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The Stress Dependence of the Paraelectric Susceptibility of KCl:OH⁻

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Abstract. The dielectric constant of weakly doped KCl:OH^- crystals under an externally applied stress was measured in the temperature range from 0.3 to 5 K. The dipolar polarizability is only slightly influenced by uniaxial stress along $\langle 111 \rangle$ whereas it can be strongly reduced by a $\langle 100 \rangle$ stress, in agreement with the generally accepted $\langle 100 \rangle$ equilibrium orientation. At low temperatures the stress dependence can only be explained by the assumption of random internal electric and elastic fields generated by lattice defects. The width of the distribution of these fields has been determined from the experimental data.

1. Introduction

The OH^- ions which substitute for the anions in alkali halides reorient still at low temperatures [1]. In most alkali halides the ion has six equivalent orientations, namely along the $\langle 100 \rangle$ crystalline axes [2]. The OH^- ion represents an electric [2] as well as an elastic [3–7] dipole. Therefore a mechanical stress can have a large influence on the paraelectric susceptibility of the system. This effect has been investigated experimentally in the temperature range from 0.3 to 5 K.

2. Experimental Details

The dielectric susceptibility was measured using a 10 kc/s a.c. field along the stress axis with an amplitude of less than 10 volt/cm.

The crystals were grown by the Kyropoulos method under argon atmosphere using as starting substance ultra pure random pieces of KCl single crystals to which heavily doped KCl:OH^- was added. To reduce internal strains the crystals were annealed during 50 hours at 650°C and slowly cooled. The concentration N_d of OH^- ions as determined from the dielectric susceptibility is so small (sample $1 : 0.85 \cdot 10^{18}/\text{cm}^3$, sample $2 : 1.29 \cdot 10^{18}/\text{cm}^3$) that the elastic and electric interaction between the hydroxyl dipoles can be neglected [1]. The infrared spectra of the samples indicated that the concentration of CO_3^- and NO_2^- was below $10^{16}/\text{cm}^3$.

The samples (Fig. 1) were composed of three parts [9]: two cubes of pure KCl (parts A and B), each with an evaporated gold electrode for electrical connection, and the dielectric sample (part C) of the same cross-section with electrodes on both sides. All three parts were carefully lapped. The thickness of the dielectric sample was about 0.4 mm and varied over the whole cross-section by less than 5 μm. After evaporation of the electrodes, the three parts were cemented together with cyanolit (Minnesota Mining Products). The thickness of the cement layers was about 10 μm, so that the electrodes of the sample and the cubes came into electrical contact.

Uniaxial pressure was applied along the long axis of the composite rod. A rather homogeneous uniaxial stress field in the dielectric sample C is assured by this method. (A thin slab between two pistons not bonded to the slab is always very inhomogeneously strained.)

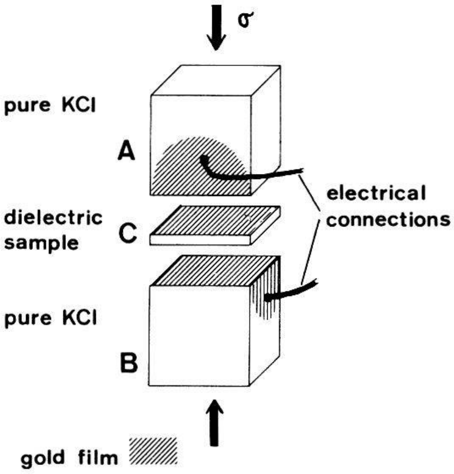

Figure 1
Composite sample for dielectric measurements under applied uniaxial stress.

3. Results

For the analysis of the dielectric measurements the Clausius–Mossotti formula was used, which relates the polarizability of the dipole system $N_d \cdot \alpha_d$, the dielectric constant ϵ of the doped crystal, and the dielectric constant ϵ_m of the pure crystal:

$$\frac{4\pi}{3} N_d \alpha_d = \frac{\epsilon - 1}{\epsilon + 2} - \frac{\epsilon_m - 1}{\epsilon_m + 2}.$$

At low dipole concentration the product $N_d \cdot \alpha_d$ is approximately proportional to $\epsilon - \epsilon_m$.

3.1. *Stress parallel ⟨111⟩*

The dielectric constant of sample 1 with stress σ applied parallel <111> (Fig. 2) does not depend upon the stress for temperatures above 0.8 K. This fact permits two conclusions:

a) The equilibrium orientations of the OH^- dipole are indeed along the ⟨100⟩ axes. By a stress parallel ⟨111⟩ the energy of classical ⟨100⟩ dipoles is not changed.
b) The strain field is sufficiently homogeneous and uniaxial.

Below 0.8 K a small dependence on stress is observed. This is due to the stress-induced rhombohedral distortion.

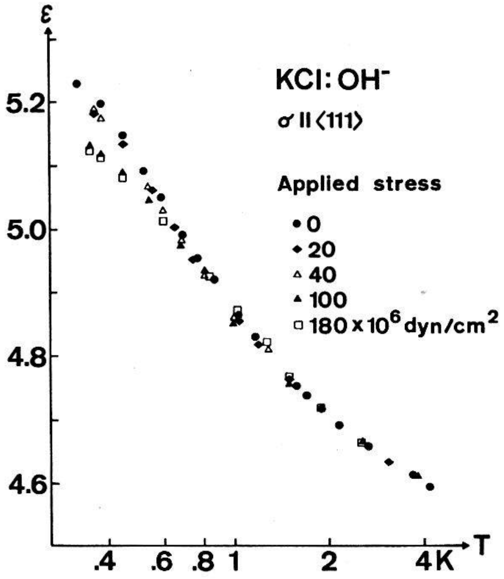

Figure 2
Dielcctric constant of KCl:OH^- with external uniaxial stress parallel ⟨111⟩.

3.2. Stress parallel ⟨100⟩ (sample 2)

The experimental data plotted in Figure 3 show that a stress applied parallel to a ⟨100⟩ direction strongly influences the dipolar polarizability, which at high stress tends to zero. After removal of the highest applied stress ($180 \cdot 10^6$ dyn/cm^2) the dielectric susceptibility still coincided with the virgin curve, thus proving that the crystal suffered no irreversible damage. The experimental results differ qualitatively from

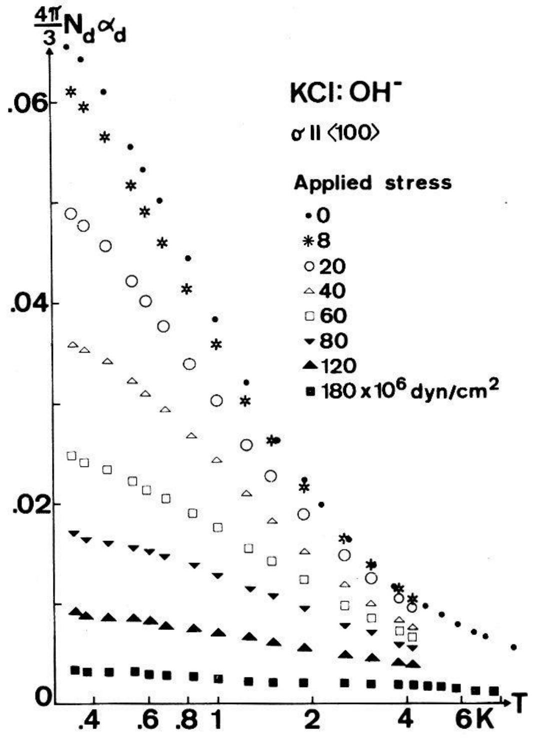

Figure 3
Dipolar polarizability of KCl:OH^- with external uniaxial stress parallel ⟨100⟩.

the theoretical curves (Fig. 4) based on the model of a ⟨100⟩ dipole that can tunnel (tunneling splitting Δ) and couples to the strain field. The stress-coupling factor α is known from elasto-optical experiments [4]. The measured stress dependence of the

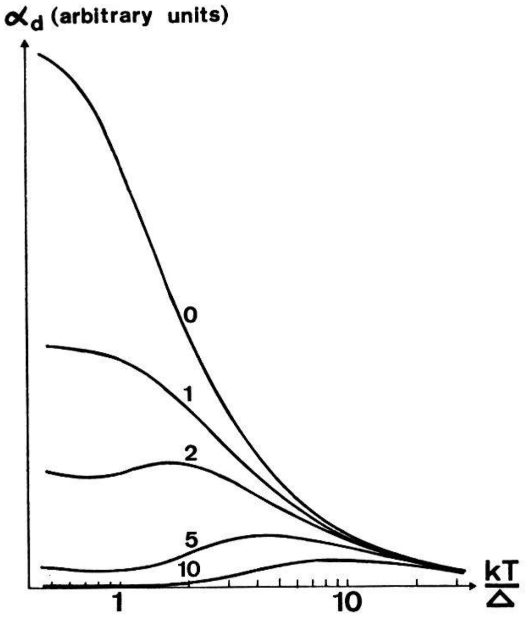

Figure 4
Theoretical dipolar polarizability for a model with ⟨100⟩ equilibrium orientation. Curve parameter is $\alpha \cdot \sigma/\Delta$. σ = applied stress, α = stress coupling factor [4], Δ = tunneling splitting (for KCl:OH$^-$ $\Delta \approx 0.3 \mathrm{K} \cdot \mathrm{k}$).

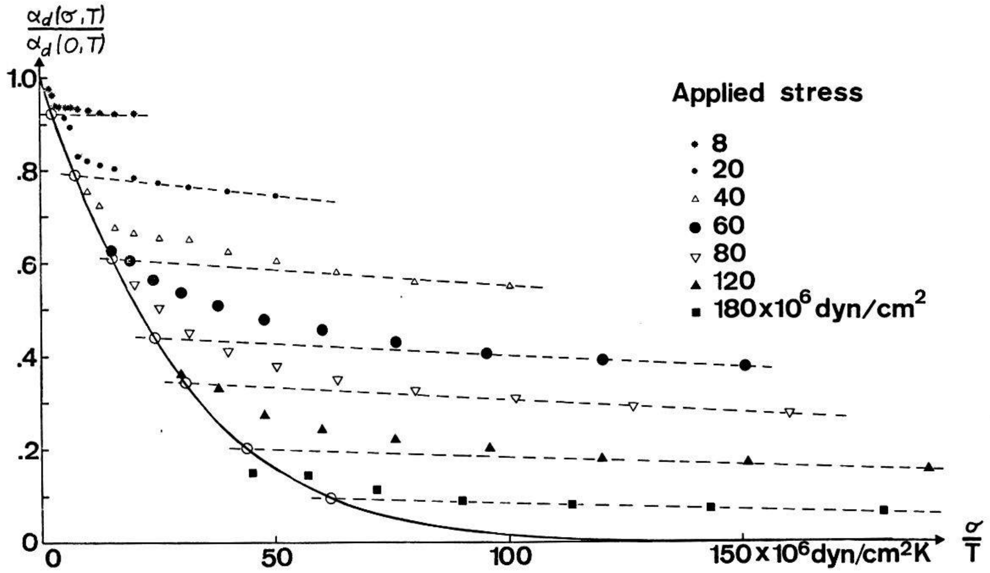

Figure 5
Ratio of the experimental dipolar polarizabilities $\alpha_d(\sigma, T)/\alpha_d(0, T)$ for KCl:OH$^-$ with external uniaxial stress parallel ⟨100⟩. The full curve represents the stress dependence for the ideal classical dipole with ⟨100⟩ equilibrium orientation.

dipolar polarizability does not exhibit the theoretically expected maximum. This discrepancy is made more transparent by plotting $\alpha_d(\sigma, T)/\alpha_d(0, T)$ against σ/T (Fig. 5). According to classical theory this ratio should depend only upon σ/T, i.e. all points should lie on a single curve. (Quantum-mechanical corrections are small even at low temperatures and low stresses and can be neglected for our purposes.)

The experimental values are at variance with this expectation. It is only at high temperatures that the experimental curve tends to the theoretical curve. At low temperatures, however, the ratio $\alpha_d(\sigma, T)/\alpha_d(0, T)$ is almost independent of the temperature and thus only a function of the applied stress. A specific value σ/T^* characterizing the deviation from the theoretical curve for each σ is found by extrapolating linearly the low temperature part and intersecting it with the theoretical curve (see Fig. 5). The temperature T^* turns out to be almost independent of σ and it has the value 2.7 ± 0.2 K.

4. Discussion

The experimental data can be explained if one assumes that the samples contain defects that produce random internal strains and electric fields [10–15]. In the present work a model was considered consisting of an ensemble of dipoles acted upon by the randomly distributed internal fields superimposed on the externally applied field. It was further assumed that the distribution of the magnitudes of these fields is Gaussian. The widths σ_{int} and E_{int} of the Gaussian distributions $\exp(-\sigma^2/2\sigma_{\text{int}}^2)$ and $\exp(-E^2/2E_{\text{int}})$, respectively, were varied to find agreement with the experimental curves. The polarizability of each dipole was calculated following the procedure given by Shore [8].

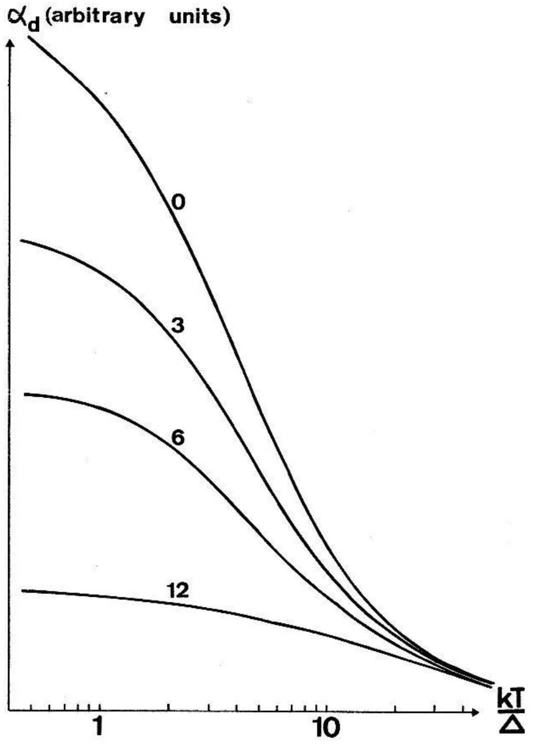

Figure 6
Theoretical dipolar polarizability for the ⟨100⟩ model with randomly distributed internal fields. In order to obtain agreement with the experimental curves the following choice had to be made: $(\alpha \cdot \sigma_{\text{int}})/\Delta = 8$ and $(p \cdot E_{\text{int}})/\Delta = 3$ (p = classical electric dipole moment). The curve parameter is $(\alpha \cdot \sigma)/\Delta$, where σ is the externally applied stress.

The resulting curves (Figs. 6 and 7) look indeed like the corresponding experimental curves (Figs. 3 and 5), suggesting that the model contains the essential features. It is important to note that neither internal electric fields alone nor internal elastic fields alone can explain the experimental data. The characteristic temperature T^*_{theor} derived from the theoretical curves of Figure 7 turns out to be independent of the

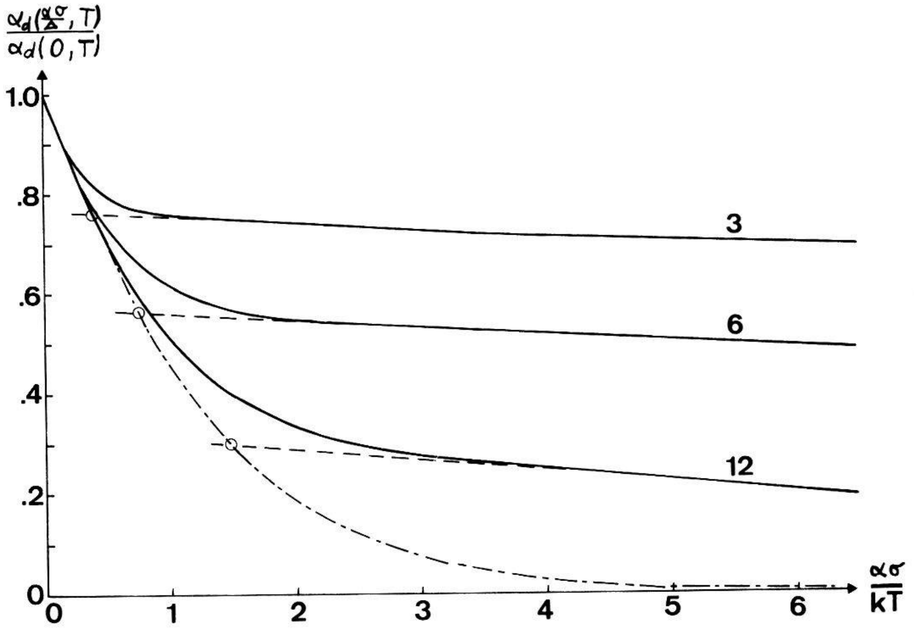

Figure 7
Ratio of the theoretical dipolar polarizabilities for the ⟨100⟩ model with randomly distributed internal fields (——) for the choice $(\alpha \cdot \sigma_{\text{int}})/\Delta = 8$, $(p \cdot E_{\text{int}})/\Delta = 3$. The curve parameter is $\alpha \cdot \sigma/\Delta$ (ideal classical ⟨100⟩ model –·–·–·–·).

external stress and is related to the width σ_{int} by the simple relation $k \cdot T^*_{\text{theor}} = \sigma_{\text{int}} \cdot \alpha$, where α is the stress-coupling coefficient defined by Lüty and coworkers [4].

If the model is applicable the experimentally determined T^* directly yields σ_{int} in the sample since α is known. From Figure 5 one obtains $\sigma_{\text{int}} = 65 \cdot 10^6$ dyn/cm^2 (corresponding to a strain of $1.5 \cdot 10^{-4}$). Other samples gave similar values. It seems that all authors arrive at this order of magnitude independent of the method.

The width E_{int} turns out to correspond to an external field of the order 9 kV/cm.

Acknowledgments

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