DULT-W 69-0510

	$v = 4$		
$1/\sqrt{2}$	1	2	5
$< 0,1$			
0,19	0,15	0,10	0,1
0,44	0,39	0,27	0,15
0,38	0,34	0,23	0,13
0,57	0,45	0,31	0,18
$< 0,1$			

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Physikalisches Institut der Johann-Wolfgang-Goethe-Universität, Frankfurt/Main

Uniaxial Stress Effects on Parity-Forbidden Transitions in NaCl:Cu$^+$ and KCl:Ag$^+$

By

W. Dultz

The temperature dependence of the stress-induced dichroism in the UV absorption bands of NaCl:Cu$^+$ and KCl:Ag$^+$ is investigated. The experiments are explained by a frequency splitting of the IR active resonance mode and an off-centre displacement of the defect in the excited state. The value of the quadratic electron–lattice interaction is determined.

Die Temperaturabhängigkeit des durch axialen Druck verursachten Dichroismus in den UV-Banden von NaCl:Cu$^+$ und KCl:Ag$^+$ wird untersucht. Die Experimente lassen sich durch eine Frequenzaufspaltung der IR-aktiven Resonanzschwingung und durch eine „off-centre"-Verschiebung der Störstelle im angeregten Zustand erklären. Der Wert der quadratischen Elektron–Gitter-Wechselwirkung wird bestimmt.

1. Introduction

The UV absorption bands of Cu$^+$ and Ag$^+$ in alkali halides show a characteristic temperature dependence, which was carefully investigated by Fußgänger et al. [1, 2]. The defect ion replaces a cation on a normal lattice site with point symmetry O_h. The electronic transitions have been interpreted as parity-forbidden electric dipole transitions $(n-1)\,d^{10} \rightarrow (n-1)\,d^9 n\,s$ ($n = 4$ for Cu$^+$, $n = 5$ for Ag$^+$). Odd parity lattice modes destroy the inversion symmetry of the defect and the transitions become allowed by mixing of even and odd electronic states [3]. Observed deviations from the expected temperature dependence of the oscillator strength gave further information about the defect properties. In NaCl:Cu$^+$ a small "off-centre" displacement of the Cu$^+$ ion in the lattice cell and a thermal contraction of the cell at higher temperature has been proposed [1, 4]. In KCl:Ag$^+$ two phonon processes in the high-temperature range cause an additional increase of the oscillator strength proportional to the square of the temperature [2].

To investigate the interactions of the defect electrons with cubic distortions of the lattice, the UV absorption of NaCl:Cu$^+$ was measured under hydrostatic pressure at room temperature [4] using a method due to Drickamer [5]. Under a hydrostatic pressure of 1 kbar, the relative shift of the peak energy $\Delta E/E$ was found to be 1.5×10^{-3} and a small decrease of the oscillator strength was observed [4]. In the present work we report on the effects of uniaxial stress (interactions with noncubic distortions of Γ_3^+- and Γ_5^+-symmetry) on the UV bands of NaCl:Cu$^+$ and KCl:Ag$^+$ at different temperatures.

2. Measurements

We measured the difference in the absorption constant K for light polarized parallel and perpendicular to the stress axis by a rotating polarizer using a lock-in technique [6, 7]. The size of the samples was about $7 \times 5 \times 1$ mm^3. To avoid

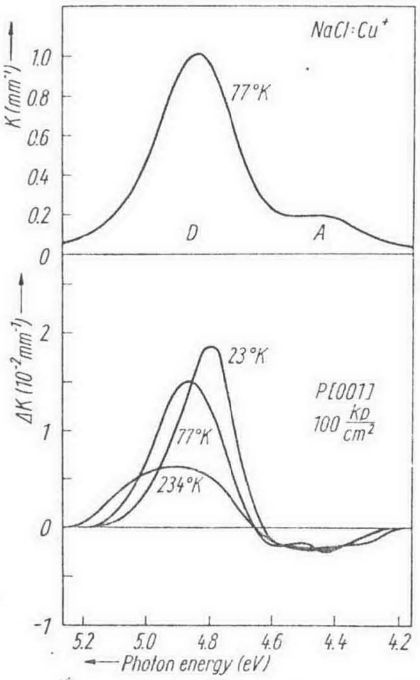


Fig. 1. Absorption constant K and its change ΔK under [001] stress versus photon energy for NaCl:Cu$^+$

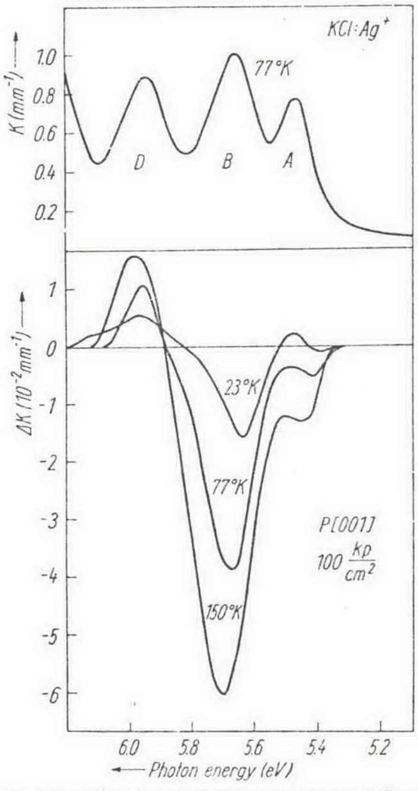


Fig. 2. Absorption constant K and its change ΔK under [001] stress versus photon energy for KCl:Ag$^+$

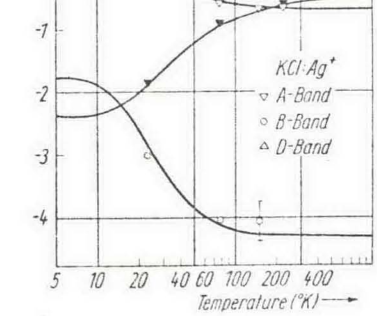
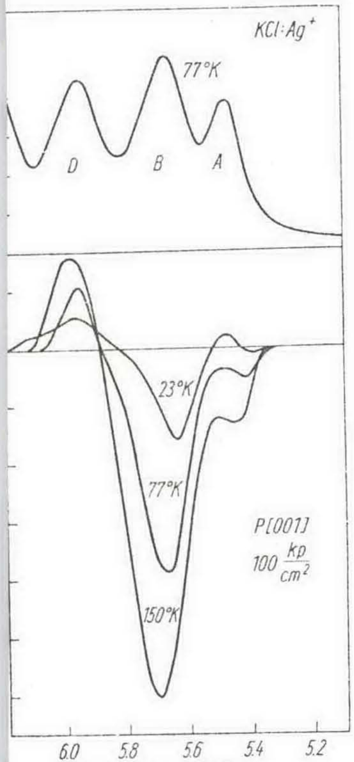


Fig. 3. Change of oscillator strength $f_{\|} - f_{\perp}$ normalized to the oscillator strength f plotted versus temperature

the formation of aggregate centres the samples were held for a few minutes at about 100 °K below the melting point and then quenched to room temperature.

The upper part of Fig. 1 shows the UV absorption of NaCl:Cu$^+$ at 77 °K. The main band at 4.8 eV, called the D-band, corresponds to a transition $\Gamma_1^+ \rightarrow \Gamma_5^-$. In the small shoulder at 4.5 eV, called the A-band, the two transitions $\Gamma_1^+ \rightarrow \Gamma_3^+$ and $\Gamma_1^+ \rightarrow \Gamma_5^+$, or briefly $\Gamma_1^+ \rightarrow \Gamma_3^+, \Gamma_5^+$, contribute to the absorption. $\Gamma_\alpha^\pm$ denotes the transformation properties of the unperturbated electronic states of the defect under the elements of the point group O_h. When uniaxial stress



orption constant K and its change ΔK un-
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is applied to the crystal the absorption constants $K_{\|}$ and $K_{\perp}$ measured with light polarized parallel and perpendicular to the stress axis are different. This difference $\Delta K = K_{\|} - K_{\perp}$ is plotted versus spectral energy for [001] stress in the lower part of Fig. 1. A comparison of $\Delta K(E)$ with the absorption spectrum $K(E)$ in the upper part of Fig. 1 shows that the change of the oscillator strength under applied stress is the dominant effect, whereas a shift of the bands due to a splitting of the excited states is negligible. ΔK is a linear function of the stress. We also note that ΔK differs in sign for the two bands.

Fig. 3 summarizes the temperature dependence of the stress effects. The oscillator strength $f(T)$ for a single band is found from a Gauss-curve analysis using the data of Fußgänger [1]. We find that $\Delta f/f = (f_{\|} - f_{\perp})/f$ has the same sign for corresponding bands in NaCl:Cu$^+$ and KCl:Ag$^+$. To explain sign and temperature dependence of $\Delta f/f$ we will discuss three effects: 1. a frequency splitting of the far IR resonance mode, 2. a small off-centre distortion of the defect, and 3. a quadratic electron–lattice interaction. We will show in the discussion of the experimental data that all three effects contribute to the observed dichroism, but the main contribution comes from the first and second effects mentioned above.

3. Theory

To investigate the interaction between the electronic states of the defect and the ionic displacements, it is convenient to classify the electronic wave functions and the normal coordinates $Q(l)$ of the perturbed lattice according to their transformation properties under the elements of the point group of the defect site. For well localized defects it is sufficient to consider the interaction within the octahedral complex Ag$^+$(Cl$^-$)$_6$ or Cu$^+$(Cl$^-$)$_6$ and introduce the symmetry coordinates $q_{\alpha i}$ of the complex which are basis functions of the irreducible representations Γ_α of O$_h$ (i denotes the row index). Small deviations from O$_h$-symmetry due to lattice vibrations and static distortions (Jahn-Teller effect, off-centre displacement) of the lattice cell will be treated as perturbations. The symmetry coordinates $q_{\alpha i}$ are linear combinations of the normal coordinates $Q(l)$ of the perturbed lattice:

$$q_{\alpha i} = \sum_l c_{\alpha i}(l)\, Q(l)\,. \tag{1}$$

Each symmetry coordinate is associated with a distortion with a potential energy $\frac{1}{2}\,\omega_\alpha^2\, q_{\alpha i}^2$ where ω_α is an effective frequency of the complex.

The Hamiltonian H of the system

$$H = H_e + H_l + H_{el} \tag{2}$$

consists of the Hamiltonian of the defect electrons H_e, the lattice Hamiltonian H_l, and the operator of the electron–lattice interaction H_{el}. We expand the electron lattice interaction in the Hamiltonian in terms of the symmetry coordinates $q_{\alpha i}$, taking linear (equation (3a)) and quadratic terms (equation (3b)) into account:

$$H_{el} = H_1 + H_2\,, \tag{3}$$

$$H_1 = \sum_{\alpha, i} V_{\alpha i}^{-}(\boldsymbol{r})\, q_{\alpha i}^{-}\,, \tag{3a}$$

$$H_2 = \sum_{\alpha, i} \sum_{\beta, j} V_{\alpha i \beta j}^{-}(\boldsymbol{r})\, q_{\alpha i}^{-}\, q_{\beta j}^{+} + \cdots\,. \tag{3b}$$

$\boldsymbol{r}$ denotes the set of electronic coordinates and the upper sign the parity of the distortion. $V_{\alpha i}^{-}(\boldsymbol{r})$ has the same transformation properties as the i-th basis function of Γ_{α}^{-}, and $V_{\alpha i \beta j}^{-}(\boldsymbol{r})$ transforms as the product $q_{\alpha i}^{-} \times q_{\beta j}^{+}$. In this approach no other terms of the same order in the distortions $q_{\alpha i}$ contribute to our effects.

The zeroth-order electronic wave function $\psi_{\mu i}$ is an eigenfunction of H_{e}. $\psi_{\mu i}$ describes the electronic state in the static complex and is the i-th basis function of the μ-th irreducible representation. Taking H_{e1} as a perturbation and the ionic displacements $q_{\alpha i}$ as parameters, we obtain a mixing between even and odd electronic states $\psi_{\mu i}$ of the defect:

$$\psi_{\mu i}' = \psi_{\mu i}^{+} + \sum_{\nu, j} \frac{\langle \psi_{\nu j}^{-} | H_{\mathrm{el}} | \psi_{\mu i}^{+} \rangle}{E_{\mu} - E_{\nu}} \psi_{\nu j}^{-} . \tag{4}$$

The electronic wave functions $\psi_{\mu j}'(q_{\alpha i})$ and the energies $E_{\mu j}(q_{\alpha i})$ are now functions of the lattice distortions $q_{\alpha i}$. The nuclear wave functions $\chi_{k}^{\mu j}(q_{\alpha i})$ are eigenfunctions of $H_{1} + E_{\mu j}(q_{\alpha i})$, where k denotes the set of nuclear quantum numbers. The wave functions of the system are products of $\psi_{\mu j}'$ and $\chi_{k}^{\mu j}$ [10]:

$$\Psi_{\mu j}^{k} = \psi_{\mu j}' \chi_{k}^{\mu j} . \tag{5}$$

The oscillator strength f of the electronic dipole transition between the ground state ψ_{0} and the excited state ψ_{μ}' is given by [10]

$$f_{0 \mu} = \frac{2}{3} \frac{m^{*}}{\hbar^{2}} \bar{\varepsilon}_{0 \mu} \, \mathrm{Av}_{0} \sum_{i} \left| \langle \psi_{0} | \sum_{j=1}^{z} \boldsymbol{r}_{j} | \psi_{\mu i}' \rangle \right|^{2} . \tag{6}$$

m^{*} denotes the effective mass of the electron, $\bar{\varepsilon}_{0 \mu}$ the mean energy of the transition, $\boldsymbol{r}_{j}$ the electric dipole operator, and Av_{0} the thermal average over the ground state.

For the present we take only the linear term (3a) of H_{el} into account. We insert (4) into (6) and take the thermal average of products of the form $q_{\alpha i} q_{\beta j}$. Since we consider static and dynamic distortions of the lattice cell, each ionic displacement $q_{\alpha i}$ consists of a static part $Q_{\alpha i 0}$ and a dynamic part $Q_{\alpha i}$:

$$q_{\alpha i} = Q_{\alpha i} + Q_{\alpha i 0} . \tag{7}$$

Using the orthogonality of the symmetry coordinates $q_{\alpha i}$ of the complex we obtain

$$\begin{aligned} \langle q_{\alpha i} q_{\beta j} \rangle &= \langle Q_{\alpha i} Q_{\beta j} + Q_{\alpha i} Q_{\beta j 0} + Q_{\alpha i 0} Q_{\beta j} + Q_{\alpha i 0} Q_{\beta j 0} \rangle = \\ &= \langle Q_{\alpha i} Q_{\beta j} \rangle \delta_{\alpha \beta} \delta_{i j} + Q_{\alpha i 0} Q_{\beta j 0} . \end{aligned} \tag{8}$$

In analogy to the Jahn-Teller effect, the $Q_{\alpha i 0}$ are the coordinates of the potential minima of the total energy of the complex including the linear electron–lattice interaction, but in contrast to the even-parity Jahn-Teller distortions, we only consider off-centre displacements with odd parity which do not contribute to the energy in first order. In linear approximation only distortions of odd parity contribute to the oscillator strength f of the transition. The octahedral complex has two threefold odd vibrations of Γ_{4}^{-}-symmetry and one threefold degenerate odd vibration of Γ_{5}^{-}-symmetry. Since IR resonance modes were observed in NaCl:Cu^{+} and in KCl:Ag^{+} we neglect effects from Γ_{5}^{-}-modes and assume that only one Γ_{4}^{-}-mode ($q_{4 i}^{-}$) contributes to the parity breaking effect. $\underset{\sim}{Q}_{4 0}^{-} = (Q_{4 x 0}^{-}, Q_{4 y 0}^{-}, Q_{4 z 0}^{-})$ is called an off-centre distortion of the defect. We take the average of all the possible off-centre positions in the lattice cell:

$$\begin{aligned} \mathrm{Av(off\text{-}centre)} \; Q_{4 i 0}^{-} Q_{4 j 0}^{-} &= \frac{1}{N} \sum_{\text{off-c.}} Q_{4 i 0}^{-} Q_{4 j 0}^{-} = \\ &= Q_{4 i 0}^{2} \delta_{i j} = Q_{4 j 0}^{2} \delta_{i j} = \frac{1}{3} Q_{0}^{2} \delta_{i j} . \end{aligned} \tag{9}$$

uct $q^-_{\alpha i} \times q^+_{\beta j}$. In this approach
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$\frac{_{\mu i}^{+}\rangle}{_{\nu}} \psi^-_{\nu j}$. (4)

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(5)

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$\sum_{=1}^{z} r_j \, |\psi'_{\mu i}\rangle \Big|^2$. (6)

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$_0 Q^-_{4 j 0} =$

$Q^2_{4 j 0} \, \delta_{ij} = \frac{1}{3} Q_0^2 \, \delta_{ij}$. (9)

N is the number of possible off-centre positions. Q_0 may be called the off-centre displacement, but note that it does not necessarily describe a static displacement of the defect ion.

Inserting (5), (7), and (8) into (6) we obtain for the oscillator strength

$$\begin{aligned} f_{\Gamma_1^+ \to \Gamma_4^+ (\Gamma_5^+)} &= A^2_{4(5)} \{\eta_x^2 (\langle Q^2_{4y}\rangle + \langle Q^2_{4z}\rangle) + \text{cyclic terms}\} + \\ &+ A^2_{4(5)} \{\eta_x^2 (Q^2_{4y0} + Q^2_{4z0}) + \text{cyclic terms}\} \,, \end{aligned} \tag{10}$$

$$\begin{aligned} f_{\Gamma_1^+ \to \Gamma_3^+} &= A_3^2 \{\eta_x^2 \langle Q^2_{4x}\rangle + \text{cyclic terms}\} + \\ &+ A_3^2 \{\eta_x^2 Q^2_{4x0} + \text{cyclic terms}\} \,. \end{aligned} \tag{11}$$

A_3, A_4, and A_5 are constants, depending on the excited state of the transition. $\eta = (\eta_x, \eta_y, \eta_z)$ is the unit vector of polarization. The first expression describes transitions from a nondegenerated state Γ_1^+ to the orbital triplet states Γ_4^+, Γ_5^+, the second one transitions to an orbital doublet state Γ_3^+. The second term represents the effect of the off-centre potential. Without stress the expressions (10) and (11) are isotropic in the polarization, because the mean square amplitudes of the lattice vibrations are equal in each direction:

$$\langle Q^2_{4i}\rangle = \langle Q^2\rangle = \frac{\hbar}{2\,\omega} \coth \frac{\hbar\,\omega}{2\,kT} \approx \begin{cases} \dfrac{kT}{\omega^2} & \text{for} \quad kT \gg \hbar\,\omega \,, \\[2ex] \dfrac{\hbar}{2\,\omega} & \text{for} \quad kT \ll \hbar\,\omega \,. \end{cases} \tag{12}$$

Inserting (12) into (10) and (11) we obtain the temperature dependence of the oscillator strength [2].

Uniaxial stress lifts the degeneracy of the resonance mode and we get different vibrational frequencies and different off-centre distortions parallel and perpendicular to the stress axis. As an example Fig. 4 shows the splitting of

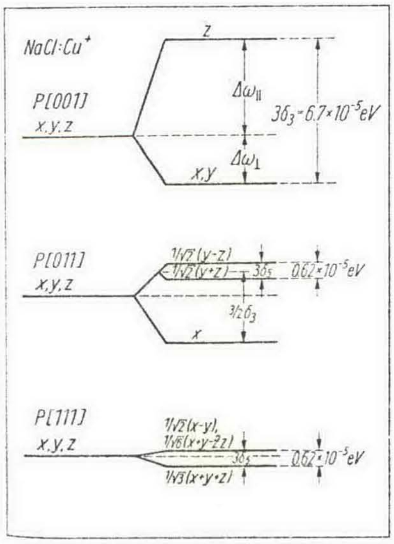


Fig. 4. Stress splitting of the local mode at 23.5 cm^{-1} in NaCl:Cu$^+$ at 4.3 °K. The applied stress is 100 kp/cm^2

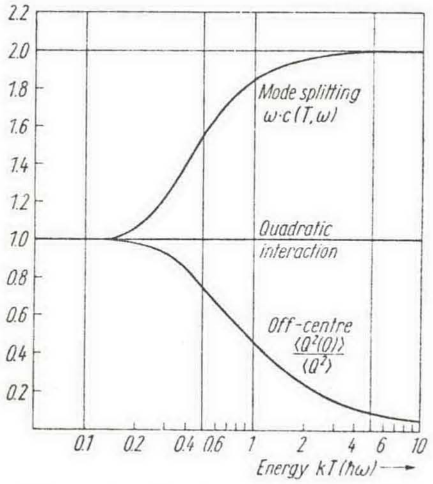


Fig. 5. Temperature dependence of the different effects contributing to $(f_{\|} - f_{\perp})/f$

the Γ_4^--resonance mode in NaCl:Cu$^+$ under uniaxial stress of 100 kp/cm^2 as taken from data given in reference [11]. The hydrostatic term of the stress Hamiltonian [12] does not enter into our formulas, since we only measure the effect of noncubic distortions. The frequency splitting changes the mean square amplitudes $\langle Q_{4\,i}^2\rangle$ as obtained from the derivative of equation (12):

$$\Delta\langle Q_{4\,i}^2\rangle = -\langle Q^2\rangle \left\{\frac{1}{\omega} + \frac{\hbar}{kT \sinh \dfrac{\hbar\,\omega}{kT}}\right\} \Delta\omega_i = -\langle Q^2\rangle\, c(T,\omega)\, \Delta\omega_i\,. \qquad (13)$$

ω is the frequency of the resonance mode, $\Delta\omega_i$ the frequency shift due to noncubic terms of the stress Hamiltonian. Fig. 5 shows the temperature dependence of $c(T,\omega)$. The high- and low-temperature limits are

$$c(T,\omega) \approx \begin{cases} \dfrac{2}{\omega} & \text{for} \quad kT \gg \hbar\,\omega\,, \\ \dfrac{1}{\omega} & \text{for} \quad kT \ll \hbar\,\omega\,. \end{cases} \qquad (14)$$

Inserting (13) into the derivative of (10) and (11) we obtain the expressions for $(f_{\parallel} - f_{\perp})/f$ (Table 1). Two effects contribute to $(f_{\parallel} - f_{\perp})/f = \Delta f/f$ in Table 1:

Table 1

Transitions	$P\,[001]$	$P\,[111]$	$P\,[011]$
${}^+_1\Gamma \to \Gamma_4^+, \Gamma_5^+$	$\frac{3}{2}\,c(T,\omega)\delta_3 - \frac{1}{2\langle Q^2\rangle} \times \{\Delta Q_{\parallel 0}^2 - \Delta Q_{\perp 0}^2\}$	$\frac{3}{2}\,c(T,\omega)\,\delta_5 - \frac{1}{2\langle Q^2\rangle} \times \{\Delta Q_{\parallel 0}^2 - \Delta Q_{\perp 0}^2\}$	$\frac{3}{2}\,c(T,\omega)\,\delta_5 - \frac{1}{2\langle Q^2\rangle} \times \{\Delta Q_{\parallel 0}^2 - \Delta Q_{\perp 0}^2\}$
$\Gamma_1^+ \to \Gamma_3^+$	$-3\,c(T,\omega)\,\delta_3 + \frac{1}{\langle Q^2\rangle} \times \{\Delta Q_{\parallel 0}^2 - \Delta Q_{\perp 0}^2\}$	$-3\,c(T,\omega)\,\delta_5 + \frac{1}{\langle Q^2\rangle} \times \{\Delta Q_{\parallel 0}^2 - \Delta Q_{\perp 0}^2\}$	$-3\,c(T,\omega)\,\delta_5 + \frac{1}{\langle Q^2\rangle} \times \{\Delta Q_{\parallel 0}^2 - \Delta Q_{\perp 0}^2\}$

δ_i, the energy splitting of the resonance mode corresponding to Fig. 4, and $\Delta Q_{\parallel 0}^2$, the change of the temperature independent $Q_{\parallel 0}^2$ by uniaxial stress. $Q_{\parallel 0}^2$ is defined by

$$Q_{\parallel 0}^2 = \frac{1}{N} \sum_{\text{off-c.}} (\boldsymbol{Q}_{40}\,\boldsymbol{\zeta})^2\,. \qquad (15)$$

$\boldsymbol{Q}_{40}$ is the displacement vector of the off-centre position and $\boldsymbol{\zeta}$ the unit vector parallel to the stress axis. $Q_{\perp 0}^2$ is defined in analogy to $Q_{\parallel 0}^2$.

The stress effect derived from the linear electron–lattice interaction (3a) in the Hamiltonian (Table 1) depends only on the energy splitting of the resonance mode and on the distortion of the lattice cell, but not on the matrix elements of the transition. The temperature dependence of the effect consists of two parts: the first part is proportional to $c(T, \omega)$ and therefore constant at high temperatures, the second part is due to the off-centre distortion and decreases with $1/T$ in the high-temperature range (Fig. 5).

Since the stress transforms as Γ_1^-, Γ_3^+, and Γ_5^+, all terms of the interaction Hamiltonian of the stress-distorted complex which are linear in q_1^+, q_{3i}^+, and q_{5i}^+ are changed. Having not observed a splitting of the absorption bands, we may neglect these terms in the linear electron–lattice interaction. In the quadratic electron–lattice interaction new terms appear, the transformation properties of which for stress in [001] direction are given by [13]

$$\begin{aligned} H_2 = {} & Q_{4x}^- \, \Delta Q_{3,1}^+ \left\{ -\frac{1}{2}\,(x) - \frac{\sqrt{3}}{2}\,(y\,z) \right\} V_{3,4} + \\ & + Q_{4y}^- \, \Delta Q_{3,1}^+ \left\{ -\frac{1}{2}\,(x) + \frac{\sqrt{3}}{2}\,(x\,z) \right\} V_{3,4} + \\ & + Q_{4z}^- \, \Delta Q_{3,1}^+ \, \{(z)\} \, V_{3,4} \, . \end{aligned} \tag{16}$$

$\Delta Q_{3,1}^+$ is the distortion coordinate of the lattice cell, and proportional to the applied stress. Using the same scheme which led to (10) and (11) we get mixed terms with (3a), being linear functions of stress. We obtain an additional term, which has to be added to the first column of Table 1:

$$\left. \begin{aligned} \frac{f_{\|} - f_{\perp}}{f} \bigg|_{\Gamma_1^+ \to \Gamma_4^+(\Gamma_5^+)}^{(3\,\mathrm{a})} &= \frac{3}{2}\,\frac{\alpha}{A}\,\Delta Q_{3.1}^+ = C_{4,5} \, , \\ \frac{f_{\|} - f_{\perp}}{f} \bigg|_{\Gamma_1^+ \to \Gamma_3^+}^{(3\,\mathrm{a})} &= -\,3\,\frac{\alpha'}{A'}\,\Delta Q_{3.1}^+ = C_3 \, . \end{aligned} \right\} \tag{17}$$

α, α' and A, A' are reduced matrix elements. We find that the relative change of the oscillator strength by uniaxial stress due to the quadratic electron–lattice interaction does not depend on temperature (Fig. 5), but in contrast to the effects of the linear electron–lattice interaction it depends on the matrix elements of the transition.

4. Discussion

We compare the absorption change ΔK of Fig. 1 and 2 with the theoretical expressions for the change of the zeroth moment stated in Table 1. The experimental values of ΔK, which are positive and negative, do not change sign within a single band. This leads to the conclusion that the main effect is due to linear electron–lattice interaction which clearly shows a difference in sign between Δf of a $\Gamma_1^+ \to \Gamma_3^+$ transition and Δf of $\Gamma_1^- \to \Gamma_4^+(\Gamma_5^+)$ transitions. Because of the transformation properties of the stress tensor, no distinction between Γ_4^+ and Γ_5^+ is possible by stress measurements.

We first discuss the B-band of KCl:Ag$^+$ assuming the resonance mode splitting to be the dominant effect. When a [001] stress of 100 kp/cm^2 is applied we find from this band a relative splitting $\Delta\omega/\omega = 2.5 \times 10^{-2}$ of the resonance mode at 38.8 cm^{-1}. The relative change of the oscillator strength for stress in [111] and [011] direction is smaller than 1/10 of the change for [001] stress, which implies a relative splitting of the resonance mode smaller than 2.5×10^{-3}. This is in good agreement with the small value of δ_5 (Fig. 4) found by Busse [11] in NaCl:Cu$^+$, and signifies a very weak interaction between the defect and the lattice for the Γ_5^+-component of the stress. The sign of the splitting $3\,\delta_3 = \omega_{\|} - \omega_{\perp}$ under [001] stress is assumed to be positive. This is consistent with the results of Nolt [14] for the splitting of the IR resonance in KI:Ag$^+$. With this sign of δ_3 we obtain the same assignments for the transitions in KCl:Ag$^+$ and NaCl:Cu$^+$ as reported in [4], [8], and [9]. Besides this we obtain the transition $\Gamma_1^+ \to \Gamma_3^+$ to be due to the A'-band (5.36 eV) in KCl:Ag$^+$ which is only separated from the A-band at low temperatures. In the A-band of both systems the $\Gamma_1^+ \to \Gamma_5^+$ transition partly compensates the effect of the $\Gamma_1^+ \to \Gamma_3$ transition. Taking the values of $\Delta\omega/\omega$ from the B-band we obtain for the A-band in KCl:Ag$^+$ the ratio of the oscillator strength $f_3/f_5 = 2.7$ which is smaller than $f_3/f_5 = 5$ obtained by Fröhlich et al. [9]. The results agree in that the $\Gamma_1^- \to \Gamma_3^+$ transition yields the larger contribution.

The quadratic electron–lattice-interaction term (17) is found to be 1 to 2×10^{-2} at 100 kp/cm^2 for each band (Table 2), but it has a negative sign for the D-bands. This is consistent with the fact that the quadratic electron–lattice interaction contributions to the oscillator strength of the transitions of Ag$^+$ in alkali halides could not be neglected [2].

Table 2

	Band	$\Delta\omega/\omega$	$\Delta Q_0^2/\langle Q^2(0)\rangle$	C	f_3/f_5
NaCl:Cu$^+$	A	2.34×10^{-2} *)	8.6×10^{-2} ***)	$+1.1 \times 10^{-2}$	1.2
	D	2.34×10^{-2} *)	8.6×10^{-2}	-2.2×10^{-2}	–
KCl:Ag$^+$	A	2.5×10^{-2} **)	0	$+2.3 \times 10^{-2}$	2.7
	B	2.5×10^{-2}	0	$+0.8 \times 10^{-2}$	–
	D	2.5×10^{-2} **)	6.3×10^{-2}	-2.7×10^{-2}	–

*) Obtained from [11].
**) Obtained from the stress effect of the B-band.
***) Obtained from the stress effect of the D-band.

So far we have not taken a static off-centre effect into account (second term in Table 1). If the off-centre effect dominates, $|\Delta f/f|$ decreases with temperature. The case of increasing $|\Delta f/f|$ is realized for the A- and B-band of KCl:Ag$^+$, whereas the A-band of NaCl:Cu$^+$ and the D-bands of both systems show the case of decreasing $|\Delta f/f|$ with temperature. For this reason we discuss these bands separately. To deduce the off-centre effect we calculate the δ_3-effect of NaCl:Cu$^+$ using the resonance mode splitting as obtained from reference [11]. For KCl:Ag$^+$ we already obtained the δ_3-effect from the analysis of our measurements of the B-band. Subtracting the δ_3-effect we find $\Delta Q_0^2 = |\Delta Q_{\|0}^2 - \Delta Q_{\perp 0}^2|$ for a stress of 100 kp/cm^2 to be 6% for KCl:Ag$^+$ and 9% for NaCl:Cu$^+$ of the square of the vibrational amplitude of the resonance mode at $T = 0$ °K (Table 2). At stresses of about 2000 kp/cm^2 a nonlinear behaviour should be expected. To test this prediction measurements of the bands under high hydrostatic pressure at low temperatures are in progress. Taking the values of $\Delta\omega/\omega$ and $\Delta Q_0^2/\langle Q^2(0)\rangle$ from Table 2 we obtain the ratio f_3/f_5 for the A-band in NaCl:Cu$^+$ to be 1.2. Inserting the parameters of Table 2 into the expressions of Table 1 and into equation (17) we obtain the theoretical temperature dependence of $\Delta f/f$ of the different bands (full lines in Fig. 3).

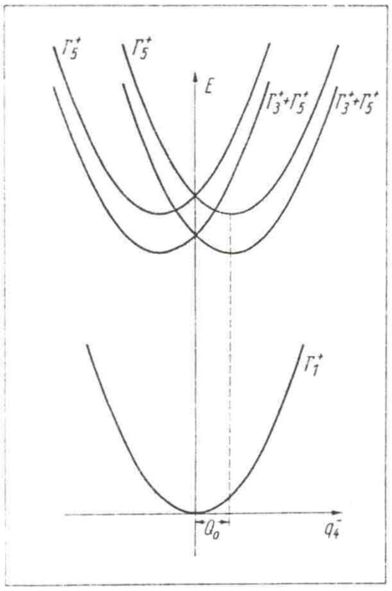
he sign of the splitting $3\,\delta_3 =$
be positive. This is consistent
f the IR resonance in KI:Ag$^+$.
gnments for the transitions in
and [9]. Besides this we obtain
nd (5.36 eV) in KCl:Ag$^+$ which
ratures. In the A-band of both
sates the effect of the $\Gamma_1^+ \rightarrow \Gamma_3^-$
the B-band we obtain for the
r strength $f_3/f_5 = 2.7$ which is
l. [9]. The results agree in that
oution.
erm (17) is found to be 1 to
, but it has a negative sign for
at the quadratic electron–lattice
gth of the transitions of Ag$^+$ in

$Q_0^2/\langle Q^2(0)\rangle$	C	f_3/f_5
$\times 10^{-2}$ ***)	$+1.1\times 10^{-2}$	1.2
$\times 10^{-2}$	-2.2×10^{-2}	–
0	$+2.3\times 10^{-2}$	2.7
0	$+0.8\times 10^{-2}$	–
$\times 10^{-2}$	-2.7×10^{-2}	–

l.
l.

effect into account (second term
$\Delta f/f|$ decreases with temperature.
he A- and B-band of KCl:Ag$^+$.
bands of both systems show the
For this reason we discuss these
effect we calculate the δ_3-effect
g as obtained from reference [11].
from the analysis of our measure-
t we find $\Delta Q_0^{=} = |\Delta Q_{\parallel 0}^{=} - \Delta Q_{\perp 0}^{=}$
Ag$^+$ and 9% for NaCl:Cu$^+$ of the
ance mode at $T = 0$ °K (Table 2).
behaviour should be expected.
nds under high hydrostatic pres-
Taking the values of $\Delta\omega/\omega$ and
f_3/f_5 for the A-band in NaCl:Cu$^+$
2 into the expressions of Table 1
tical temperature dependence of
).

Fig. 6. Schematic plot of the energy versus interaction coordinate of the odd mode q_4^- (linear coupling)



The off-centre effect found in NaCl:Cu$^+$ raises the question why no off-centre effect was found at the IR absorption of the resonance mode. Obviously the effect is only connected with the excited state Γ_5^+ of KCl:Ag$^+$ which is distorted by the odd parity mode. This distortion may be described in terms of a relatively strong admixture of Γ_4^- electronic states to the Γ_5^+-state which gives rise to a small off-centre displacement of the ion in the excited state. In NaCl:Cu$^+$ the off-centre effect is bigger and is also found in the lower excited states. Fig. 6 shows this concept in a configuration coordinate model. The potential energy has been plotted versus one of the three symmetry coordinates q_{4i}^-. We note that the modes described in Fig. 6 do not cause a broadening of the bands, but make the parity-forbidden transitions allowed. Q_0 denotes the off-centre displacement. The different energy parabolas of one excited state are degenerate at the inversion centre, where the ground state has minimal energy. This model explains the fact that no off-centre splitting of the IR resonance mode at low temperatures has been found by experiments.

In Section 2 we have seen that the first-moment change under stress was negligible. It was this fact which made a detailed analysis of the zeroth moment possible. But this lack of a stress splitting in NaCl:Cu$^+$ and KCl:Ag$^+$ is in contrast to the properties of other colour centres as F-centres, U-centres, and Tl$^+$ ions. In all these systems a relatively strong splitting under Γ_3^+- and Γ_5^+-stress was observed. We conclude that the coupling of the excited states to Γ_3^-- and Γ_5^--modes is small in NaCl:Cu$^+$ and KCl:Ag$^+$ and much too weak to cause a Jahn-Teller distortion. In such a case a second-order perturbation by odd modes (Γ_4^- and Γ_5^-) is no longer negligible and might cause an off-centre effect if there is a sufficiently strong coupling to the vibration of an impurity resonance mode. This seems to be the case for the A-band and the D-band of NaCl:Cu$^+$ and for the D-band of KCl:Ag$^+$. Stark effect measurements [4] and absorption measurements [1] indicate that the excited states of these bands have a strong ligand character which may increase the "orbital radius" and the polarizability of these states over those of the A- and B-bands in KCl:Ag$^+$, and give rise to the observed stress effects.

5. Summary and Conclusions

The stress dichroism of the UV absorption bands in NaCl:Cu$^+$ and KCl:Ag$^+$ shows a change of the zeroth moment which is linear in stress, but no stress splitting. The dominant effect is explained by a splitting of the frequency of the IR active resonance mode. The splitting for Γ_5^+-stress is smaller than 1/10 of the splitting for Γ_3^+-stress which is in good agreement with measurements of the IR active mode under stress [11, 14].

The temperature dependence of the stress dichroism was used to evaluate the effect of the quadratic electron–lattice interaction. This effect was found to be of the same order of magnitude as that due to the resonance mode. It is positive for the A- and B-bands and negative for the D-bands.

The temperature dependence of the stress dichroism in the D-bands gives evidence of a small off-centre effect in the excited states. This is explained as a result of the small coupling to Γ_3^+- and Γ_5^+-lattice vibrations which made higher-order coupling to odd modes observable. The D-bands are understood to have a strong ligand character which favours this coupling.

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