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Determination of the off-center parameters in NaBr:Cu$^+$ by pressure effects of the absorption bands

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The temperature dependence of the oscillator strength and the peak position of the parity-forbidden absorption bands of the Cu$^+$ ion in NaBr and NaCl crystals under various hydrostatic pressures up to 14.8 kbar are measured in detail. These results reveal the state of the Cu$^+$ ion in a shallow off-center system NaBr:Cu$^+$; the distance of the Cu$^+$ ion from the lattice site (off-center distance) is estimated to be 0.5_5 Å and the depth of the valley of the adiabatic potential (off-center valley) to be 25 ± 3 meV. The distance between the Cu$^+$ ion and Br$^-$ ion suggests that the $\langle 110 \rangle$ or the $\langle 111 \rangle$ directions are preferable for an off-center displacement. The plausible off-center potential for the Cu$^+$ ion in NaBr is represented in a summary of these quantitative results. The adiabatic potential for the Cu$^+$ ion in NaBr is changed by pressure from a shallow off-center type to a harmonic on-center type passing through an anharmonic on-center type.

I. INTRODUCTION

The cation centers with the small ionic radius such as Li$^+$, Cu$^+$, and Ag$^+$ propose an intensive interest with the uniqueness that the ions arrange in the various ways in host crystal lattice of each alkali halide.[1-6] The defect systems in alkali halide crystals are classified into four types from a harmonic on-center to a deep off-center according to the adiabatic potential;[7] (a) a normal substitutional position with a harmonic oscillation of the defect ions, (b) a normal substitutional position but with an anharmonic oscillation extended over the several host lattices around the defect ion, (c) an off-center position with a shallow valley in potential that is called a shallow off-center, (d) an off-center position with a deep valley, called a deep off-center. Each type is related to the characteristic temperature dependence of the oscillator strength of a parity-forbidden transition. The Cu$^+$ center in NaCl and NaBr studied here are understood as the types (b) and (c), respectively. It has been indicated that the off-centers transfer to the on-centers under hydrostatic pressures,[7,8] which was confirmed by monitoring the oscillator strength of the parity-forbidden transition, $nd^{10} \rightarrow nd^9(n+1)s$ ($^1D, ^3D$) ($n=3$ for Cu$^+$, and $n=4$ for Ag$^+$) in free ion.

The distance of the Ag$^+$ ion in RbCl and RbBr from regular lattice site (off-center distance) has been examined experimentally.[6] The semiclassical theoretical work was devoted to the minimum-energy configuration and predicted the direction of the off-center displacement and the off-center distance for Cu$^+$ and Ag$^+$ systems.[9] However, no experimental report on the off-center distance of Cu$^+$ defect systems is found.

In this paper, we will present the temperature dependence of the oscillator strength of the parity-forbidden absorption band of NaBr:Cu$^+$ and NaCl:Cu$^+$ systems under various hydrostatic pressures in detail. The off-center distance and the depth of the valley of the adiabatic potential (off-center vally) for the Cu$^+$ ion are estimated from pressure effects of the oscillator strength and from the pressure shift of the D_1 absorption peak, respectively. The preferable direction for an off-center displacement is given. The change from a shallow off-center [type (c)] to a harmonic on-center [type (a)] due to the applied pressure is shown under higher pressure than in the previous papers.[7,8]

II. EXPERIMENTAL

The high-pressure system is constructed with a 50-ton oil press, a uv light guide, a cooling bath, and an optical-pressure cell of a piston-cylinder type. The cross section of the optical-pressure cell is schematically presented in Fig. 1. This pressure cell is available up to about 16 kbar at room temperature. The high-quality sapphire windows were used to lead the uv light up to 195 nm to the sample. As the uv light source, a D$_2$ lamp was operated with the power of 100 to 200 W. The pressures upon the

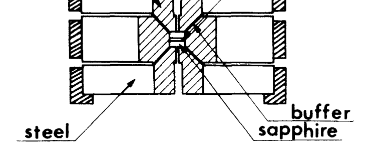

FIG. 1. Cross section of the optical-pressure cell. The crystal of which diameter is 5 mm and thickness is 1 mm is sandwiched in between the two sapphire windows.

phase transition of rubidium halides were available to correct the applied pressure. Quality of hydrostatic pressure by this cell is examined with the sharpness of the phase transition of rubidium halides. At room temperature, the phase transition occurs very sharply, and the sharpness is slightly lost at liquid-helium temperature.

The single crystals doped Cu^+ ions were grown by Kyropoulos method in air. Before melting, powder was hold at 400 °C for one day to eliminate hydroxyl ions. Cuprous halides of 0.02 to 1.0 mol % were added to the melt of the host substances. The concentration of Cu^+ ions in NaBr was obtained by the atomic-absorption analysis. The oscillator strength of D absorption band (letter D is hereafter used to denote the D_1 and D_2 absorption bands simultaneously) in NaBr:Cu^+ was determined from Smakula's equation corrected by Dexter[10] using the refractive index of 1.84, and evaluated to be 0.067 at room temperature.

The crystals were annealed for 1 to 2 min at 50 °C below the melting points, then rapidly quenched to room temperature. Consequently, the aggregation of Cu^+ ions or the formation of small particles of cuprous halides in the crystal was avoided.

III. DETERMINATION OF THE OFF-CENTER PARAMETERS

There are mainly three parameters with respect to the state of the off-center Cu^+ ion, and hydrostatic pressure will exert significant influence upon the circumstance of the Cu^+ ion. Then, we can reveal the off-center parameters from the pressure effects of the absorption bands. The off-center distance can be determined from the reduction rate of the oscillator strength due to pressure, the energy depth of the off-center valley from the pressure shift of the D_1 absorption peak, and the off-center direction from the consideration of the nearest-neighbor distance. In this section, we will discuss three off-center parameters in the above-mentioned sequence.

A. Estimation of the off-center distance

The oscillator strength for a parity-forbidden transition is connected with the normal coordinate Q_{odd} of an odd parity as follows:[10]

$$f=\frac{2}{3}\left[\frac{m}{e^2}\right]\left[\frac{\nu}{h}\right]\left[\frac{2}{\delta E}\right]^2 M_{ab}^2 \sum |\langle \chi | Q_{\text{odd}} | \chi' \rangle|^2 , \tag{1}$$

where δE is the mean value of the transition energy, ν the incident photon frequency, M_{ab} the dipole matrix element, and χ is the wave function of the relevant phonon. The normal coordinate Q_{odd} is divided into the vibrational term Q_v and the distortional term Q_d which are orthogonalized. The off-center displacement belongs to the term Q_d. If the $Q_d \gg Q_v$, the oscillator strength insensitive to temperature is expected. This case is found in KBr:Cu^+ and KCl:Cu^+ with considerably strong oscillator strength[1,2] in spite of a forbidden transition. Vanishing of Q_d from the term Q_{odd} results in that the oscillator strength linearly increases with temperature at high temperature. Figure 2 shows the pressure dependence of oscillator strength of the D absorption band at three temperatures which is a parity-forbidden transition assigned to ${}^1\Gamma_1^+ \rightarrow {}^1\Gamma_5^+$.[3,11] The abrupt decrease observed under about 1.8 kbar at 2.0 K will respond to vanishing of the distortional term Q_d by applied pressures. That is, the phase transition from off-center to on-center (off-on transition) occurs at this point of pressure. The larger contribution of the term Q_v to the oscillator strength at higher temperature smears out the above abrupt decrease as shown in Fig. 2.

Assuming that the dipole matrix element M_{ab} in Eq. (1) does not change upon the off-on transition by pressure, the ratio of the oscillator strength f (off) at the off-center position to the f (on) at the on-center position is given by

$$R_f=\frac{f(\text{off})}{f(\text{on})}=\frac{\sum \langle |Q_{\text{odd}}^2| \rangle}{\sum \langle |Q_v^2| \rangle} , \tag{2}$$

where

$$Q_{\text{odd}}^2=Q_d^2+Q_v^2 . \tag{3}$$

Here, the off-center displacement is only taken into account as Q_d and for the time, is considered to lie isotropically. At sufficiently low temperature, the term Q_v is given by the average fraction in zero-point vibration,

$$\langle |Q_v^2| \rangle=\frac{\hbar}{2\mu\omega} , \tag{4}$$

where μ is the mass of the Cu^+ ion and ω relevant phonon frequency which will be adopted from the resonant mode because it has a large amplitude on the defect ion and may strongly contribute to the oscillator strength of

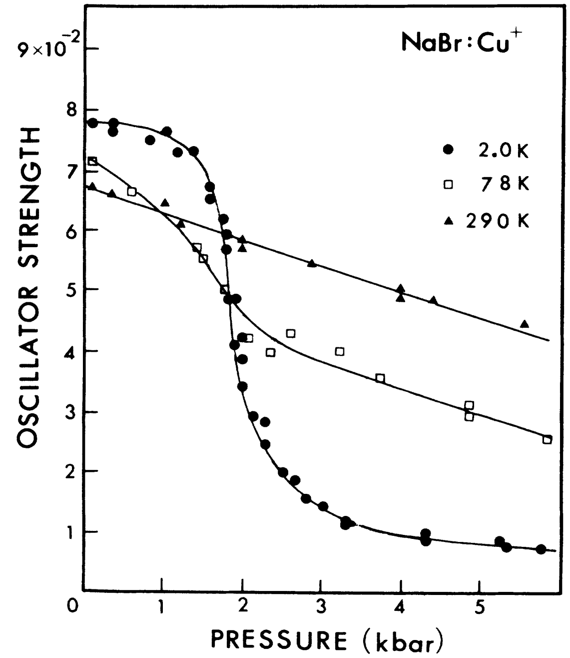

FIG. 2. Hydrostatic pressure dependence of the oscillator strength of the D absorption band in NaBr:Cu^+ at selected temperatures 2.0, 78, and 290 K.

the D absorption band. The resonant mode in NaCl:Cu$^+$ is found at 23.6 cm^{-1}.[12,13] This frequency may be taken as that of resonant mode in NaBr:Cu$^+$ under 8.2 kbar; it is because the Cu$^+$ ion in the above circumstances is considered to be in the almost same adiabatic potential as the Cu$^+$ ion in NaCl at atmospheric pressure. This situation is afterwards described in detail with the temperature dependence of the oscillator strength under various pressures. Then $\langle |Q_v^2| \rangle$ for NaBr:Cu$^+$ under 8.2 kbar is 1.13×10^{-18}cm^2.

As known well, the oscillator strength $f(T)$ of the absorption band assisted by the phonon that has essentially the temperature dependence of the hyperbolic cotangent type, i.e., $f(T)=f(0)\coth(\hbar\omega/2k_BT)$, is linearly proportional to temperature at a high-temperature region, and this asymptote crosses zero at absolute-zero temperature. However, the asymptote of the experimental curve under 14.8 kbar does not drop to zero (see Fig. 6). The residual value is rather large. It cannot be ascribed to an electric quadrupole transition or a magnetic-dipole transition. It could be attributed to the distortion of six ligand halide ions with odd symmetry. It should be subtracted from the experiment value because we must use the net ratio of the oscillator strength change upon the off-on transition to estimate the off-center distance. Thus we get 28 for R_f.

$$Q_d=[(R_f-1)\langle\,|Q_v^2|\,\rangle]^{1/2}=0.5_5\ \text{Å}\ . \tag{5}$$

This experimental value should be referred to the value calculated with CTE theory by Nagasaka.[14,15] From Fig. 6 in Ref. 15 the displacement along the $\langle 110\rangle$ or the $\langle 111\rangle$ axis is read out as 0.532 Å with the Na—Br bond length of 2.99 Å. The agreement is excellent.

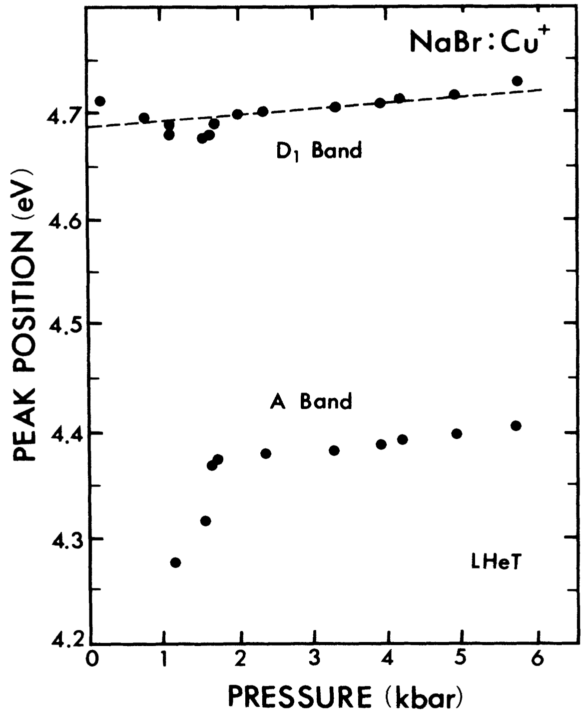

FIG. 3. Pressure dependence of the peak positions of the D_1 and A absorption bands at liquid-helium temperature. The A absorption band appears on the low-energy side of the D_1 absorption band on the off-on transition (see Ref. 8).

B. Estimation of the depth of the off-center valley

We will try to estimate the depth of the off-center valley from the change of the D_1 absorption peak by hydrostatic pressure. The D_1 absorption peak does not monotonously shift in contrast with usual blue shift of the on-center systems. Figure 3 shows the pressure shifts of the D_1 absorption band at liquid-helium temperature. It displays first red shift and then blue shift, while the peak shifts only to the higher energy at the rate of 6.7±0.7 meV at a temperature at which the thermal motion of the Cu$^+$ ion exceeds the off-center valley. It is the probable reason for the linear blue shift at higher temperature that the Cu$^+$ ion does not feel the off-center potential. The turning pressure from the red shift to the blue shift virtually coincides with the off-on transition pressure.

Drickamer and Frank,[16] and Drickamer, Frank, and Slichter[17] expressed pressure shift of the absorption peak with a linear term of hydrostatic pressure. For the shallow off-center system, we can briefly present the expression of the peak shift by adding an off-center term g to Drickamer's expression as follows:

$$E(p)=E_0+V_e(Q_d)+Ap+g\ , \tag{6}$$

or

$$dE(p)=E(p)-E_0-V_e(Q_d)=Ap+g\ , \tag{7}$$

where

$$g=\begin{cases} f(p), & p<p_c\ ,\\ 0, & p>p_c\ .\end{cases} \tag{8}$$

Here, E_0 is a transition energy at an origin of the normal coordinate and $V_e(Q_d)$ the energy measured from E_0 at the off-center displacement Q_d of the adiabatic potential $V_e(Q)$ in the excited state. The terms E_0, $V_e(Q_d)$, and g, are indicated in Fig. 4. It is assumed that $V_e(Q_d)$ is not changed by pressure in spite of the change of Q_d under pressure. The validity of the assumption is described below. A, which is related to a configuration coordinate and a force constant of an adiabatic potential in the ground and excited state,[16] is assumed to be constant. The off-center term g will be expressed adequately by a monotonically decreasing function $f(p)$ of pressure p, and responds only to the change of the ground-state potential, since the adiabatic potential in the relevant excited state of NaBr:Cu$^+$ is found to be an on-center type with a strong anharmonicity.[18,19] Therefore, g is effective until the off-on transition pressure p_c. We need not know the function $f(p)$ in detail. Since the hydrostatic pressure is totally symmetric, the term Ap acts only in A_{1g} space and gives a linear blue shift for the absorption band.

The red shift of the D_1 absorption peak could be responsible for g. At p_c, the off-center valley vanishes and consequently g drops to zero. Under higher pressure than p_c, the peak represents a linear blue shift at the rate of 5.7±0.6 meV/kbar at 4.2 K, i.e., $A=5.7\pm0.6$

meV/kbar. The extrapolation of this blue shift to zero applied pressure reaches 4689 meV. It is depicted with a broken line in Fig. 3. The difference 25±3 meV between the peak energy at atmospheric pressure and 4689 meV gives the value of g that corresponds to the depth of the off-center valley. According to Nagasaka's theory,[14,15] the temperature $T_{\min}$ at which the oscillator strength of the D absorption band is a minimum is related to the depth of the off-center valley dV as $dV = k_B T_{\min}$, where k_B is Boltzmann's constant. Then we can obtain the energy depth of 18±1 meV from the curve 1 in Fig. 6. This discrepancy is out of error range. In the latter case, the zero-point vibration is not taken into account to estimate the depth. Hence, this value of 18 meV corresponds to the potential barrier energy measured from the zero-point energy level. In contrast with it, the value of 25±3 meV obtained from the pressure shift of the D_1 absorption peak refers to the potential barrier energy from the bottom of the off-center potential. The difference of 7±4 meV corresponds to the zero-point vibrational energy of the Cu$^+$ ion. We can expect to find the resonance mode NaBr:Cu$^+$ system in the range 6 to 22 meV.

There exists another contribution to the initial red shift of the D_1 absorption peak. The slight and gradual decrease of the oscillator strength under the initial pressure as shown in Fig. 2 has its origin in a small movement of the Cu$^+$ ion toward the lattice site, which makes the transition energy to the optically excited state reduce by $dV_e = V_e(Q_d) - V_e(Q_d')$ $(Q_d > Q_d')$, in T_{1u} space. It is difficult to evaluate the dV_e because the adiabatic potential function in the excited state is not known precisely. However, the dV_e may be small to be covered in our experimental error, since the decrease of Q_d will be small up to the off-on transition pressure. Furthermore, the measurements of the life time by Piccirilli and Spinolo,[18] and Bertoloccini *et al.*[19] show very strong biquadratic anharmonic potential in the excited state. This strong biquadratic potential could become less biquadratic and finally harmonic as increases the applied pressure, as observed in the ground state,[7,8] making the optically excited state push up higher and resulting in the blue shift. These two kinds of the pressure effects cancel each other for the pressure shift of the D_1 absorption band. This situation can be seen schematically in Fig. 4.

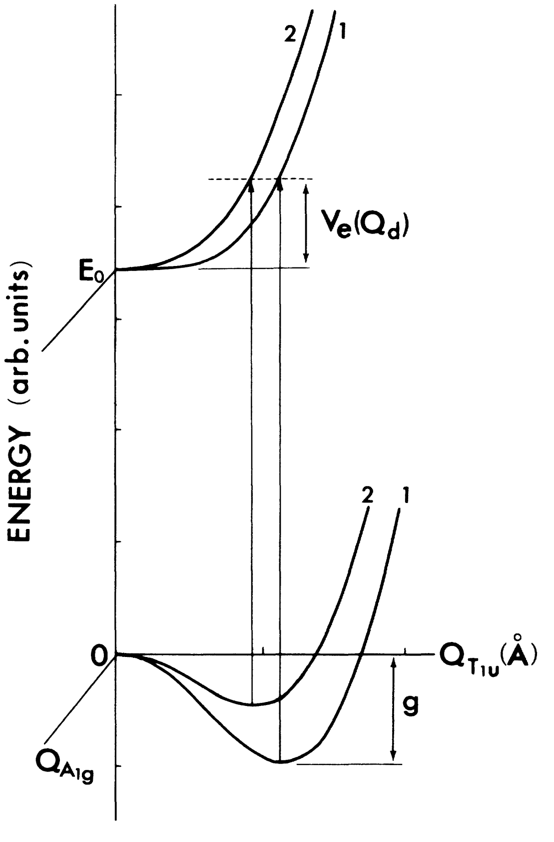

FIG. 4. Schematic explanation of the potential energy change for both the ground state and the excited state in T_{1u} space due to applied pressure. Curve 1 stands for the potential energy at atmospheric pressure and curve 2 under applied pressure. The optical final energy is depicted to be equal for two cases. The change of the potential in A_{1g} space (Ap) is omitted to avoid the confusion of schema.

Across the transition pressure, the absorption peak uniquely shifts in a unique fashion. The oscillator strength around the transition pressure shows a temperature dependence like a cubic function with one maximum and one minimum at temperatures lower than 100 K. This suggests that the Cu$^+$ ion is in a complicated potential around the transition pressure.

C. Off-center direction

The amount 0.5_5 Å of the off-center distance is a very interesting value in the view-point of a nearest-neighbor distance. Figures 5(a) and 5(b) illustrate the situation for the Cu$^+$ ion in NaBr with three possible different off-center displacements along the $\langle\bar{1}00\rangle$ axis, the $\langle 110\rangle$ axes, and the $\langle 111\rangle$ axes. Figure 5(a) illustrates the cross-sectional view in the (100) plane and 5(b) the cross-sectional view in the (110) plane. The framework built with Br$^-$ and Na$^+$ is illustrated just as it is in host crystal, and the Cu$^+$ ion is located at the position of 0.5_5 Å apart from the lattice site along each axis. Here the radii of Br$^-$, Na$^+$, and Cu$^+$ ions are chosen as 1.95, 0.98, and 0.96 Å, respectively, and a lattice constant of NaBr is chosen as 5.98 Å. The exact value of the ionic radius is not necessary for these considerations.

As seen in the figures, the overlap of the ionic radii of Cu$^+$ and Br$^-$ ions is recognized, implying that the partial covalent bonding arises between Cu$^+$ ion and Br$^-$ ions. The largest overlap is seen in the case along the $\langle\bar{1}00\rangle$ axis. In this case, the nearest-neighbor distance, i.e., Cu—Br bond length, is about 2.44 Å close to Cu—Br bond length of 2.464 Å in CuBr. When the displacement would occur along the $\langle 110\rangle$ axes and along the $\langle 111\rangle$ axes, the nearest Cu-Br distances are 2.63 and 2.71 Å, respectively.

The recent experimental results of EXAFS (extended x-ray-absorption fine-structure) gives an interesting aspect on the bond length in solid solution. For example, on the dilute limit in $In_xGa_{1-x}As$ alloy semiconductor[20-22] with zinc-blende structure, the deviation of In—As bond length in GaAs:In from the bond length of In—

As in InAs is only quarter of the difference between In—As bond length in InAs and Ga—As bond length in GaAs, and on the dilute limit in a rock-salt structure the deviation is half.[23] Adopting the above results to our case, as the difference of bond length between Cu—Br (2.464 Å) in CuBr and Na—Br (2.99 Å) in NaBr is 0.53 Å, the Cu—Br distance in NaBr in the dilute solution will take either 2.60 or 2.73 Å depending on the local structure of zinc-blende-like type or rock-salt-like type which is taken by the Cu^+ ion in NaBr. In any case, the displacement of 0.5_5 Å along the $\langle 100 \rangle$ axis makes the Cu^+ ion too close to the Br^- ion. These distances of 2.60 and 2.73 are close to the Cu—Br distances on the off-center displacement of 0.5_5 Å along the $\langle 110 \rangle$ and the $\langle 111 \rangle$ axis, respectively. Accordingly, the Cu^+ ion will displace either along the $\langle 110 \rangle$ axis or along the $\langle 111 \rangle$ axis. The $\langle 111 \rangle$ direction seems to be more desirable than the $\langle 110 \rangle$ direction from a standpoint of covalent bonding between Cu^+ and Br^- ions, because the Cu^+ ion overlaps with three Br^- ions on displacing along the $\langle 111 \rangle$ axis.

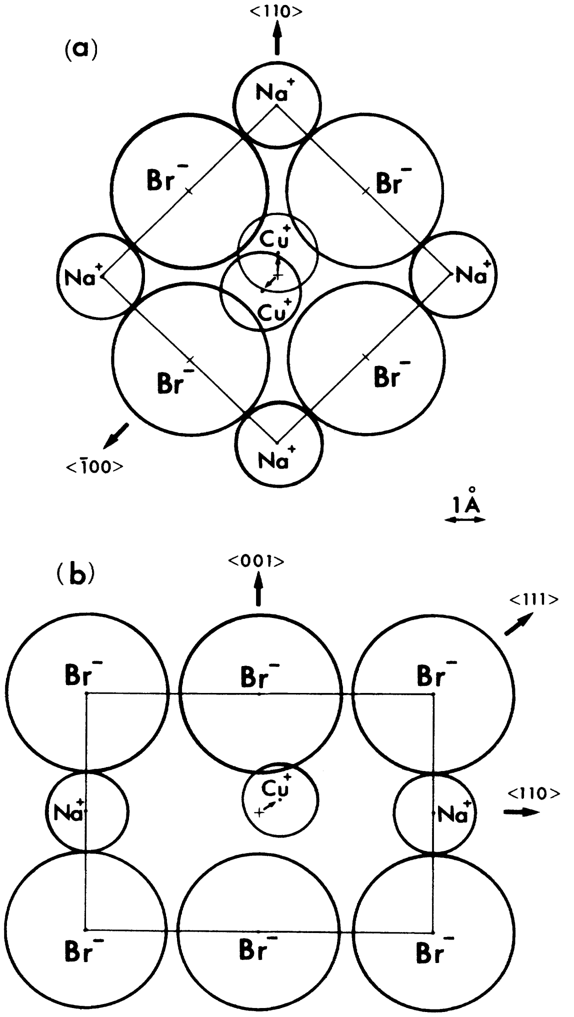

FIG. 5. Illustration of the off-center displacements in NaBr framework. (a) A cross-sectional view in the (100) plane , in which two different directions of the off-center displacement of 0.5_5 Å are presented. (b) A cross-sectional view in the (110) plane, in which the displacement of 0.5_5 Å along the $\langle 111 \rangle$ axis is presented.

Our preliminary analysis[24] of the fluorescent EXAFS at 50 K presents a favorable sight to the $\langle 111 \rangle$ direction. A peak at the distance from the lattice center to the Br^- ion does not appear. That will be negative evidence for the existence of the central valley.

IV. CHANGE OF THE OFF-CENTER TYPE

Figure 6 shows the temperature dependence of the oscillator strength of the D absorption band in NaBr:Cu^+ under various pressures up to 14.8 kbar. Nagasaka[14,15] introduces an instability parameter α determining the off-center type in his charge-transfer excitation (CTE) theory. This α is defined as $B/2k\varepsilon$ where B is an electron-lattice coupling constant for a T_{1u} type lattice distortion, k the bare force constant, and 2ε energy separation between the ground state and the charge transfer state. In NaBr:Cu^+, α is estimated to be 0.56 at atmospheric pressure and at 0.44 under 8.2 kbar which is almost the same value as the value of NaCl:Cu^+ at atmospheric pressure. The slight and gradual decrease of the oscillator strength under low pressure results from the gradual decrease of parameter (see Fig. 2). This situation is also supported from the fact that the temperature $T_{\min}$ at which the oscillator strength is a minimum, which is related to the depth of the potential valley as described in Sec. III B, becomes lower with increasing pressure as shown in Fig. 6. In Fig. 7, corresponding data for $f(T;P)$ for NaCl:Cu^+ are represented. The oscillator strength at atmospheric pressure shows a temperature dependence proportional to $\sqrt{T}$, indicating that the bi-

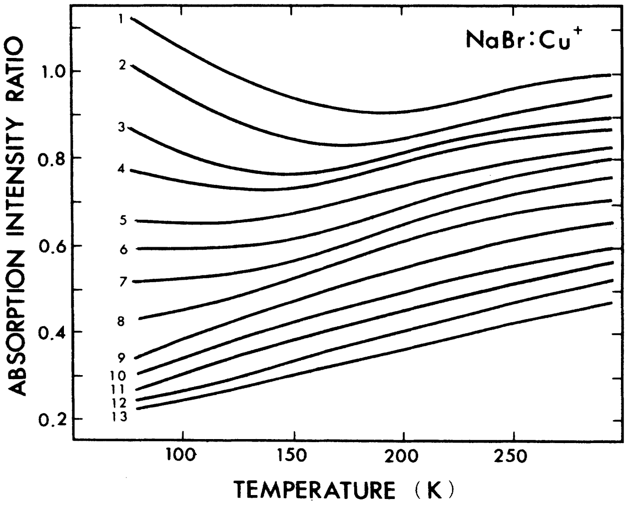

FIG. 6. Temperature dependence of the intensity of the D absorption band in NaBr:Cu^+ under fixed pressures. The absorption intensity at 300 K at atmospheric pressure is normalized to the one that corresponds to the oscillator strength of 0.067. Pressures for each curve are given as follows: 1, 1 atm; 2, 0.6 kbar; 3, 1.5 kbar; 4, 1.9 kbar; 5, 2.6 kbar; 6, 3.1 kbar; 7, 3.5 kbar; 8, 4.8 kbar; 9, 6.1 kbar; 10, 8.2 kbar; 11, 9.2 kbar; 12, 12.5 kbar; 13, 14.8 kbar.

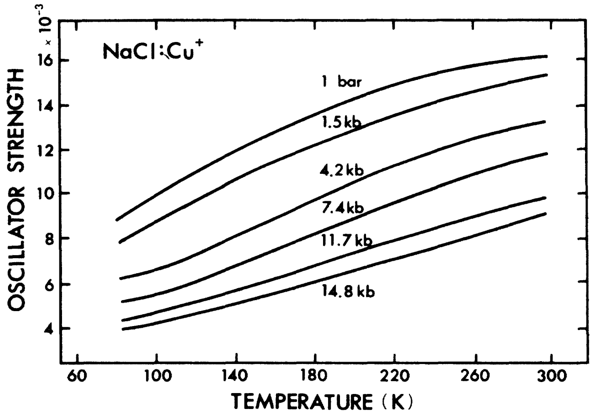

FIG. 7. Temperature dependence of the oscillator strength of the D absorption band in NaCl:Cu^+ under fixed pressures.

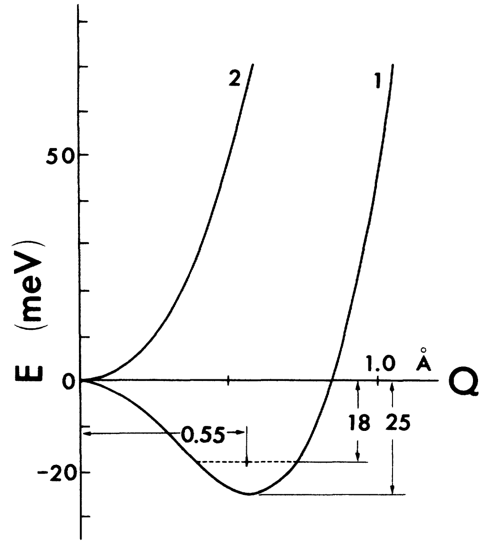

FIG. 8. Adiabatic potential energy for the Cu^+ ion in NaBr. Curve 1 stands for the adiabatic potential at atmospheric pressure and curve 2 under high pressure (~8 kbar). The abscissa denotes the displacement of the Cu^+ ion from lattice center along the ⟨111⟩ or the ⟨110⟩ axis. The broken line indicates the zero-point vibrational level of the Cu^+ ion.

quadratic anharmonicity (Q_v^4) is predominant in the adiabatic potential. This feature gradually changes to a linear relation $f \propto T$ with increasing pressure. The linear relation at high-temperature range is characteristic of type (a). A similar tendency is seen in NaBr:Cu^+ around the uppermost pressure studied here. Therefore, we can conclude that in NaBr:Cu^+ system the adiabatic potential is changed from the shallow off-center type to the harmonic on-center type under hydrostatic pressure, and that in the NaCl:Cu^+ system from the anharmonic on-center type to the harmonic on-center type.

V. SUMMARY

Hydrostatic pressure strongly affects the circumstances of the Cu^+ ion in NaBr crystal. We can quantitatively reveal the off-center parameters on the Cu^+ ion in NaBr with pressure effects of the oscillator strength and the absorption peak. From the change of the oscillator strength of the parity-forbidden D absorption band by hydrostatic pressure, we can estimate the off-center distance for NaBr:Cu^+ to be 0.5_5 Å, and from the pressure shift of the D_1 absorption band, the depth of the off-center valley to be 25±3 meV. The Cu—Br distance at the off-center position suggests that the ⟨110⟩ directions or the ⟨111⟩ directions are preferable to the ⟨100⟩ directions for the off-center displacement. The temperature dependence of the oscillator strength of the D absorption band in NaBr:Cu^+ varies with increasing pressure from the peculiar style, which takes a minimum value at 200 K, to the one ruled by simple function $\coth(\hbar\omega/2k_BT)$ for the usual forbidden transition, indicating that the adiabatic potential for the Cu^+ ion changes from the shallow off-center type to the harmonic on-center type passing through the anharmonic on-center type.

Hence, under the assumption of the rigid framework, the above quantitative result can be summarized in the scheme of the adiabatic potential energy depicted in Fig. 8, where two kinds of adiabatic potential are represented. One (curve 1) stands for the adiabatic potential at atmospheric pressure and the other one (curve 2) under high pressure (~8 kbar). The latter potential with a strong biquadratic anharmonicity is almost the same as that for the Cu^+ ion in NaCl at atmospheric pressure. These potential curves are depicted following Eq. (2.5) in Ref. 14.

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