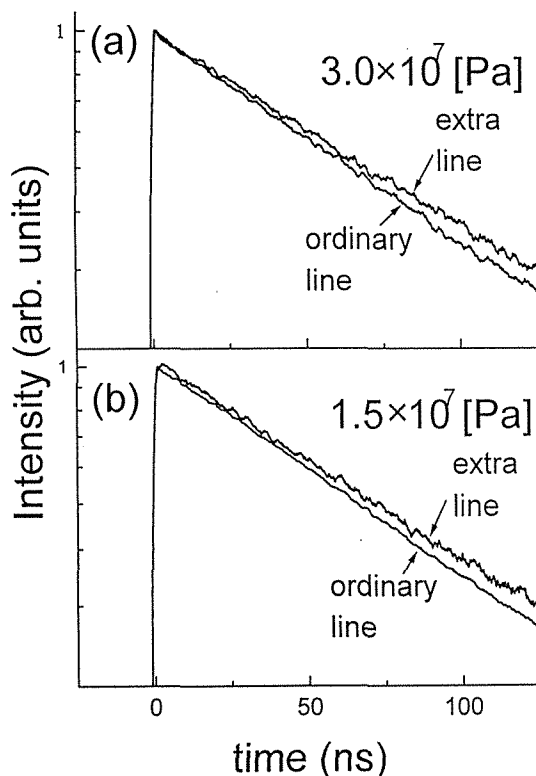

Fig. 5 : Decay curves of the ordinary and extra lines of O_2^- luminescence at 2 K; (a) under <100> stress of 3.0× 10^7 Pa and (b) 1.5× 10^7 Pa.

Figure 5 shows the decay curves of the ordinary and extra lines under <001> stress at 2K. All the decay curves are well expressed by a single exponential function $exp(-t/\tau)$. By applying convolution analysis, the decay times of the ordinary and extra lines are determined to be $\tau_{ord} = 92 \pm 1$ns and $\tau_{ext} = 96 \pm 1$ns, respectively. Both decay times are independent of the magnitude of the stress. The different decay times show that the ordinary and extra lines certainly have different origins.

Figs.6(a) and 6(b) show polarized spectra of the O_2^- luminescence in KBr under <001> stress. As seen in the figures, extra lines are strongly polarized perpendicular to the stress. As mentioned in §1 the ordinary lines of the O_2^- luminescence in KBr originate from <111> centers. Their intensities of E⊥P and E∥P polalizations are expected to be the same under <001> stress, since the O_2^- center of four equivalent <111> orientations make the same contribution to the luminescence of both E⊥P and E∥P. The observed
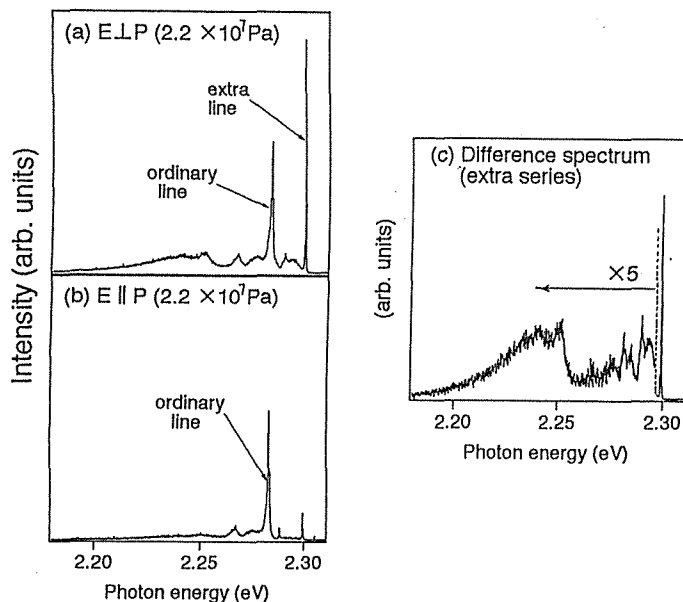
Fig. 6 : Polarized spectra of particular lines ($v = 8$) and their sidebands of O_2^- luminescence in KBr under
<001> stress: (a) spectrum polarized perpendicular to the stress (E⊥P), (b) spectrum polarized
parallel to the stress (E∥P), and (c) the difference spectrum of (a) and (b).

ordinary lines of E⊥P and E∥P show a little difference in their intensities on account of
the contribution of the background due to the sidebands of the extra series of E⊥P. The
difference is almost removed by the subtraction of the background. The difference spec-
trum shown in Fig.6(c) is obtained by subtracting the spectrum in Fig.6(b) from that in
Fig.6(a). The difference spectrum shows the extra line accompanied by the clear double-
structure sideband.

Here we note that the results in this experiment are well explained by the scheme
which is shown in Fig.2 and discussed in §1. The double-structure sidebands are ascribed
to the crystal field splitting of the $^2\Pi_g$ state of the O_2^- centers with <110> orientation. The
energy separation Δ_{opt} between two parts of the double-structure sideband corresponds to
the magnitude of the crystal field splitting which will be discussed in the following sec-
tion.

3.2. Relation between Δ_{opt} and λ/Δ

As noted in the previous section the double-structure sidebands which appear in the
luminescence from <110> centers are ascribed to the crystal field spitting of the ground
state $^2\Pi_g$. Figure 7 shows the spectrum of particular zero-phonon lines and their double-
structure sidebands of the O_2^- luminescence in several host crystals including the difference
spectrum of the luminescence in KBr shown in Fig.6(c). They correspond to the transition
to the $v = 8$ vibrational levels of the ground state $^2\Pi_g(^2B_{2g}$ and $^2B_{3g})$. Following the discus-
sion in the previous section, we take the energy separation Δ_{opt} between the two parts of
the double-structure sideband in each spectrum shown in Fig.7 to be the magnitude of the
crystal field splitting for the 8th vibrational level of the $^2\Pi_g$ state.

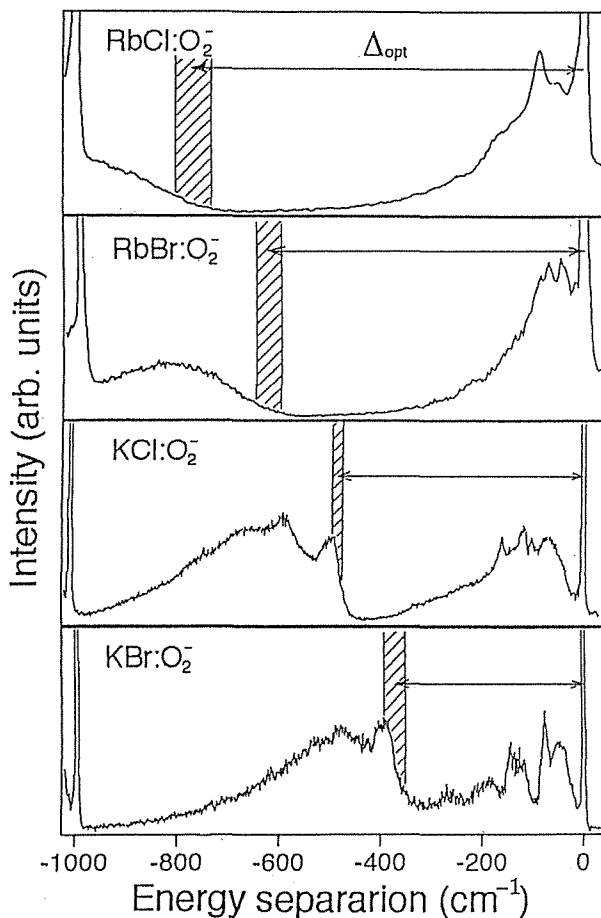On the other hand, from the EPR study on the O_2^- centers in various host crystals[6]

Fig. 7 : Spectra of the zero-phonon lines ($v = 8$) and their double-structure phonon sidebands of O_2^-
luminescence in KCl, KBr, RbCl and RbBr. The spectrum of KBr is the difference spectrum
of $E \perp P$ and $E /\!/ P$ under <100> stress (see Fig. 6).

were obtained values of λ/Δ, where λ and Δ are the spin orbit coupling constant and crystal field splitting of the $^2\Pi_g$ state of the O_2^- molecule in the crystal, respectively. Figure 8 shows the relation between $\Delta_{opt}(v = 8)$ for the 8th vibrational level and $(\lambda/\Delta)^{-1}$ for several host crystals. A good proportionality holds between the two quantities. The magnitude of $\Delta_{opt}(v)$ for each host crystal shows a gradual increase with the decrease in v. This indicates that $\Delta_{opt}(v)$ is affected by the anharmonicity of the vibrational levels in each crystal. The value of λ/Δ determined from the EPR study is that for the lowest vibrational level ($v = 0$) of the $^2\Pi_g$ state. Then in order to discuss the relation between Δ_{opt} and $(\lambda/\Delta)^{-1}$ further, we have to get $\Delta_{opt}(v = 0)$ for each crystal. Since the $v = 0$ lines and their phonon sidebands are too weak to be observed, we obtained $\Delta_{opt}(v = 0)$ for each host crystal by extrapolation of $\Delta_{opt}(v)$ values obtained from the luminescence spectra in the present experiment. This leads to plots of $\Delta_{opt}(v = 0)$ values similar to those shown in Fig.8. A good proportionality
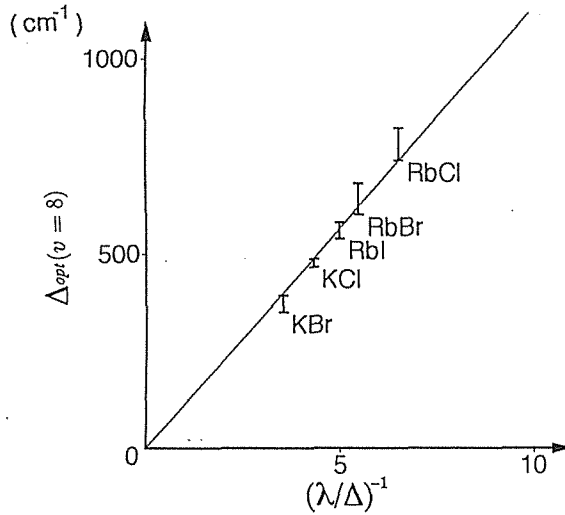
Fig. 8 : Relation between $\Delta_{opt}(v=8)$ and (λ/Δ)

also holds between the quantities, $\Delta_{opt}(v = 0)$ and $(\lambda/\Delta)^{-1}$, for RbCl, RbBr, KCl and KBr: the slope of the line fitted to the plots is slightly steeper than that in Fig.8.

Since the magnitude of Δ in $(\lambda/\Delta)^{-1}$ should be equal to $\Delta_{opt}(v = 0)$ for each crystal, we obtain $\lambda \approx 125$ cm^{-1} from the constant of proportionality between these two quantities. Rolfe et al. also made a brief discussion on the crystal field splitting of O_2^- centers in KCl and Rb halides.[9] The present estimation of values of Δ_{opt} are different from theirs. A good proportionality has been obtained between $\Delta_{opt}(v = 0)$ and $(\lambda/\Delta)^{-1}$ for the spectra of group (b) crystals, including the difference spectrum of O_2^- centers in KBr. The value of λ(about 125 cm^{-1}) is relatively small as compared with that (150~200 cm^{-1}) roughly estimated by Zeller and Känzig.[6] Nevertheless it should be noted that the magnitude of λ obtained here is the same for O_2^- centers in the several host crystals. This fact seems reasonable because the size of the O_2^- molecule is smaller than those of halogen ions. For example the inter-atomic distance of the O_2^- molecule is about 1.3 Å, while the ionic radius of Cl$^-$ is about 1.8Å. The above result also supports the conclusion that the extra series of the O_2^- lumi-nescence in KBr is due to <110> centers as in the case of that in KCl and Rb-halides.

§ 4. Temperature dependence of the intensities of luminescence lines: reorientation of the O_2^- centers

4.1 Temperature dependence of the luminescence under zero stress

In the previous section, it was confirmed that almost all of the O_2^- centers in KBr change their orientations from the <110>'s to <111>'s when excited optically under zero stress at 2 K and give the luminescence of the ordinary series. Weak extra lines observed at 2 K originate from the centers which retain <110> orientations in the excited state probably due to the effect of residual strain caused by impurities or defects in the host crystal. In this section is investigated the reorientation of the O_2^- centers for the change of

temperature.

Figure 9 shows the spectra of the $\upsilon = 8$ lines in the series of luminescence lines on an expanded scale under zero stress at several temperatures. In this case the spectra polarized parallel and perpendicular to the <001> axis show no difference. At 2K, the intensity of the extra line is about 1% of that of the corresponding ordinary line. With increasing temperature the ratio of the integrated intensity of the extra line to that of the ordinary line increases up to about 10% at ~ 20 K. In Fig.10 is plotted the ratio as a function of temperature. For the estimation of the intensities of the lines, contribution of the background due to the phonon sideband is properly subtracted.

Here we analyze, at first, the temperature dependence of the luminescence intensity under zero stress and discuss the reorientation of the O_2^- centers in their excited state. Figure 11 shows a schematic illustration for the reorientation of the O_2^- center in the excited state under zero stress. By absorbing UV light at 2 K, O_2^- centers in the ground state $^2B_{2g}$ are excited into the higher vibrational levels of excited state $^2B_{3u}$ shown in Fig.2. During the relaxation in the excited state, most of the O_2^- centers change their orientations from the <110>'s to <111>'s and quickly reach the bottom of ^2E_u state and then return to the ground state emitting the luminescence of the ordinary series with the decay time of 92 ± 1 ns. With an increase in temperature, some of the <111> centers at the bottom of the excited state are thermally activated and change their orientations from the <111>'s to <110>'s and reach the bottom of $^2B_{3u}$ state. Then they return to the ground state emitting the series of weak extra lines with the decay time of 96 ± 1 ns.

The energy level of the <111> center is 4-fold degenerate orientationally, while that of the <110> center is 6-fold degenerate. The total number of the <111> or <110> centers in their excited states is denoted as $N_{ord}(=\sum_{i=1}^{4} n_i^o)$ or $N_{ext}(=\sum_{j=1}^{6} n_j^e)$, where n_i^o or n_j^e is the number of the centers with the orientation i or j, respectively. Under zero stress, all n_i^o's ($i=1 \sim 4$) are equal and are denoted as n^o. Similarly, all n_j^e's ($j=1 \sim 6$) are equal and are denoted as n^e. Then the rate equations for N_{ord} and N_{ext}, which describe the reorientaion and luminescence processes, are given as follows by neglecting the non-radiative decay process,
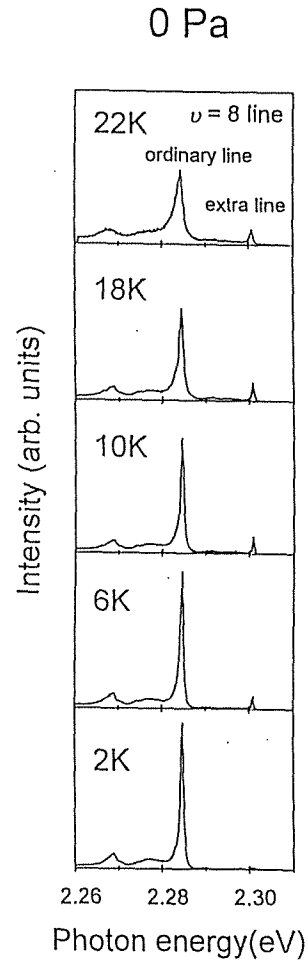

0 Pa

22K $\upsilon = 8$ line
ordinary line
extra line
18K
10K
6K
2K

2.26   2.28   2.30

Photon energy(eV)

Fig. 9 : Spectra of $\upsilon=8$ lines of O_2^- luminescence at several temperatures under zero stress.
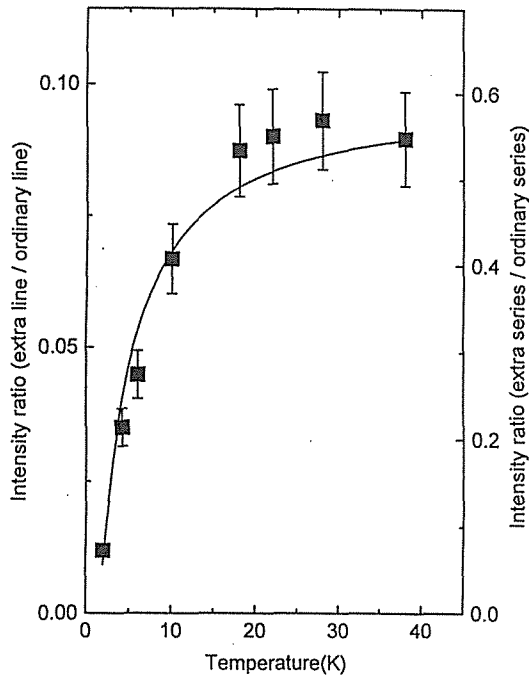
Fig. 10 : Temperature dependence of the intensity ratio of the extra to ordinary luminescence under 0 Pa: the ratio of υ=8 lines on the left hand scale and the ratio of the total intensities of the extra to ordinary series on the right hand scale. Solid curve shows the calculated one fitted to the observed points using Eq. (8) in the text.
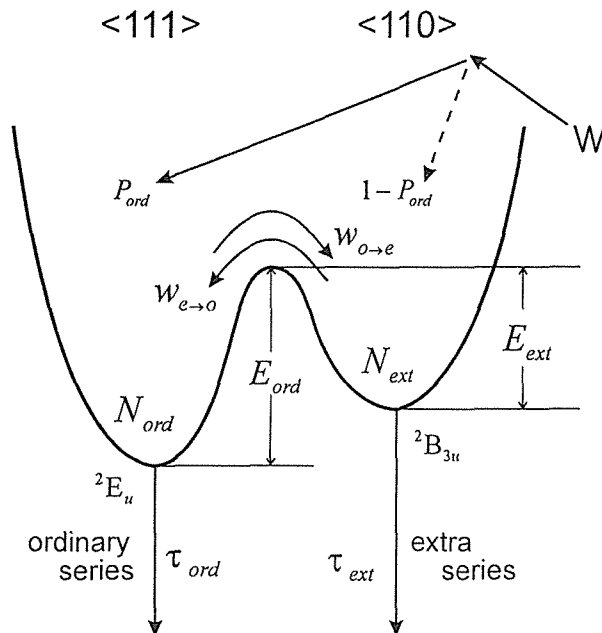

Fig. 11:. Adiabatic potential curve for reorientation of the O$_2^-$ center in the excited state under 0 Pa.

$$\frac{dN_{ord}}{dt} = WP_{ord} - N_{ord}\left\{ \frac{1}{\tau_{ord}} + w_{o \to e} \right\} + w_{e \to o} N_{ext}, \tag{1}$$

$$\frac{dN_{ext}}{dt} = W(1 - P_{ord}) - N_{ext}\left\{ \frac{1}{\tau_{ext}} + w_{e \to o} \right\} + w_{o \to e} N_{ord}, \tag{2}$$

where W is the pumping rate and P_{ord} expresses branching ratio into the $<111>$ orientations. The notations $w_{o \to e}$ and $w_{e \to o}$ are the rates of reorientations $<111> \to <110>$ and $<110> \to <111>$, respectively. They are expressed as $w_{o \to e} = v_{ord}\exp(-E_{ord}/kT)$ and $w_{e \to o} = v_{ext}\exp(-E_{ext}/kT)$, respectively, where E_{ord} and E_{ext} are barrier heights, and v_{ord} and v_{ext} are the frequency factors for the reorientations (see Fig.11). For the steady state, we get the solutions,

$$N_{ord} = \frac{w_{e \to o} + P_{ord}/\tau_{ext}}{w_{o \to e}/v_{ext} + w_{e \to o}/v_{ord} + 1/\tau_{ord}\tau_{ext}} W, \tag{3}$$

$$N_{ext} = \frac{w_{o \to e} + (1 - P_{ord})/\tau_{ord}}{w_{o \to e}/v_{ext} + w_{e \to o}/v_{ord} + 1/\tau_{ord}\tau_{ext}} W. \tag{4}$$

Since the transition dipole moment is parallel to the direction of the O_2^- axis, the intensities of the ordinary and extra lines are expressed as follows, by taking account of the direction cosine of the O_2^- axis, (see upper half of Fig.14 with $P = 0$.)

$$I_{ord} \propto \frac{2}{3} N_{ord}/\tau_{ord}, \tag{5}$$

$$I_{ext} \propto \frac{2}{3} N_{ext}/\tau_{ext}. \tag{6}$$

For the steady state, the total number of the excited O_2^- centers is constant, that is,

$$N_{ord} + N_{ext} = 4n^0 + 6n^e = \text{const.} \tag{7}$$

The decay times τ_{ord} and τ_{ext} are almost the same as noted in the previous section, then we get $I_{ord} + I_{ext} \sim$ constant, which reflects the conservation of the total luminescence intensity. Since $I_{ext}/I_{ord} = \frac{N_{ext}/\tau_{ext}}{N_{ord}/\tau_{ord}}$, we get from eqs.(3) and (4) the following relation,

$$\frac{I_{ext}}{I_{ord}} = \frac{(v_{ord}/\tau_{ext})\exp(-E_{ord}/kT) + (1 - P_{ord})/\tau_{ext}\tau_{ord}}{(v_{ext}/\tau_{ord})\exp(-E_{ext}/kT) + P_{ord}/\tau_{ext}\tau_{ord}}. \tag{8}$$

In Fig.10 is plotted the intensity ratio of the $v = 8$ lines of the ordinary and extra series as a function of temperature. As seen in Fig.4 and as discussed in the previous section, the intensity of the phonon sidebands of the extra lines are much stronger than that of the ordi-

nary lines. Therefore we have to include both intensities of the lines and their phonon side-bands of each series in I_{ext} or I_{ord}. The intensity ratio I_{ext}/I_{ord} was then estimated to be about 6.1 times as large as that of the $v = 8$ lines themselves. The ratio is expressed by the points in Fig.10 on the right hand scale. Observed points are well fitted with the solid curve calculated by eq.(8). Best fit values of the parameters are as follows;

$$E_{ord} = 11 \pm 1 \text{cm}^{-1} \ , \ v_{ord} = 4 \pm 1 \times 10^9 \text{ sec}^{-1} \ ,$$

$$E_{ext} = 9 \pm 1 \text{cm}^{-1} \ \ , \ v_{ext} = 6.1 \pm 1 \times 10^9 \text{ sec}^{-1} \ ,$$

$$\text{and} \ \ P \approx 0.99 \ .$$

It is noted that the excited state of the <111> center is situated about 2cm^{-1} below that of the <110> center and the barrier height between both orientations is about 11cm^{-1} as measured from the <111> orientation. In addition, it is noted that almost all of the O$_2^-$ centers in KBr relax into the lowest vibrational level of the excited state with the <111> orientation after optical excitation. Above 15 K, populations of <111> and <110> orientations reach nearly thermal equilibrium and the intensity ratio is approximated by $I_{ext}/I_{ord} \sim (v_{ord}/v_{ext})\exp\{-(E_{ord}-E_{ext})/kT\}$, since $\tau_{ord} \approx \tau_{ext}$, $P_{ord} \approx 1$ and v_{ext}, v_{ord}, $\gg \tau_{ord}^{-1}$, τ_{ext}^{-1}. The decay times of <111> and <110> centers approach to the same value of about 93.5 ns.

§5. Temperature dependence of the intensities of the extra lines under <001> stress

In this section the reorientation of the O$_2^-$ centers under uniaxial stress is investigated for the change in temperature. Figure 12 shows polarized spectra of the $v = 8$ lines under <001> stress of 3.4×10^7 Pa. The intensities of the spectra are normalized at the peaks of the ordinary lines. The intensities of the ordinary lines of E⊥P and E∥P polarizations are nearly the same at each temperature and show a gradual increase with temperature. The intensity of the extra line of E⊥P is much stronger than that of E∥P. The former shows a remarkable decrease with an increase in temperature, while the latter shows a slight change. In Fig.13 is plotted the intensity ratio of the extra to ordinary lines as a function of temperature. The ratio decreases monotonically for each polarization and approaches to nearly the same value of ~0.1 above 30K.

At 2 K, the decay time of the ordinary line is 92±1ns, while that of the extra line is 96±1ns under the stress of ~3×10^7 Pa as mentioned *3.1*. On the other hand, above 17 K, both decay times become equal to about 93.5 ns under the stress. Under zero stress both decay times approach to about 93.5 ns above ~ 8 K.

As mentioned above, the extra lines, especially the E⊥P lines of KBr:O$_2^-$ are strongly enhanced at low temperature under uniaxial stress (see Fig.12). This indicates that the number of the <110> centers in the relaxed excited state increases significantly. Under <001> stress, the orientational degeneracy of the <110> centers is lifted as shown in Fig.14. while that of the <111>centers is not. The levels of the <110> centers under the
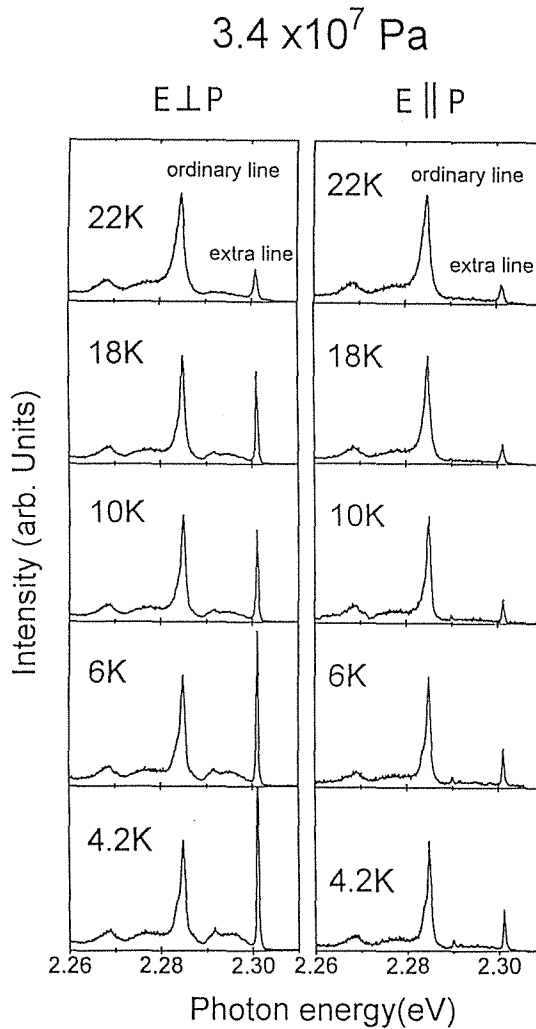
3.4×10^7 Pa

Fig. 12 : Spectra of $v=8$ lines of O_2^- luminescence under 3.4×10^7 Pa at several temperatures. The spectra are depicted being normalized at the peaks of the ordinary lines.

stress are denoted as shown in Fig.14. The $<110>_{90°}$ level is located below the $<110>_{45°}$. The observed extra lines, however, show no splitting for the increase in the stress. This fact suggests that the energy separation between the $<110>_{90°}$ and $<110>_{45°}$ levels is the same for the excited state and the ground state under the stress.

Here we note the total numbers of the $<110>_{90°}$ and $<110>_{45°}$ centers as $N_{90°}(=2n_{90°})$ and $N_{45°}(=4n_{45°})$, respectively. Then the intensities of the extra lines parallel and perpendicular to the stress under the condition shown in Fig.14 are expressed as follows,

$$I_{\parallel}^e \propto (\frac{1}{\sqrt{2}})^2 \times 4n_{45°}^e / \tau_{ext} , \tag{9}$$

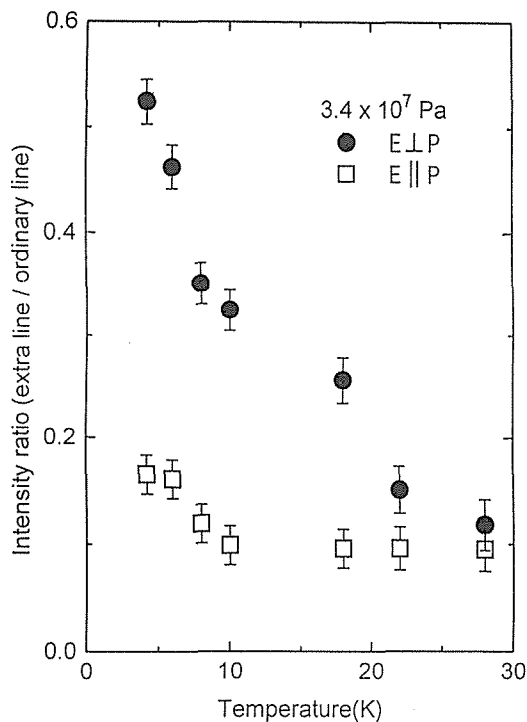$$I_{\perp}^e \propto (\frac{1}{\sqrt{2}})^2 \times (2n_{90°}^e + 2n_{45°}^e) / \tau_{ext} . \tag{10}$$

Fig. 13 : Temperature dependence of the intensity ratios of $\nu = 8$ lines of extra and ordinary series under 3.4× 10^7 Pa. (•) for E⊥F; (○) for B//P polarizations.

<111> center   <110> center
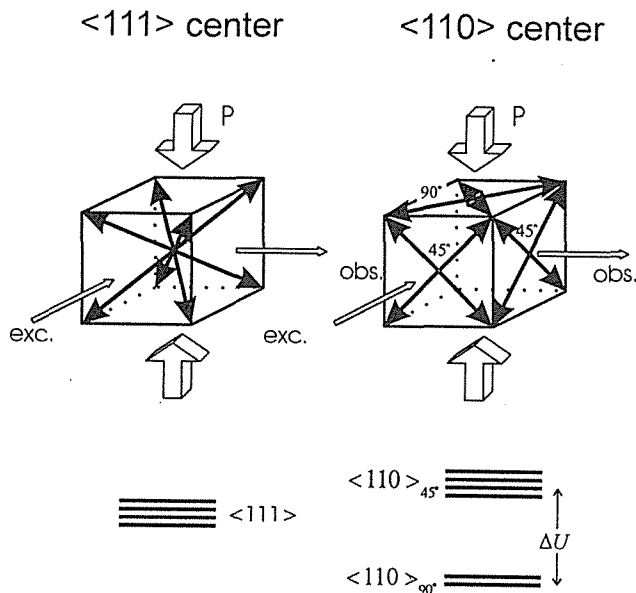
Fig. 14 : Schematic illustrations for <111> and <110> orientations of O$_2^-$ centers under <001> stress (upper half) and for orientational degeneracy and splitting of energy levels (lower half). Excitation light is along the <100> direction and luminescence is observed along the <010> direction.

At high temperatures, populations of the excited $<110>_{90°}$ and $<110>_{45°}$ centers seem to approach thermal equilibrium. Then we may put

$$n^e_{45°} / n^e_{90°} \propto \exp(-\Delta U/kT) , \tag{11}$$

where ΔU is the energy separation between the relaxed excited states of $<110>_{45°}$ and $<110>_{90°}$ centers. The excited states of both orientations are assumed to be separated by an appropriate potential barrier from each other. Then we get the following relation between $I^e_\parallel$ and $I^e_\perp$ at high temperatures,

$$\frac{I^e_\parallel}{2I_\perp - I^e_\parallel} \propto \exp(- \frac{\Delta U}{kT}) . \tag{12}$$

Here it is assumed that ΔU is proportional to the magnitude of the applied stress P, that is, $\Delta U = \beta P$, as in the case for the ground state.[13] It is also assumed that the frequency factors for the reorientations are much larger than the decay rates.

In Fig.15 is plotted the intensity ratio $\ln[(2I_\perp^e - I_\parallel^e)/I_\parallel^e]$ as a function of P/kT. As seen in the figure, observed points lie on a straight line for small values of P/kT, but deviate from it for large values of P/kT. This fact indicates that $n^e_{45°}$ and $n^e_{90°}$ are in thermal equilibrium for small P/kT, that is, for high temperature and/or weak stress. From the slope of

the line in Fig.15, we get $\beta = 6.4 \times 10^{-24}$cm^3 for the excited state of the $<110>$ center in KBr under $<001>$ stress. This value of β gives $\Delta U \approx 10$ cm^{-1} for $P \approx 3 \times 10^7$ Pa.

Känzig *et al.* obtained $\beta = 6.41 \times 10^{-24}$cm^3 for the ground state of the $<110>$ center in KBr in their EPR study.[13] The present value of β for the excited state coincides with that for the ground state. This result is consistent with the fact that the extra lines show no splitting for the increase in the stress as mentioned before. In the case of O_2^- centers in KCl and other host crystals, zero-phonon lines show shifts and clear splittings with the increase in the

Fig. 15 : Plots of the intensity ratio $\ln[(2I^e_\perp - I^e_\parallel)/I^e_\parallel]$ of $v = 8$ extra lines as a function of P/kT. The straight line corresponds to thermal equilibrium distribution of $n^e_{45°}$ and $n^e_{90°}$ under $<001>$ stress (see text).

stress, indicating that the energy splitting due to the stress are different for the excited and ground states in those crystals.

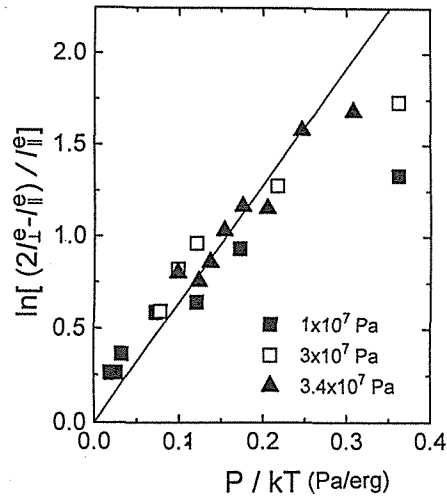## §6. Summary and conclusion

The changes in the spectrum and the decay time of the O_2^- luminescence in KBr caused by <001> stress have been studied in the temperature range of 2~40 K. The following results have been obtained:

1) The zero-phonon lines of the extra series are strongly enhanced and are accompanied by the double-structure sidebands at 2K, while the intensity of the ordinary lines are significantly reduced. The intensities of extra lines under the stress decrease as temperature rises.

2) The ordinary and the extra zero-phonon lines under the stress show decay times of τ_{ord} = 92±1ns and τ_{ext} = 96±1 ns at 2K, respectively.

3) The intensities of the E⊥P components of the extra lines under the stress are much stronger than those of E//P at 2K. Both intensities becomes nearly the same magnitude above 20K reflecting the thermal equilibrium of the luminescent levels.

The separations of the two parts of the double structure sidebands Δ_{opt} in several alkali halide crystals KCl, KBr, and Rb-halides are proportional to $(\lambda/\Delta)^{-1}$ for the O_2^- centers of <110> orientation estimated from the EPR study. From these results, it is concluded that the extra lines of the O_2^- luminescence in KBr originates from <110> centers and they are accompanied by double structure sidebands. If we take $\lambda \approx 125$ cm^{-1}, then Δ_{opt} is equal to crystal field splitting Δ of $^2\Pi_g$ level for the <110> O_2^- centers in these crystals. The facts support that the double structure sidebands of O_2^- centers in these crystals are caused by the crystal field splitting of the energy levels of the <110> O_2^- centers.

In addition, the temperature dependence of the luminescence intensities is discussed by taking account of the reorientation of the excited O_2^- centers between the <110> and <111> orientations in KBr. The potential barrier height between both orientations is estimated to be about 11 cm^{-1} as measured from the <110> center under zero stress.

The 6-fold degeneracy of the energy levels of the <110> center is lifted by application of uniaxial stress. The energy separation between the <110>$_{90°}$ and <110>$_{45°}$ centers under <001> stress is nearly the same for the excited and the ground states. This result is consistent with the fact that the extra lines do not show splitting by application of the stress in contrast to the case of KCl:O_2^- and other crystals. The curious behavior of the O_2^- luminescence in KBr for the change in temperature and upon application of the uniaxial stress is well understood in terms of the reorientation of the O_2^- centers in the crystal.

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