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## A dielectric study of the domain freezing in $\text{KH}_2\text{AsO}_4$

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**Abstract.** We have studied the frequency and temperature dependence of the dielectric constant parallel to the ferroelectric  $c$  axis in the ferroelectric phase of  $\text{KH}_2\text{AsO}_4$ . The dielectric dispersion found in the high-frequency range (1 MHz–1000 MHz) could be described by a Vogel–Fulcher-dependent Gaussian distribution of relaxation times, similarly as in  $\text{KH}_2\text{PO}_4$ . However, the use of a Vogel–Fulcher law is less convincing than in  $\text{KH}_2\text{PO}_4$ . Below the freezing temperature  $T_f$  the relaxation times strongly increase resulting in a decrease of the domain wall mobility. This may be due to the non-linear superposition of the piezoelectric resonance and the relaxational dispersion.

### 1. Introduction

Dielectric studies of the ferroelectric phase in potassium dihydrogen phosphate (KDP) type crystals [1] have shown that the low-frequency dielectric constant  $\epsilon_3$  parallel to the ferroelectric  $c$  axis exhibits an anomalous high value as compared to the value predicted by the phenomenological Landau theory. On cooling  $\epsilon_3$  shows a plateau-like temperature dependence below the Curie temperature  $T_C$  and then at a temperature  $T_f$  abruptly decreases down to its phenomenological value. The anomalously large dielectric constant in the temperature interval  $T_f < T < T_C$  is believed to be due to the motion of the walls between the ferroelectric domains [2]. The abrupt decrease of the dielectric constant is then attributed to the freezing of the domain wall motion.

Although the domain freezing phenomenon has been known for a long time and was intensively studied in recent years [2–8], the problem has not been solved yet. At least three different approaches were used to describe this phenomenon: a statistical model of Fedosov and Sidorkin [2] where it is assumed that for a domain wall there exist two possible configurations with different energy (the ground state and the saddle configuration depending on temperature), the microscopic study of Bornarel [3, 4] according to which the domain walls are pinned at their tips to dislocations, which leads to the interaction between vibrations of the domain wall and the longitudinal vibrations of corresponding tips, and finally a phenomenological description for the high-frequency relaxational dispersion of Kuramoto and Nakamura [5–8] indicating an abrupt increase of the relaxation times of the dipole flipping in two-dimensional clusters (at the domain wall) on approaching the domain freezing temperature.

Up to now, most attention has been paid to KDP. In this paper we present dielectric measurements in the isomorphous  $\text{KH}_2\text{AsO}_4(\text{KDA})$ . The dielectric properties of KDA in the

vicinity of the domain freezing temperature  $T_f$  have not been studied yet. Since the domain wall mobility in KDA is supposed to be more rigid than in KDP [9] (i.e. it possesses a lower domain wall mobility), it might be interesting to compare the results of dielectric studies on them. Recently similar measurements on  $\text{KD}_2\text{AsO}_4$  (DKDA) [10] have been performed.

The experimental arrangement is described in section 2, results are given in section 3 and the discussion and conclusions are contained in section 4.

## 2. Experimental details

Good-quality samples of KDA were obtained from the pyramidal growth sector of a crystal grown from an aqueous solution. Samples with the shape of a rectangular plate (with dimensions about  $3 \times 5 \times 0.4 \text{ mm}^3$ ) and a circular plate (with diameter  $d = 4.98 \text{ mm}$  and thickness  $t = 1.39 \text{ mm}$ ) were plated with electrodes of evaporated silver or Degussa silver paint. Comparing both types of electrode no differences could be observed. The complex dielectric constant parallel to the ferroelectric  $c$  axis was measured using the impedance analysers HP 4284A, HP 4192A and HP 4191A, in the frequency range 20 Hz–1 MHz, 100 Hz–13 MHz and 1 MHz–1 GHz respectively. The applied AC electric measuring field was  $E \approx 7 \text{ V cm}^{-1}$ .

The measurements were performed on heating and on cooling with 10 min dwelling time at each temperature before measuring. The temperature was stabilized using an Oxford Instruments continuous-flow cryostat ( $\Delta T = \pm 0.03 \text{ K}$ ) or a CTI-Cryogenics Cryodyne 22 helium closed cycle refrigerator ( $\Delta T = \pm 0.05 \text{ K}$ ) respectively. The sample was mounted in the cryostat surrounded by helium gas (thermal gradients were less than 0.1 K) in such a way that it could vibrate freely. The piezoelectrically induced resonance vibrations were used for the determination of the elastic constant  $C_{66}^E$ .

## 3. Results

Temperature dependences of  $\epsilon'$  and  $\epsilon''$  measured for various frequencies are shown in figure 1. The dielectric constant  $\epsilon'$  shows for frequencies up to about 10 MHz a 'plateau' region between  $T_f \approx 82 \text{ K}$  and  $T_C = 96 \text{ K}$ . For the dielectric loss  $\epsilon''$  two frequency regimes can be distinguished in the data: the first for frequencies lower than the first piezoelectric resonance frequency of the sample (which was about 200 kHz), where one finds a peak in  $\epsilon''$  at  $T_f$  and practically no frequency dependence of this peak is observed. The second regime, for frequencies higher than the resonance frequencies, is characterized by increasing values of  $\epsilon''$  with increasing frequency in the temperature region  $T_f$ – $T_C$ . The maximum of  $\epsilon''$  with respect to temperature shifts to higher temperatures for increasing frequencies. This tendency can be observed up to a frequency of 47 MHz, where the maximum of  $\epsilon''$  reaches the transition point  $T_C$ . For higher frequencies no clear domain freezing is found.

The frequency dependence of the real and imaginary part of the dielectric constant  $\epsilon$  at several temperatures in the ferroelectric phase is shown in figure 2 and figure 3. Two dispersions are evident: a relaxational one at high frequencies and one of resonance type in the kHz region. Both dispersions are temperature dependent and their characteristic frequencies start to overlap for temperatures  $T < T_f$ .

The lowest resonance frequency of the face shear mode can be used for the calculation of the elastic constant  $C_{66}^E$ . For this reason measurements of the dielectric constant with a high frequency resolution around the resonance frequency have been performed for temperatures

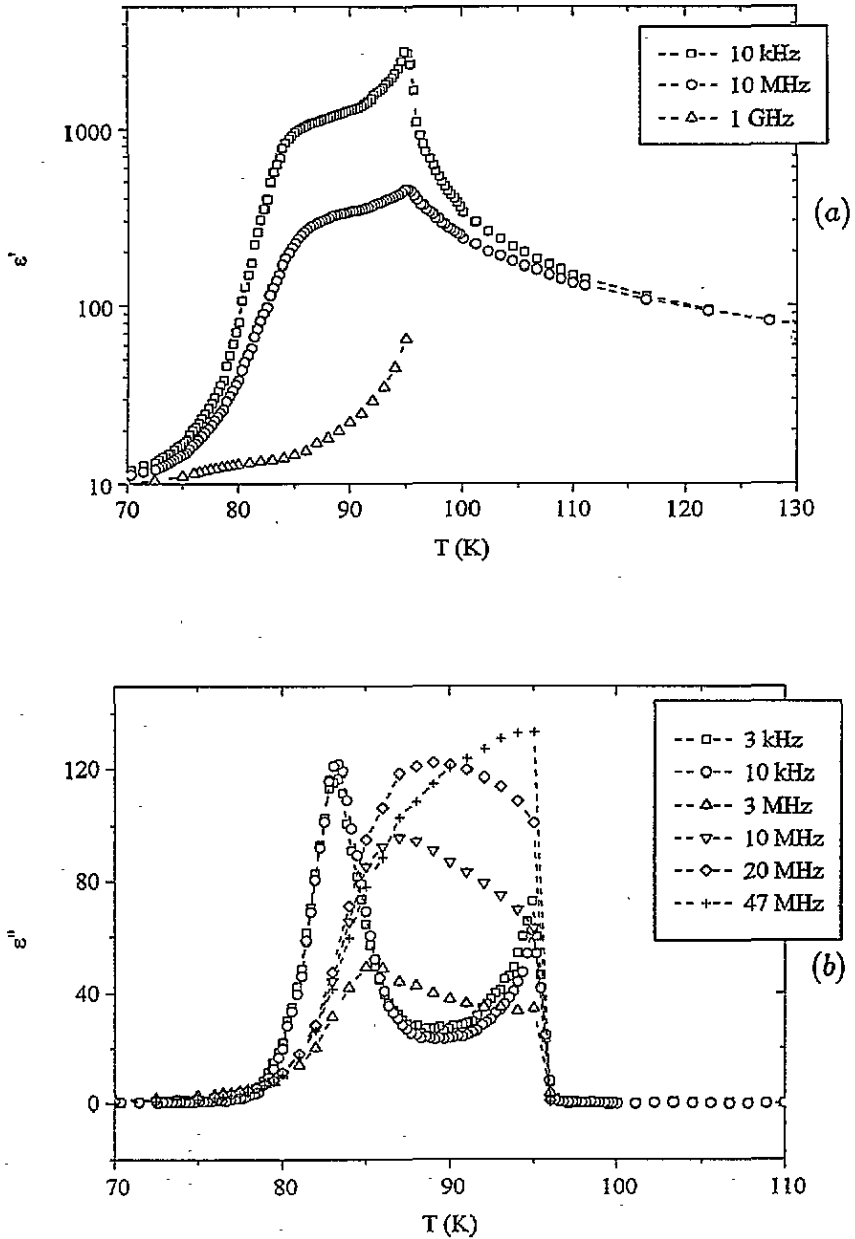


Figure 1. The temperature dependence of the dielectric constant  $\epsilon'$  (a) and the dielectric loss  $\epsilon''$  (b) for several frequencies.

between 80 K and 115 K. The shear elastic constant was determined using the known formula [11]

$$C_{66}^E = \rho(2f_r l)^2 \tag{1}$$

where  $\rho$  is the density of the sample,  $f_r$  is the first resonance frequency and  $l$  is the shorter dimension of the sample. This leads to the temperature dependence of  $C_{66}^E$  as shown in

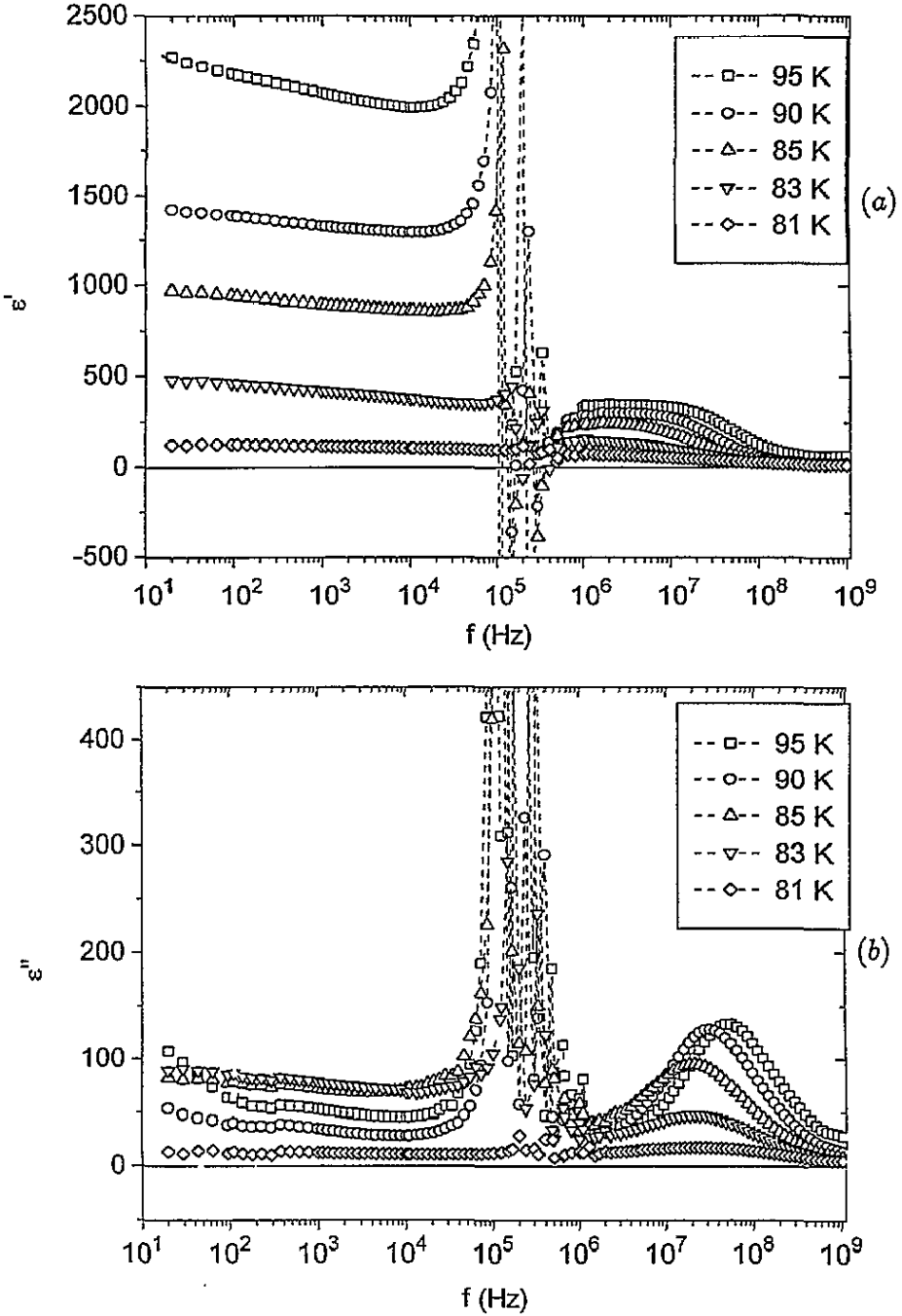


Figure 2. The frequency dependence of the dielectric constant  $\epsilon'$  (a) and the dielectric loss  $\epsilon''$  (b) for several temperatures in the plateau region.

figure 4(a). Here, between  $T_f$  and  $T_C$ , the field induced motion of domain walls manifests itself in a clear softening of  $C_{66}^E$ . In the vicinity of the domain freezing temperature  $T_f$  the

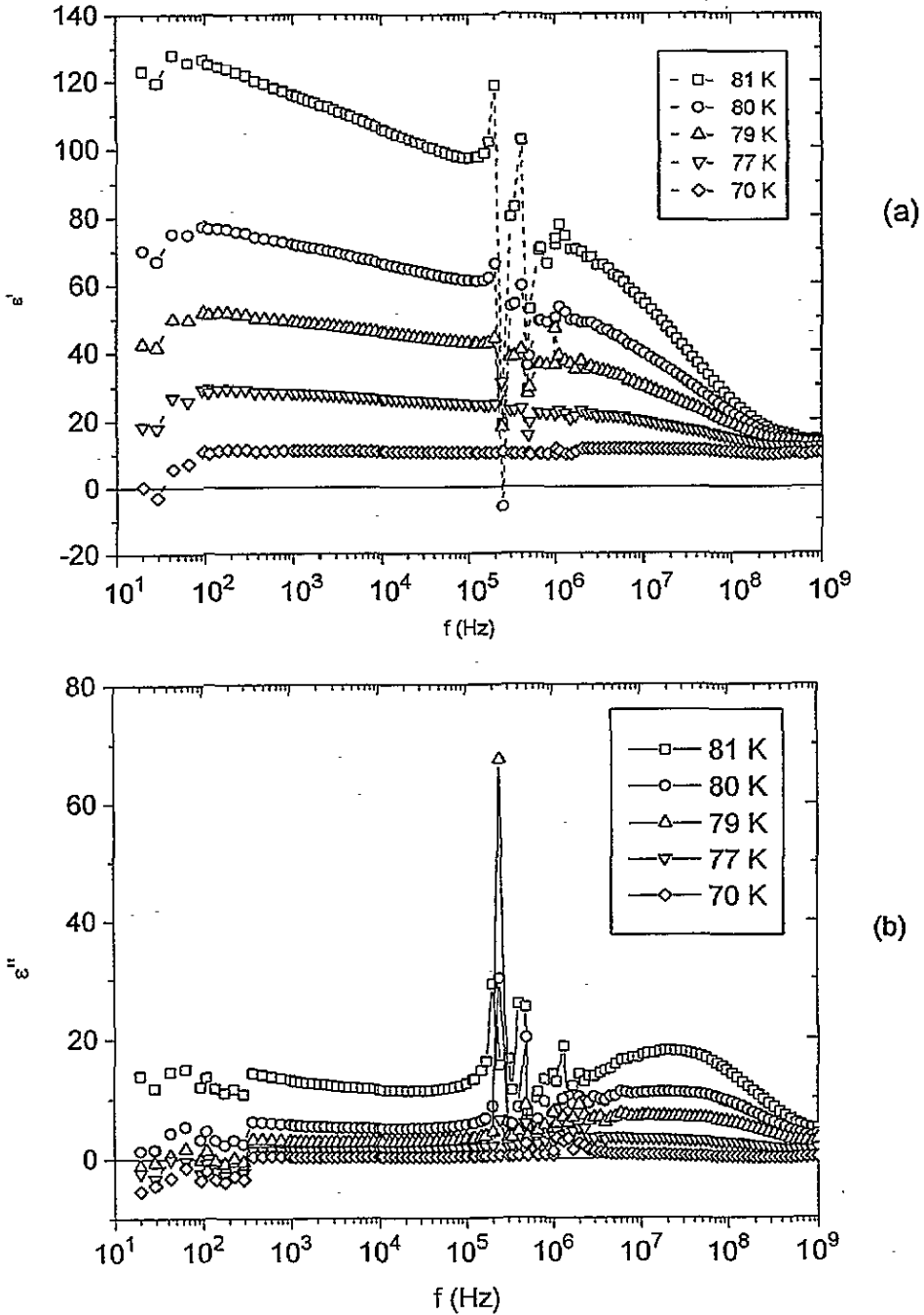


Figure 3. The frequency dependence of the dielectric constant  $\epsilon'$  (a) and the dielectric loss  $\epsilon''$  (b) for several temperatures below the domain freezing temperature.

resonance is damped and its intensity decreases (figure 3). The damping constant  $\gamma$  has been determined from the width of the resonance and its temperature dependence is shown

in figure 4(b). Note that the maximum of  $\gamma$  coincides with the domain freezing temperature  $T_f$ .

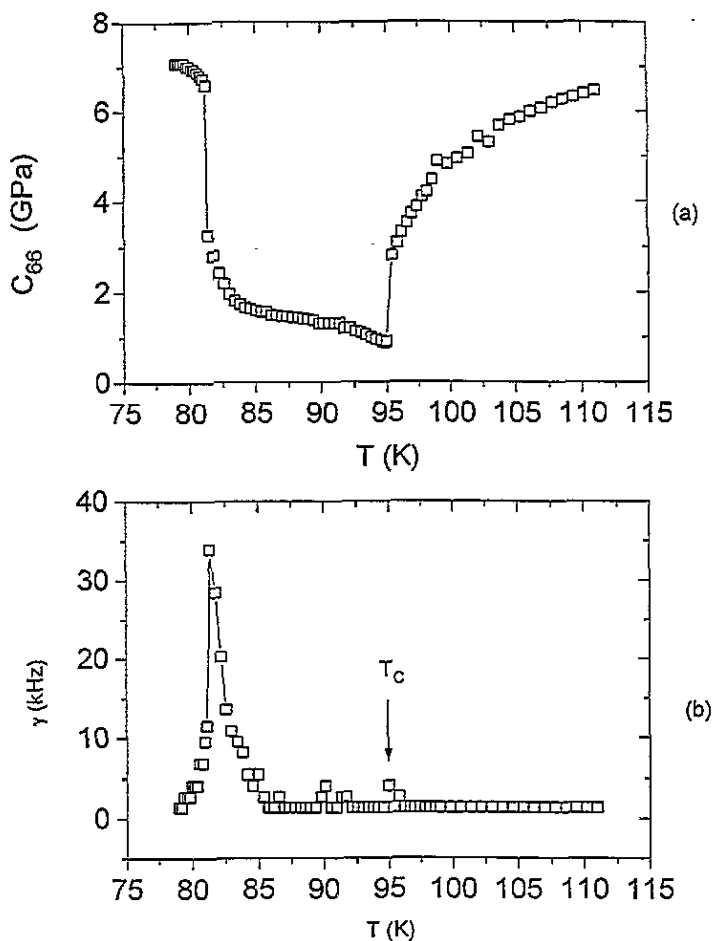
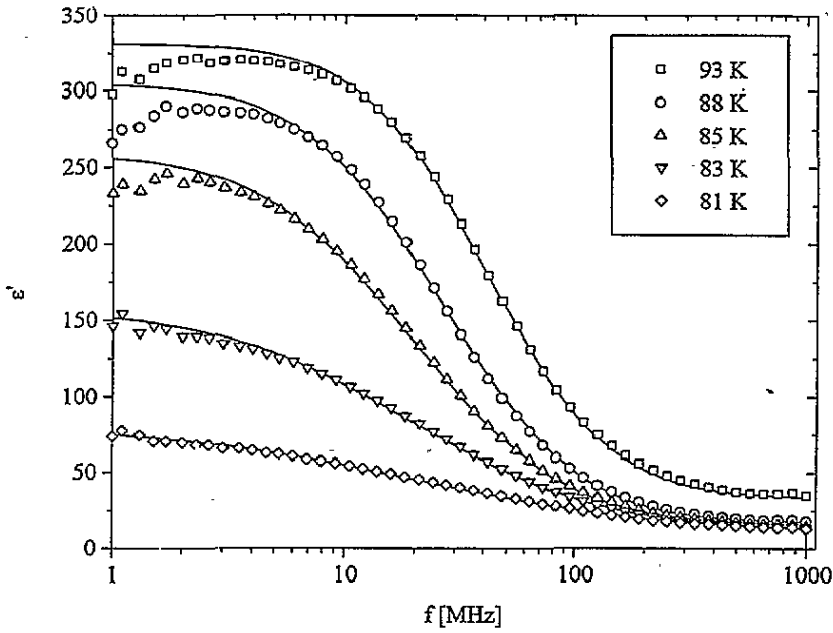


Figure 4. The temperature dependence of the elastic constant at constant electric field  $C_{66}^E$  (a) and the corresponding damping constant  $\gamma$  (b).

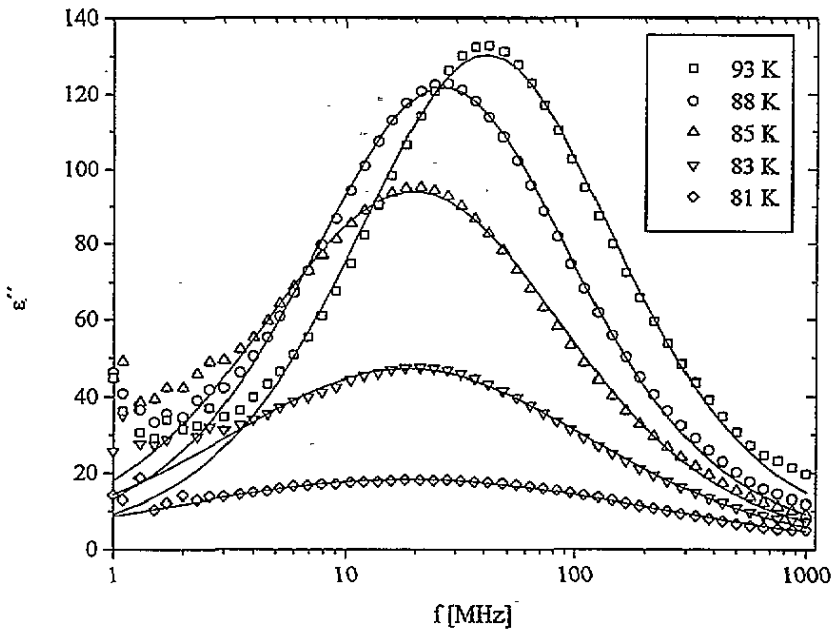
The frequency dependence of  $\epsilon'$  and  $\epsilon''$  above the resonance frequency is shown in figure 5 where one can clearly see a dispersion of the relaxational type. Similarly as in KDP the peak in  $\epsilon''$  is symmetric on a logarithmic frequency scale. For lower temperatures the peak in  $\epsilon''$  shifts to lower frequencies and becomes lower and wider. This leads to a temperature-dependent distribution function of relaxation times. This relaxational dispersion vanishes above  $T_c$ .

#### 4. Discussion and conclusions

The above mentioned results resemble those in KDP [5–7]. We therefore use the approach of Kuramoto [5] for describing the experimental data. The dielectric constant can be written



(a)



(b)

Figure 5. The frequency dependence of  $\epsilon'$  and  $\epsilon''$  in the range 1 MHz–1 GHz. Full lines represent fits to the experimental data using (11) and (12).

as

$$\epsilon(\omega, T) = [\{\epsilon_1(T) - \epsilon_2(T)\}\bar{A} + \epsilon_2(T) - \epsilon_\infty(T)]\bar{B} + \epsilon_\infty(T) \quad (2)$$

where



$$\bar{A} = \frac{\omega_r^2}{\omega_r^2 - \omega^2 + i\gamma\omega} \quad (3)$$

corresponds to the piezoelectric resonance and

$$\bar{B} = \int_0^\infty \frac{g(\tau, T) d\tau}{1 + i\omega\tau} \quad (4)$$

describes the high-frequency relaxational dispersion.  $\epsilon_1(T)$  and  $\epsilon_\infty(T)$  are the low- and high-frequency limits of the dielectric constant, respectively,  $\epsilon_2(T)$  is the value of the clamped crystal dielectric constant,  $\omega_r$  is the angular resonance frequency,  $\gamma$  is the damping constant and  $g(\tau, T)$  is the distribution function of the relaxation times  $\tau$ .

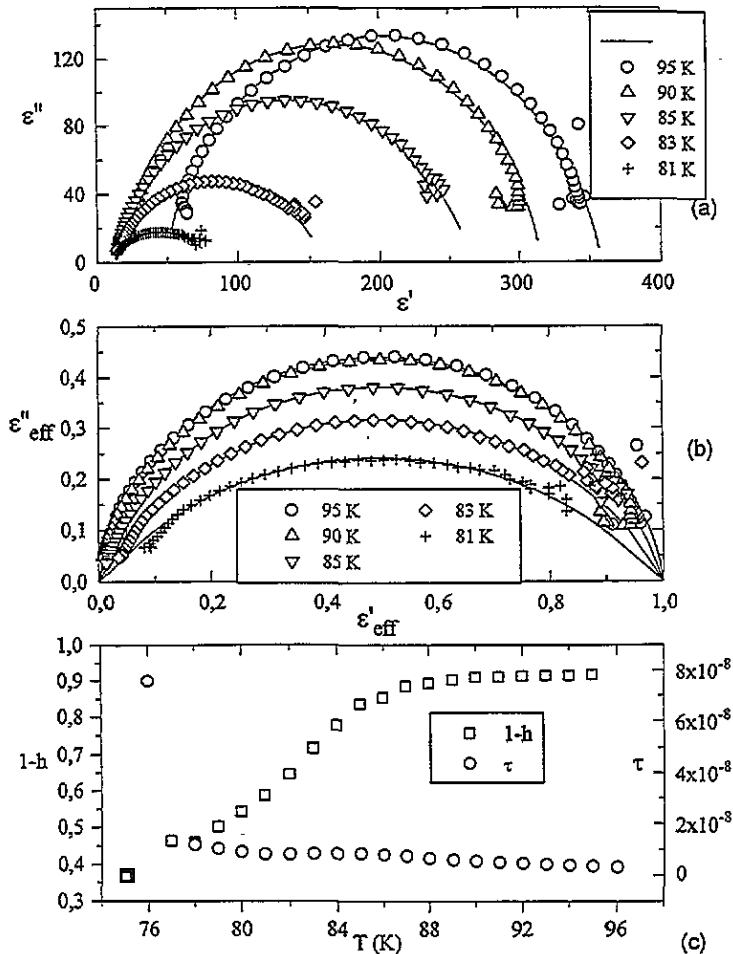


Figure 6. Cole-Cole diagram (a) and reduced Cole-Cole plot (b) of the high-frequency dispersion for several temperatures. Solid lines are fits to (7). (c) Temperature dependence of the parameters  $(1-h)$  and  $\tau$ .

To illustrate the rather peculiar temperature dependence of the distribution function  $g(\tau, T)$  of the high-frequency dispersion, one can draw a Cole-Cole diagram for various

temperatures (figure 6(a)). Using the notation

$$\epsilon'_{\text{eff}}(\omega, T) = \frac{\epsilon'(\omega, T) - \epsilon_{\infty}(T)}{\epsilon_2(T) - \epsilon_{\infty}(T)} \quad (5)$$

and

$$\epsilon''_{\text{eff}}(\omega, T) = \frac{\epsilon''(\omega, T)}{\epsilon_2(T) - \epsilon_{\infty}(T)} \quad (6)$$

one obtains the normalized Cole–Cole plot (figure 6(b)). A clear deviation from a Debye semicircle, corresponding to a single relaxation time, is observed. It follows that the distribution of the relaxation times becomes broader for lower temperatures. This feature might indicate that the high-frequency dispersion is a kind of glass forming phenomenon [7]. To determine this dispersion in more detail, one can use a least-squares fit of the experimental data according to an empirical Cole–Cole relation

$$\epsilon(\omega, T) = \epsilon_{\infty}(T) + \frac{\epsilon_2(T) - \epsilon_{\infty}(T)}{1 + (i\omega\tau)^{1-h}} \quad (7)$$

The results of this fit are shown for several temperatures in figure 6 by solid lines. The temperature dependence of the exponent  $(1-h)$  exhibits a rather large decrease in the temperature range of 78 K–88 K only (where a steep decrease of  $\epsilon'$  is observed), while for higher temperatures it remains nearly constant (figure 6(c)). This might signal the connection between the domain freezing phenomenon and the high-frequency relaxation. The fitted relaxation time shows a gradual increase  $((3-13) \times 10^{-9}$  s) with decreasing temperature. Unlike in KDP [5] fitting the slowing down of the relaxation time to a Vogel–Fulcher law

$$\tau = \tau_0 \exp \left[ \frac{E}{T - T_0} \right] \quad (8)$$

is rather problematic. In the above equation  $T_0$  denotes the Vogel–Fulcher temperature and  $E$  the activation energy.

For a description of the distribution function of relaxation times a Gaussian type distribution function of the activation energies  $f(E)$  (see [5]) was used

$$f(E) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[ \frac{-(E - E_0)^2}{2\sigma^2} \right] \quad (9)$$

We note that a Gaussian type distribution of the energies entering in the relaxation time seems to be quite acceptable also from the physical point of view, although it does not correspond to the empirical Cole–Cole relation (equation (7)). It may be shown, however, that such a distribution of relaxation times agrees with the results obtained above. As we will see later, the data may be well described by this distribution.

For further analysis the temperature dependence of the relaxation time will be assumed to be more general than according to a Vogel–Fulcher law:

$$\tau = \tau_0 \exp \frac{E}{a(T)} \quad (10)$$

where  $a(T)$  is a function of temperature.

Using equations (2)–(4) and (9), (10) one gets in the high-frequency limit ( $\omega \gg \omega_r$ )

$$\epsilon'(\omega, T) - \epsilon_\infty(T) = B(T) \int_{-\infty}^{\infty} \exp\{-[C(T)z - D(T)]^2\} \frac{1}{1 + \omega^2 e^{2z}} dz \quad (11)$$

and

$$\epsilon''(\omega, T) = B(T) \int_{-\infty}^{\infty} \exp\{-[C(T)z - D(T)]^2\} \frac{\omega e^z}{1 + \omega^2 e^{2z}} dz \quad (12)$$

where

$$B(T) = \frac{\epsilon_2(T) - \epsilon_\infty(T)}{\sqrt{2\pi}\sigma} a(T)$$

$$C(T) = \frac{1}{\sqrt{2}\sigma} a(T)$$

$$D(T) = \frac{\ln \tau_0}{\sqrt{2}\sigma} a(T) + \frac{E_0}{\sqrt{2}\sigma}$$

and

$$z = \ln \tau.$$

Thus the parameters  $B(T)$ ,  $C(T)$  and  $D(T)$  are functions of temperature, too. By an investigation of the temperature dependence of  $a(T)$  one can deduce whether a Vogel–Fulcher type law describes the situation properly or not.

For the determination of the parameters  $B(T)$ ,  $C(T)$  and  $D(T)$  a least-squares fit to the values of  $\epsilon''(\omega)$  from 1 MHz to 1 GHz using equation (12) was performed. The results obtained are shown in figure 5 by solid lines. Calculated values of  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  according to (11) and (12) agree in a wide frequency range and for temperatures 77–95 K quite well with the experimental data. We tried to fit  $\epsilon''(\omega)$  over the whole frequency range from 10 Hz to 1 GHz using equation (2). This aim could not be achieved. Unlike in KDP [6] and DKDA [10] where the  $\epsilon'(\omega)$  values below the first resonance frequency remain constant as long as there is no overlap of the two contributions ( $T_f > T > T_C$ ) and the  $\epsilon''(\omega)$  decreases to zero as expected, in KDA an increase of  $\epsilon'(\omega < \omega_r)$  and a relatively large value of  $\epsilon''(\omega < \omega_r)$  can be observed. The origin of this additional phenomenon is not yet clear but was observed in KDP [8] and was said to be a highly non-linear dispersion (relaxation) which vanishes in the limit of zero external field. The need for further investigations concerning this low-frequency relaxation is evident.

One should note that for fitting the values of  $\epsilon'(\omega)$  calculated parameters  $B(T)$ ,  $C(T)$  and  $D(T)$  as obtained above were used and only one free parameter  $\epsilon_\infty(T)$  was left. The values of  $\chi^2$  for the fits according to (11) and (12) were somewhat lower than those obtained using the Cole–Cole relation (equation (7)). This may indicate that the Gaussian distribution of the activation energy is more probable.

The temperature dependence of  $C(T)$  and  $D(T)$  (shown in figure 7) can be approximated by a linear function in the temperature range 80–90 K. This yields the parameters  $T_0 = (76.7 \pm 0.2)$  K,  $\sigma = (7.7 \pm 0.2)$  K,  $\tau_0 = (4.5 \pm 2.8) \times 10^{-9}$  s and  $E_0 = (3.5 \pm 5.7)$  K.

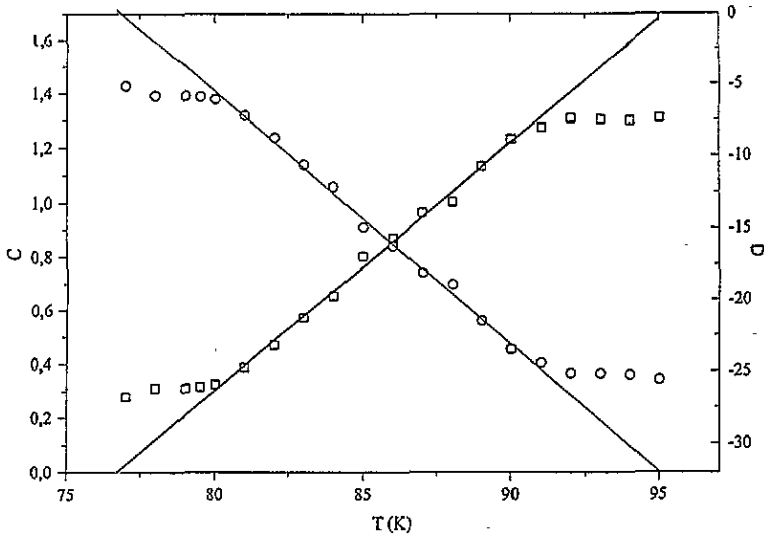


Figure 7. The temperature dependence of the parameters  $C(T)$  and  $D(T)$ . The straight lines correspond to the relation  $a(T) = T - T_0$  (see text).

One should note the big error in the determination of the value  $E_0$ . As  $E_0$  and  $\sigma$  are of the same order this is an indication of a large disorder and may be due to a wide distribution of domain sizes. Unlike the results obtained in KDP [5] the fit is linear only in a narrow temperature region (similarly to the lossy KDP [6]). This might signal that the Vogel-Fulcher law should be replaced by a more complicated dependence.

Comparing the results to those of DKDA [10] we have found smaller values for the relaxation time  $\tau_0$ , the activation energy  $E_0$  and the Vogel-Fulcher temperature  $T_0$ , similarly as was found in KDP-DKDP crystals [7]. This may point to the role of the protons or the  $H_2PO_4^-$  ions in this high-frequency dispersion.

In conclusion one can state that the model of domain freezing proposed for KDP [5] describes the properties of this phenomenon in KDA, too. The application of the Vogel-Fulcher law for the relaxation time seems to be suitable in a rather narrow temperature range only. In accordance with this model the motion of the domain walls is easy above  $T_f$ . One possible origin for this may be dipole flipping in two-dimensional clusters [4]. This softens the crystal in the shear mode  $C_{66}$ , too. Below  $T_f$  the motion of the domain walls stops because of an abrupt increase of the relaxation time of the dipole flipping which is probably due to the decrease of the configuration entropy of the dipoles.

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