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PHONONS

Comptes rendus de la conférence internationale.
Proceedings of the international conference.

RENNES, FRANCE
1971

Flammarion Sciences
20, rue de Vaugirard
75-Paris 6^e^

THE EFFECT OF UNIAXIAL STRESS ON THE OFF-CENTER POTENTIAL OF CU^+ AND AG^+ DEFECTS IN ALKALI HALIDE CRYSTALS

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Odd parity lattice distortions near Cu^+ and Ag^+ defect ions on normal lattice sites in alkali halide crystals mix electronic defect states of different parity and give rise to a noticeable oscillator strength of the parity-forbidden electric dipole transitions $nd^{10} \rightarrow nd^{9}s$ ($n = 3$ for Cu^+, $n = 4$ for Ag^+) in the UV-spectral range. In this way the intensity of the absorption bands indicates the behaviour of the local lattice distortions under extranious fields or at different temperatures and enables us to study the potential of the defect ion. Here we report on the effect of uniaxial stress on the potential of Cu^+ in KCl and Ag^+ in rubidium halides, where the small defect ion shifts from the symmetry center of the lattice cell to an off-centre position.

For sufficiently large off-center distortions the defect potential can be approximated by a number of separated and symmetrically arranged potential wells with high walls between them (1). We describe the defect displacement from the symmetry center by the symmetry coordinate $\vec{Q}_4$ which transforms as a vector under the elements of the point group O_h. The relevant odd-parity term of the electron-lattice interaction for the defect ion in the n-th potential well is given by:

$$H'_{el} = \sum_{i=1}^{3} V_{4i} \left\{ Q^{-}_{4in} + Q^{-}_{4i} \right\} \qquad [1]$$

where $\vec{Q}_{4n}$ is the static displacement of the defect ion and $\vec{Q}_4$ describes vibrational distortions of the symmetry Γ_4^-. For the oscillator strength of a parity forbidden electric dipole transition from the ground state $|j^+\rangle$ to the excited state $|k^+\rangle$ we obtain by using perturbation theory:

$$f_{j\rightarrow k} = \sum_n \frac{e^{-\frac{E_n}{kT}}}{\sum_n e^{-\frac{E_n}{kT}}} \cdot \sum_{l,m=1}^{3} B_{lm}(j,k)\,(Q^-_{4ln}\, Q^-_{4\underset{mn}{\cancel{lm}}} + \langle Q^-_{4l}\, Q^-_{4m}\rangle) \qquad [2]$$

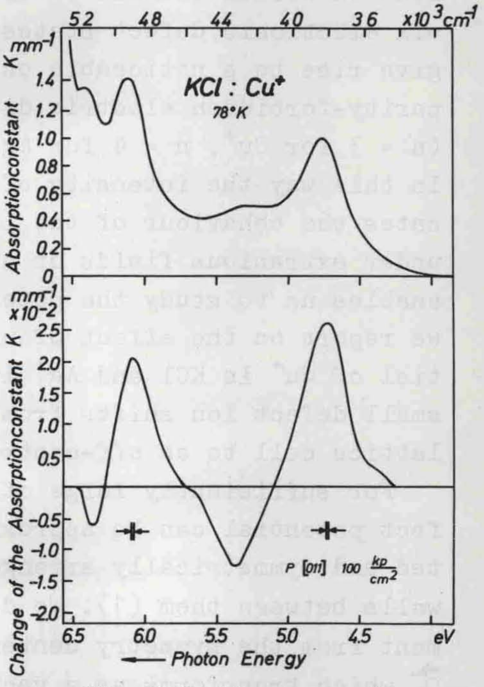

Fig.1.Difference of absorption constant of KCl:Cu$^+$ for light polarized parallel and perpendicular to the stress axis.

The Boltzmann-factor considers the occupation probability of the n-th potential well with minimum energy E_n. The first term of [2] is due to static off-center distortions, the second term describes the the component of the oscillator strength which is due to vibrations. $\langle\ \rangle$ means the thermal average.

Uniaxial stress affects the oscillator strength [2] in three different ways: First the off-center elongation $\vec{Q}_{4n}$ of the defect ion in the stressed crystal depends on the projection of $\vec{Q}_{4n}$ on the stress axis, and secondly the frequency ω of the "odd" mode in a single well may split (1),(2). Here we report on the change of the oscillator strength due to stress-induced changes of the occupation probability of the defect ion in a single off-center well. This effect is only observable if uniaxial stress lifts the equivalency of the different potential wells i.e. if the minimum energy E_n in equ. [2] depends on the position of the n-th well relative to the stress axis.

In KCl:Cu^+ we observe a change of the UV-bands only under [011]-stress, but there is no change due to tetragonal distortions ([001]-stress), see Fig.1. This means that eight off-center wells are arranged on the corners of a cube in the [111] directions which remain equivalent under tetragonal distortions of even parity. Moreover it follows that the two stress effects on the band intensitiy mentioned above could be neglected for KCl:Cu^+. Under [011]- stress the position degeneracy of the eight wells is lifted and we observe a change of the band intensity due to transitions between two inequivalent sets of potential wells, which is proportional to the difference of the occupation probability δW.

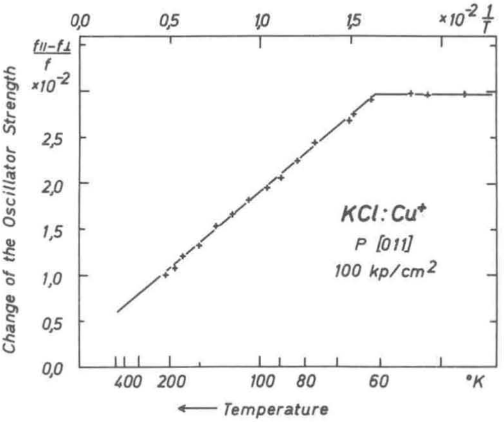

Fig.2. Stress effect of the oscillator strength of the band at 4.7 eV in KCl:Cu^+ versus temperature.

$$\delta W \approx \frac{\Delta}{8kT}\left\{e^{-\frac{t}{\tau}}-1\right\} \qquad \text{for } \frac{\Delta}{2} \ll kT \qquad [3]$$

Δ is the energy difference of the two sets and τ the relaxation time for establishing thermal equilibrium.

$$\tau = \frac{\pi}{2\omega} e^{\frac{E_o}{kT}} \qquad [4]$$

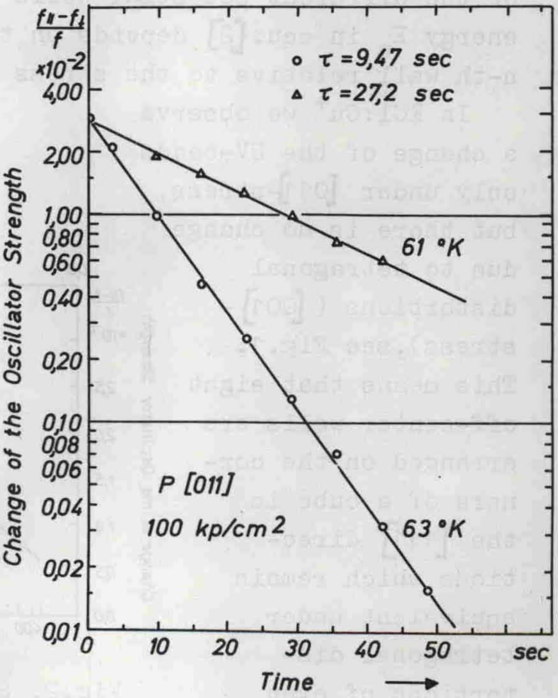

Fig.3. Time dependence of $(f_{\parallel} - f_{\perp})/f$ of the band at 4.7 eV in KCl:Cu$^+$ after having removed the stress.

E_o is the minimum height of the wall between adjoining potential wells. At low temperatures τ becomes very long and the initial distribution freezes in.

Fig.2 shows the stress change of the oscillator strength of the UV-band at 4.7 eV in KCl:Cu$^+$ versus 1/T. The effect increases proportional to 1/T, but becomes a constant below the freezing point at 60°K. Near 60°K τ is of the magnitude of about a minute see Fig.3 and we obtain the frequency ω and the wall height E_o from its measurement:

$$E_o\ (\mathrm{KCl{:}Cu^+}) = 1.6 \pm 0.1\ \mathrm{eV} \mathrel{\hat{=}} 1850 \pm 100^{\circ}\mathrm{K}$$

$$\omega \mathrel{\hat{=}} 4\ \mathrm{cm}^{-1}\ ;\quad 0.4 \leq \omega \leq 40\ \mathrm{cm}^{-1} \qquad [5]$$

In $RbCl:Ag^+$ and $RbBr:Ag^+$ the off-center wells are shallower and no freezing point was observed down to 23°K. As in $KCl:Cu^+$ the stress effects of the band intensity are proportional to $1/T$ and come up to $(f_{\parallel}-f_{\perp})/f = 0.2$ in $RbBr:Ag^+$ at 100 kp/cm^2. This temperature dependence indicates the same stress-induced mechanism we found for $KCl:Cu^+$, but off-center positions in [011]-directions give the only possible arrangement which is consistent with our measurements. Since Kapphan and Lüty (3) found no electro-caloric effect in $RbBr:Ag^+$ at 5°K, we conclude that the freezing point of the Ag^+ ion in RbBr lies between 5°K and 23°K. We point out that [011]-off-center positions in contrast to [111] positions indicate a ds hybridisation of axial symmetry for the ground state of the Ag^+ defect ion.

This work was supported by the Deutsche Forschungsgemeinschaft.

REFERENCES

(1) W.DULTZ. - Thesis Frankfurt (Main) 1970

(2) W.DULTZ. - Phys.Stat.Sol. 34 95 (1969)

(3) S.KAPPHAN and F.LÜTY. - Sol.Stat.Com. 6 907 (1968)

OPTICAL PHONONS AND PHASE TRANSITIONS IN SOME ORDER-DISORDER AND DISPLACIVE FERROELECTRICS*

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I - INTRODUCTION

The optical vibrational modes of SbSI and KH_2PO_4 and its isomorphous crystals have received considerable investigation in the past using optical techniques (1)-(3). However, assignment of the modes to the irreducible representations of the proposed space groups in both the paraelectric and the ferroelectric phases has not been complete and the mechanism of the phase transition has not been fully understood in all these crystals. In the present work the polarized Raman spectra of SbSI and KH_2PO_4, $KD_{2x}H_{2(1-x)}PO_4$ ($x = .3, .8, .98$), KH_2AsO_4 and $NH_4H_2PO_4$ have been measured as a function of temperature in the range 15-300°K.

Complementary polarized far infrared reflectance spectra of all the materials have been measured over the same temperature range. In the present work we have obtained the frequencies and symmetries of the phonon modes as allowed by group theory, and provided confirmation of the proposed structures. The data indicate that the low frequency phonons are 'soft' modes and are responsible for the ferroelectric behaviour. The results confirm current theories concerning the different mechanism of the phase change in ferroelectrics.

II - EXPERIMENTAL

The polarized far infrared reflectance measurements were made using a Fourier transform Michelson interferometer and a low temperature detector. A mosaic was constructed from the SbSI single crystal needles mounted with their c axes parallel to provide about 5 mm x 10 mm surface area. The KDP type crystals were in the form of large polished plates with the c axis parallel to one face.

The Raman spectra were recorded using a Spex 1401 double monochromator, ITT FW130 photomultiplier tube and photoelectron counting detection electronics. A ~ 80 mw 6328Å He-Ne laser with oblique angle scattering was used for SbSI and a ~ 300 mw 5145Å Ar^+ laser with a right angle scattering was used for the KDP type crystals.

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*Supported in part by NASA grant NGL 22-011-051 and by Northeastern University.