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# Anomalous dielectric behaviour of $\text{NH}_2(\text{CH}_3)_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystals in the ferroelectric phase

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**Abstract.** The temperature- and frequency-dependent dielectric susceptibility parallel to the ferroelectric axis of  $\text{NH}_2(\text{CH}_3)_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  crystals was studied in the ferroelectric phase. The dispersion corresponding to a critical slowing down of the thermal dipole relaxation was observed in the vicinity of  $T_c$  in the frequency range 1–10 MHz. Besides, a dispersion which is related to the dipole reversal within the domain walls was found at lower frequencies. The latter is much more pronounced in the deuterated sample and is thought to be connected with the dynamics of hydrogen bonds.

## 1. Introduction

Crystals of dimethylammonium aluminium sulphate hexahydrate  $\text{NH}_2(\text{CH}_3)_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (DMAAS) have been widely studied recently using different experimental methods. In particular it has been found that DMAAS shows ferroelastic properties at room temperature and undergoes a proper ferroelectric phase transition of second order  $2/m \rightarrow m$  at  $T_c = 150$  K [1, 2]. The transition was associated with a polar cooperative ordering of DMA cations when instead of four bonds averaged in time only two more strong N–H...O bonds appear. This leads to the reorientation of  $[\text{SO}_4]^{2-}$  tetrahedra which come closer to the DMA cations. In such a case noncompensated dipoles arise, which is followed by the appearance of the macroscopic polarization [3]. Besides, according to [4] freezing of jump motion of water molecules participating in the formation of the  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  complex also may be considered as one of the possible reasons for the phase transition. It should be remarked that water creates strong hydrogen bonds O–H...O (length 2.55–2.70 Å) with the sulphate tetrahedra.

Valuable information about the nature of the ferroelectric and ferroelastic phases has been drawn from the investigations of spectral [5], dielectric [6] and mechanical [7] properties of DMAAS. Besides, the anomalous behaviour of the electrooptic and pyroelectric coefficients was observed at  $T_1 = 110$  K [8, 9]. Dielectric investigations showed that in a cooling run the dielectric permittivity remains comparatively high below the phase transition and decreases only at a certain temperature close to  $T_1$ , whereas the dielectric losses show broad maxima in this region. Moreover, the temperature position of the corresponding anomalies depends on the frequency of the applied field [10]. Such a dielectric behaviour observed in the directions perpendicular to the ferroelectric axis was supposed to be due to a

'freezing' of the H-bond reorientation. This effect may be considered as a manifestation of the so-called domain freezing connected with the temperature dependence of the domain wall mobility [11]. Previous investigations also have ascertained the availability of a dielectric constant anomaly at  $T_2 = 75$  K which obviously corresponds to another phase transition [10].

The effect of domain freezing was widely investigated, especially, in the compounds of the KDP family [12,13]. Under such circumstances it would be interesting to study the aforementioned phenomenon in a new type of material such as DMAAS crystals. This is why detailed dielectric measurements in these crystals were performed in a wider frequency range of  $10^{-1}$ – $10^7$  Hz. Taking into account the important role of the H-bond dynamics in the genesis of a spontaneous polarization in the ferroelectric phase, considerable attention was devoted to deuterated dimethylammonium aluminium sulphate crystals (DMAASD).

## 2. Experimental details

Good quality samples of DMAAS were grown by slow evaporation of water from aqueous solution of dimethylammonium and aluminium sulphates with addition of sulphuric acid. The deuterated crystals were grown from solution of the corresponding salts in 'heavy water'. Measurements were performed on rectangular plates of DMAAS cut perpendicular to the ferroelectric axis [1]. After polishing, conducting silver paste electrodes were used. The complex dielectric constant was measured using an SR-850 lock-in amplifier and a Hewlett-Packard 4192 A impedance analyser in the frequency ranges 0.1 Hz–10 kHz and 1 kHz–10 MHz respectively. The applied AC measuring electric field was  $E = 10$  V cm<sup>-1</sup>.

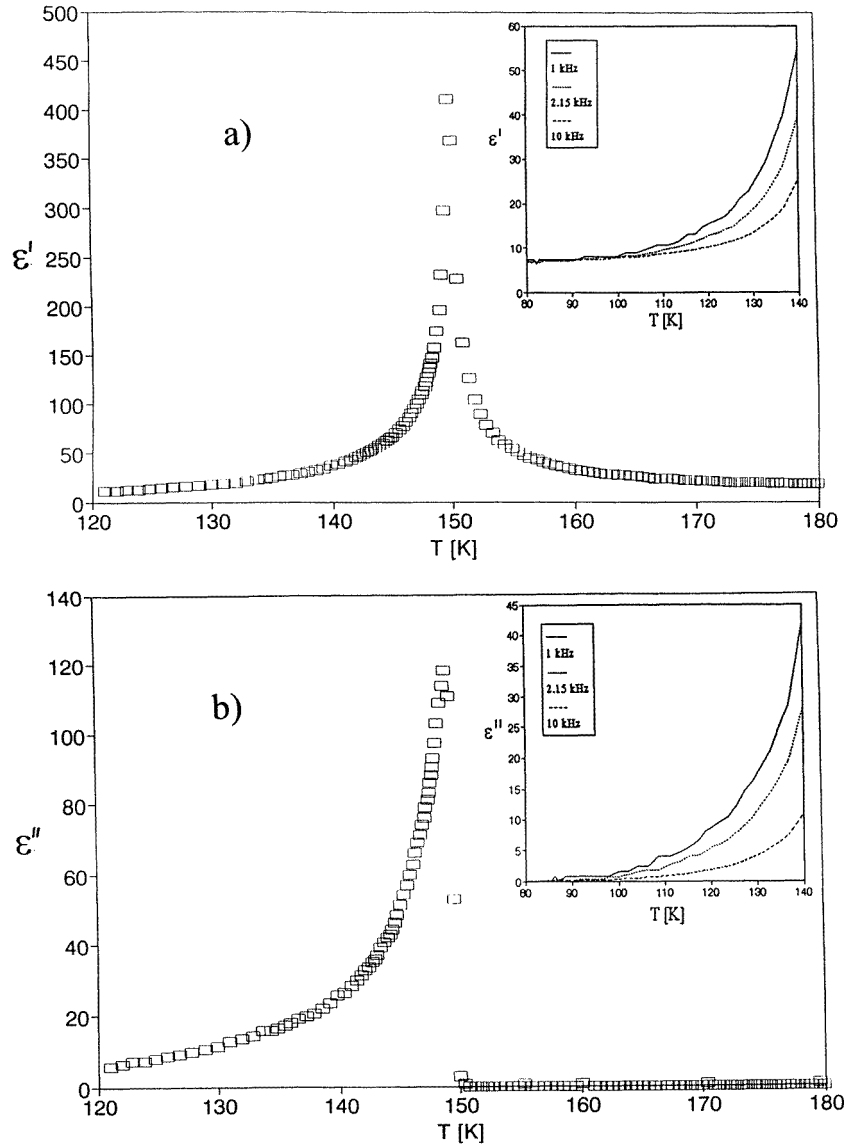
Measurements were performed on heating and on cooling with a rate of about 0.4 K min<sup>-1</sup>. The temperature was stabilized by a CTI-Cryogenics Cryodyne 22 helium closed-cycle refrigerator.

## 3. Results and discussion

### 3.1. DMAAS

The temperature dependences of the real and imaginary parts of the dielectric constant manifest sharp peaks at  $T_c = 150$  K, characteristic of proper ferroelectric phase transitions (figure 1(a), (b) respectively). On the other hand it is difficult to find clear evidence of the existence of domain freezing, although one could note a slight decrease both of  $\epsilon'$  and  $\epsilon''$ , measured at low frequencies in the vicinity of the temperature  $T = 100$  K (insert figure 1). Another interesting feature is the disappearance of dielectric dispersion below this temperature region, that could be explained in terms of domain freezing, in good agreement with data of previous investigations [10].

A much more pronounced dielectric dispersion can be observed at higher frequencies. Starting from  $f = 1$  MHz the temperature dependence of  $\epsilon'$  shows sharp minima at  $T_c$  instead of the clear peak usually observed in ferroelectric substances at lower frequencies (figure 2). The minimum becomes broader and deeper with increasing frequency. Simultaneously both shoulders of  $\epsilon'$  are shifted away from the transition point. It is also interesting to note that the imaginary part shows maxima at  $T_c$ . Such anomalous behaviour of the dielectric parameters is characteristic of 'order-disorder' type ferroelectric phase transitions and is related to a critical slowing down (paraelectric phase) and respectively

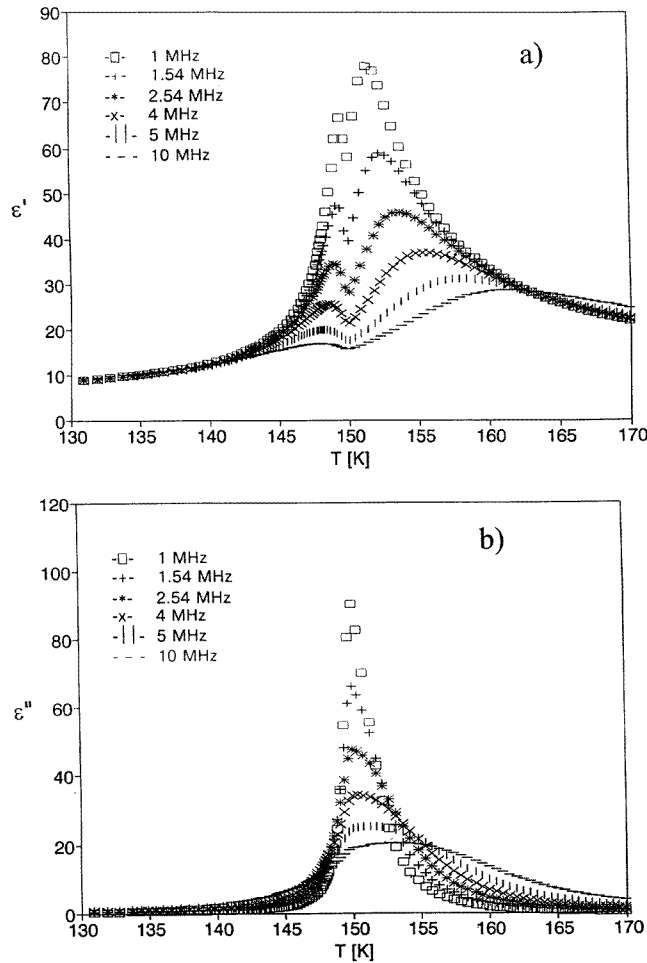


**Figure 1.** Temperature dependences of (a) the real  $\epsilon'$  and (b) the imaginary  $\epsilon''$  part of the dielectric constant of DMAAS obtained at  $f = 1$  kHz. Insets, the freezing regime for 1, 2.15 and 10 kHz.

speeding up (ferroelectric phase) of the dipole (order parameter) relaxation time. The observed phenomenon is directly connected to increase of the relaxation time  $\tau$  in the vicinity of the phase transition according to the equation [14]

$$1/\tau = (T - \theta)/\tau_0 \quad (1)$$

where  $\theta$  denotes the Curie–Weiss temperature for  $\epsilon'$  and  $\tau_0$  is considered as the temperature parameter of relaxation time.



**Figure 2.** Temperature dependences of (a)  $\epsilon'$  and (b)  $\epsilon''$  for DMAAS obtained at high frequencies (1–10 MHz).

The dispersive equation for  $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$  in this case may be obtained from the Debye equation:

$$\epsilon^*(\omega) = (\epsilon_0 - \epsilon_\infty)/(1 + i\omega\tau) + \epsilon_\infty \quad (2)$$

taking into account that  $\epsilon_0 - \epsilon_\infty = C(T - \theta)$  and relation (1):

$$\epsilon^*(\omega, T) = C/(T - \theta + i\omega\tau_0) + \epsilon_\infty. \quad (3)$$

In the equations (1)–(3)  $\epsilon_\infty$  denotes the high-frequency limit and  $\epsilon_0$  is the permittivity obtained by static measurements.

According to (3) the temperature maximum of  $\epsilon'$  in the region of dispersion is observed at

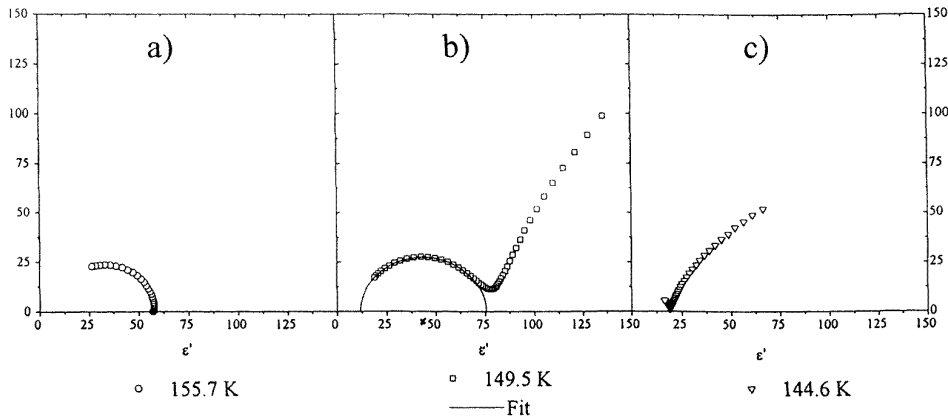
$$T_{max} = \theta \pm \omega\tau_0. \quad (4)$$

As follows from the obtained experimental results (figures 1 and 2),  $\theta = 150.0$  K, for both the ferroelectric and the initial phase, i.e. the phase transition is of second order. Thus

using the available data concerning the frequency shift of the corresponding  $\epsilon'$ -maxima and equation (4) one could calculate  $\tau_0^\pm$  (where + corresponds to the paraelectric phase and – to the ferroelectric phase)

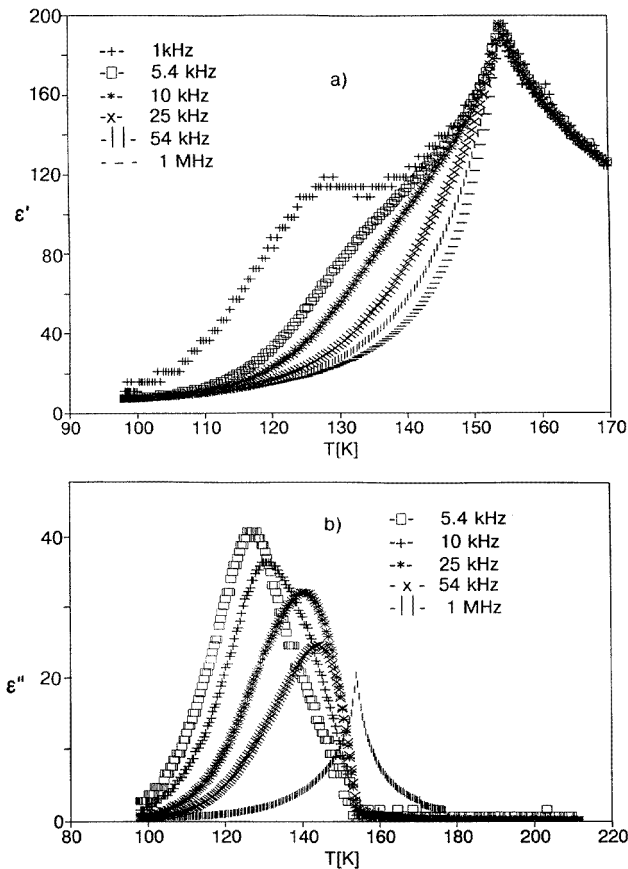
$$\tau_0 = \pm(T_{max} - \theta)/\omega. \quad (5)$$

It has been found that  $\tau_0^+ = 2.49 \times 10^{-7}$  s and  $\tau_0^- = 6.01 \times 10^{-8}$  s. These values are much higher than those usually observed in the ferroelectrics of ‘order–disorder’ type [14], obviously due to the availability of comparatively massive dipoles such as the DMA groups. A calculation using the data for  $\text{CH}_3\text{NH}_3\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  leads to similar relaxation times [15].



**Figure 3.** Cole–Cole diagrams for DMAAS obtained at different temperatures (a) above and (b), (c) below the transition point  $T_c$ . The solid line shows a fit according to a Cole–Cole function.

Cole–Cole diagrams for DMAAS are shown in figure 3. In accordance with the previous consideration the diagram obtained at  $T = 149.5$  K is clearly divided into two parts—the full semicircle which corresponds to the aforementioned order parameter relaxation and the low-frequency part which is thought to be due to domain freezing. Unfortunately the latter could not be observed on the whole in the frequency measurement window between 1 kHz and 1 MHz. Therefore one could obtain only a part of the expected diagram. At the same time the high-frequency relaxation is described by the semicircle which, however, is centred below the X-axis. This implies some distribution of relaxation times due to interaction between the dipoles [16]. The aforementioned relaxation is observed in a narrow temperature range only. Indeed, with decreasing temperature the characteristic relaxation time  $\tau^-$  decreases in the ferroelectric phase. This is connected with the diminishing of regions of correlated dipoles under the influence of increasing spontaneous polarization and coercive field. Due to this the relaxation shifts toward higher frequencies. As a result, one could observe only a small part of the corresponding Cole–Cole plot (see figure 3,  $T = 144.6$  K). Meanwhile, the low-frequency wing of the Cole–Cole diagram manifests itself at least until vanishing at 110 K due to a freezing of the domain motion. Nevertheless it is difficult to perform the detailed analysis of the supposed domain freezing, for the effect is very weak in the investigated frequency window. Therefore it would be interesting to search for the mentioned phenomenon in the deuterated crystals (DMAASD). According to Nakamura [12] proton dynamics play an important role for the domain freezing in the compounds with H bonds. Indeed the deuteration of DMAAS leads to a considerable change of its dielectric properties.

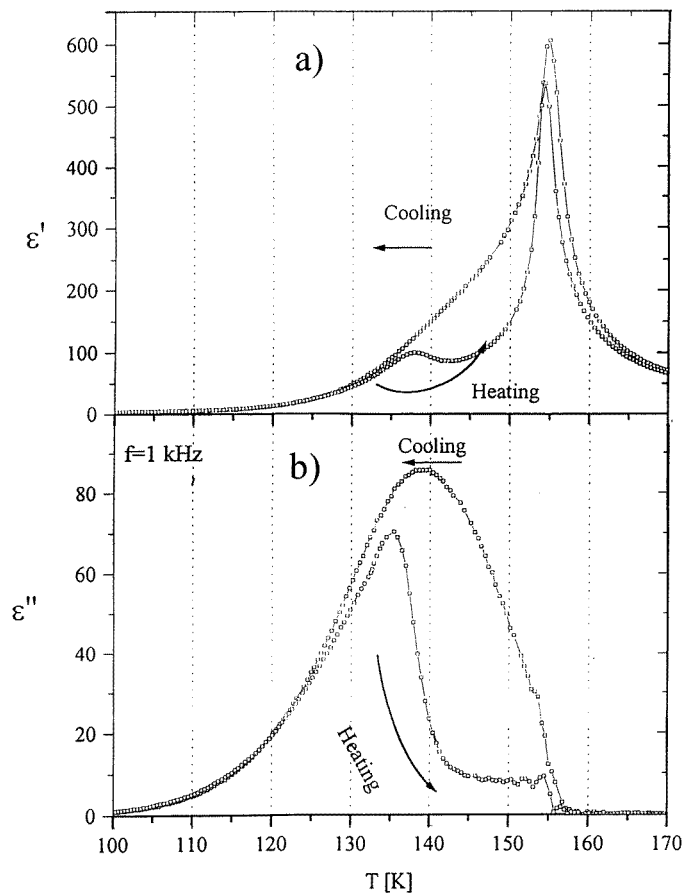


**Figure 4.** Temperature dependences of (a)  $\epsilon'$  and (b)  $\epsilon''$  for DMAASD obtained at different frequencies between 1 kHz and 1 MHz. The sample thickness is  $d = 1$  mm.

### 3.2. DMAASD

As it can be seen clearly from the temperature dependence of  $\epsilon'$  (figure 4(a)) the phase transition point is shifted toward higher temperatures due to the deuteration ( $T_c = 155.5$  K). The dielectric permittivity gives rise to a sharp peak at  $T_c$ , characteristic of proper ferroelectric phase transitions. At low frequency (at least, below 100 kHz) the temperature dependence of the dielectric permittivity clearly deviates from a Curie–Weiss law. At  $f = 1$  kHz, for example,  $\epsilon'$  shows a plateau between 120 K and  $T_c$  and steeply falls with further cooling. The imaginary part  $\epsilon''$  (figure 4(b)) displays clear maxima at the temperatures corresponding to the regions of the sharpest decrease of the dielectric permittivity (the most intensive peak of  $\epsilon''$ , obtained at  $f = 1$  kHz, is omitted to preserve the details of other dependences). These anomalies shift towards lower temperatures with decreasing frequency. Meanwhile, at higher frequencies, e.g. at  $f = 1$  MHz, the ordinary peak of  $\epsilon''$  is observed exactly at the phase transition point  $T_c$ . Similar anomalous behaviour of the dielectric constant has been observed in the crystals of the KDP family and has been related to the dipole reversal within the domain walls in the AC field [12]. Due to this fact the domain walls can move and the reorientation of the corresponding dipoles enlarges the

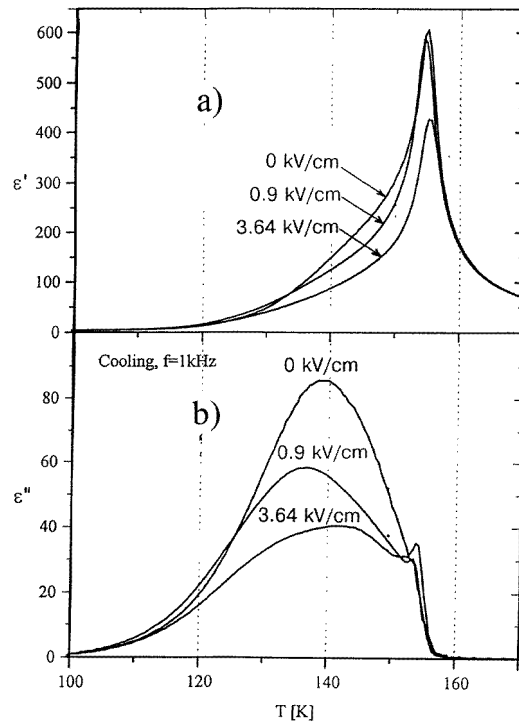
susceptibility. When approaching a certain temperature of freezing  $T_f$ , dipoles are no longer easily removable and consequently the mobility of the domain walls vanishes, leading to an abrupt decrease of the dielectric constant [12]. For DMAASD one can conclude that the considered phenomenon depends on the specimen size and strongly on the temperature cycling (cooling or heating runs) even in the same sample. Because of this the value and the shape of the dielectric constant's anomalies below  $T_c$  depend on the aforementioned factors. This can be seen from the temperature dependences of  $\epsilon'$  and  $\epsilon''$  for DMAASD obtained in the cooling and heating run at  $f = 1$  kHz (figure 5). On heating the dielectric permittivity shows a more noticeable plateau below  $T_c$ , although the values of the dielectric constant are lower in this region in comparison with the cooling run. On the other hand, the relaxation maxima of  $\epsilon''$  in a heating run are observed at lower temperatures. Comparing figures 4 and 5 one can notice the difference between the data obtained by applying the same AC field on samples with the thicknesses of 1.0 and 0.55 mm respectively.



**Figure 5.** Temperature dependences of (a)  $\epsilon'$  and (b)  $\epsilon''$  obtained on cooling and on heating at  $f = 1$  kHz for a sample of DMAASD with a thickness of  $d = 0.55$  mm.

It seems that the observed phenomenon is closely connected with the crystal defects and the domain texture formed in the ferroelectric phase. Besides we have to bear in mind that the DMAAS crystals are ferroelastic already at room temperature in the paraelectric phase





**Figure 6.** The influence of a DC bias electric field (0 kV, 0.9 and 3.64 kV cm<sup>-1</sup>) on the dielectric constant (a)  $\epsilon'$  and (b)  $\epsilon''$  of DMAASD.

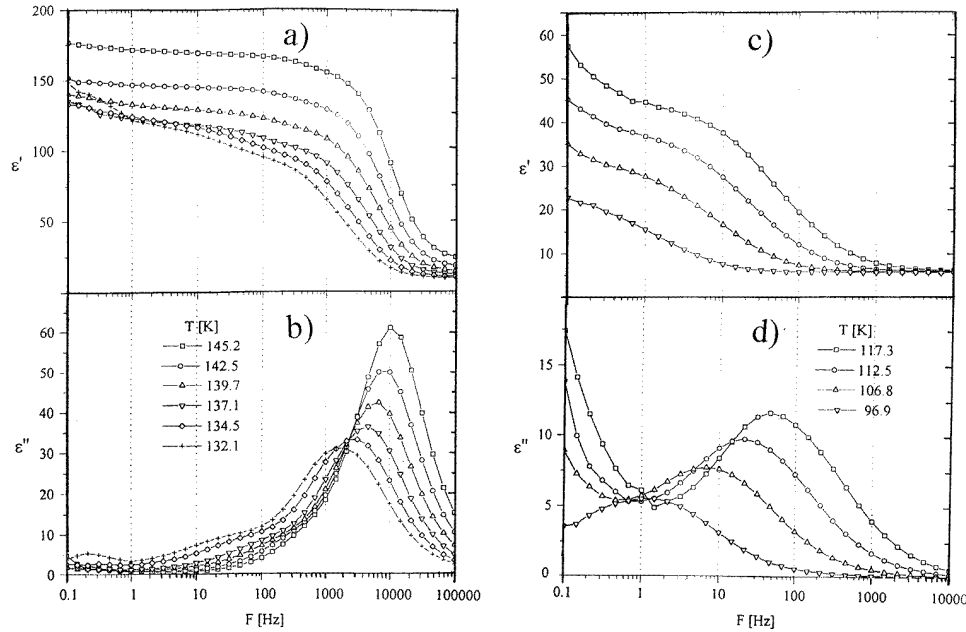
and are in a multidomain state with respect to the ferroelasticity. One could say that in a heating run the (ferroelectric) domain walls remain partly frozen even at the temperatures above  $T_f$ .

A bias electric field also strongly influences the considered anomalies (figure 6). The observed decrease of the dielectric constant's anomalies can be related to the process of sample transformation into the single-domain state.

Figure 7 shows the frequency dependences of  $\epsilon'$  and  $\epsilon''$  for DMAASD in the frequency range  $10^{-1}$ – $10^5$  Hz. A clear dispersion of a relaxational type is found just below  $T_c$ . The profiles of  $\epsilon''$  in figure 7(b), (d) are symmetric with respect to the frequency in the logarithmic scale. When the temperature is lowered the peak of  $\epsilon''$  shifts to the low-frequency region and becomes broader in width and lower in height. This result implies a peculiar behaviour of the relaxation times whose distribution function strongly depends on the temperature. The relaxational dispersion completely disappeared above  $T_c$  in the frequency range measured.

Cole–Cole diagrams for the deuterated crystal obtained at different temperatures within the ferroelectric phase are shown in figure 8. Although the shape of the plots is close to the semicircle, they deviate from a pure Debye relaxation behaviour since the semicircles are not centred on the  $X$ -axis. This implies some distribution of relaxation times. In this case the complex dielectric constant can be written as [17]

$$\epsilon^*(\omega, T) = (\epsilon_0(T) - \epsilon_\infty(T)) \int_0^\infty \frac{g(\tau, T) d\tau}{1 + i\omega\tau} + \epsilon_\infty(T). \quad (6)$$



**Figure 7.** The dielectric constant (a), (c)  $\epsilon'$  and (b), (d)  $\epsilon''$  for DMAASD as a function of frequency for various temperatures in the ferroelectric phase.

Here  $g(\tau, T)$  results from a Gaussian distribution of activation energies  $E$  centred around  $E_0$  with variance  $\sigma$  which enter a Vogel–Fulcher law for the relaxation time [17]:

$$\tau(T) = \tau_0 \exp\{E/(T - T_0)\}. \quad (7)$$

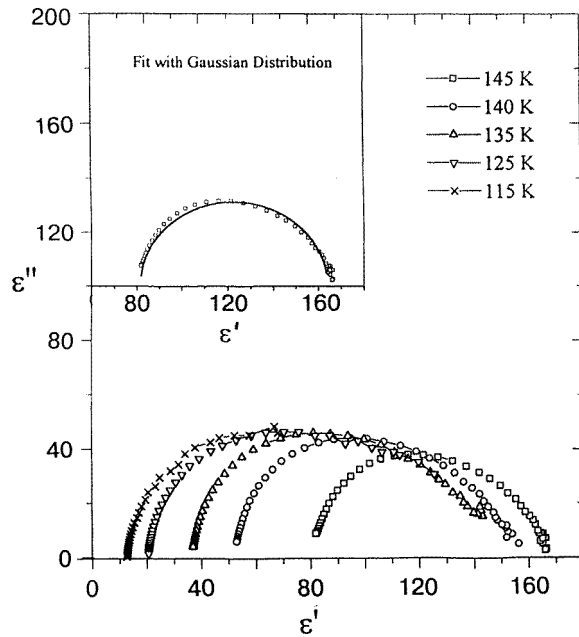
Working out least-squares fits to the data and using a procedure described in detail elsewhere [13,18] one can obtain the important parameters such as Vogel–Fulcher temperature  $T_0$ , relaxation time at infinite temperature  $\tau_0$  and mean value ( $E_0$ ) and variance ( $\sigma$ ) for the distribution of activation energies:

$$\begin{aligned} T_0 &= 111.0 \pm 0.1 \text{ K} \\ \tau_0 &= (3.4 \pm 0.2) \times 10^{-7} \text{ s} \\ E_0 &= 77.7 \pm 0.3 \text{ K} \\ \sigma &= 16.0 \pm 0.1 \text{ K}. \end{aligned}$$

#### 4. Conclusion

We have investigated DMAAS crystals and their deuterated analogues DMAASD in the ferroelectric phase by means of dielectric measurements over a wide frequency range.

The thermal dipole relaxation with a critical slowing down at  $T_c$  was observed in the hydrogenated sample at frequencies rather low for such a type of phenomenon. Perhaps this is due to the availability of comparatively massive dipoles in the structure of DMAAS (compare also [15]). The relaxation connected with the domain freezing was observed at lower frequencies (at least, below 100 kHz) and was found to be much more pronounced in the deuterated crystals. This effect is thought to be due to the reversal of the dipoles in the



**Figure 8.** Cole–Cole diagrams for DMAASD obtained at different temperatures. The solid line is the fit to equation (6).

AC field. As a result, the domain walls can move and the reorientation of the corresponding dipoles enlarges the susceptibility. When approaching a certain ‘freezing’ temperature the dipoles are no longer easily removable and consequently the mobility of the domain walls vanishes, leading to an abrupt decrease of the dielectric constant. The observed phenomenon is considerably connected with proton dynamics since the deuteration strongly influences the amplitude as well as the frequency and temperature positions of the anomalies. Moreover in DMAASD the relaxation corresponding to the domain motion is observed in a more wide frequency range. This situation correlates with the model proposed by Nakamura. According to [12] the dipole reversal may arise around the domain walls with the cooperative reorientation of the ions with minor violation of the ice rule for the proton configuration. In this case a certain size of the cooperative region will be required. According to a theory of Adam and Gibbs concerning glass forming processes [19] the increase in the size of such cooperative clusters with decreasing temperature gives a non-Arrhenius type temperature dependence of the relaxation time containing the Vogel–Fulcher law, as a result of a decrease of the configurational entropy for dipole reorientation. It seems that the limiting size of the clusters depends on the defect and domain wall density. Due to this the dielectric parameters measured at different conditions of the experiment (sample thickness, regime of temperature change etc) display divergent features in the region of anomalous relaxation.

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