Dynamical Dielectric Instability of the Ferroelectric $AgNa(NO_2)_2$

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The characteristic ferroelectric dispersion of the complex dielectric constant of $AgNa(NO_2)_2$ is measured in a wide temperature range enclosing the transition point. It can be well described by a Debye monodispersive process except for a small temperature intervall around T_c. The relaxation strength obeys a Curie-Weiss law in the paraelectric phase, whereas in the ferroelectric phase there are deviations from this behaviour. A first order phase transition is observed which is close to a second order one. The maximum value of the dielectric constant at T_c is 10^4.

I. Introduction

It has been shown by several recent investigations that $AgNa(NO_2)_2$ is a ferroelectric crystal which undergoes a phase transition of the first order, close to a second order one, at about 38 C. In particular, dielectric measurements[1, 2] show that the transition may be assumed to be of the order-disorder type with the NO_2^--groups forming the permanent electrical dipoles. In contrast to most of the order-disorder ferroelectrics in this substance an extremely small, strongly temperature dependent, characteristic relaxation frequency can be observed indicating that the critical polarization dynamics appear in the kHz regime.

However, there are some problems with the macroscopic dielectric behaviour which, so far, have not been cleared up with a sufficient accuracy. So e. g. it is not known how close the phase transition is to a second order one. Of course, this problem is related to the question, what is the maximum value of the dielectric constant, which can be reached at the transition point. Furthermore the temperature dependence of the macroscopic characteristic dielectric relaxation frequency, so far, is not known in a wide temperature range. If this quantity were known with a better accuracy the activation energy for the motions of the electrical dipoles could be estimated more accurately. It is the purpose of the present paper to contribute to a solution of these problems. The experimental results which will be reported in the following could only be obtained by growing single crystals of an extreme quality. Special care must be taken when preparing the samples because the crystals are very sensitive to external manipulations.

II. Sample Preparation and Experimental Details

It is well known[3] that single crystals of $AgNa(NO_2)_2$ can be grown from an aqueous solution of $AgNO_2$ and $NaNO_2$ in a range of composition of 9.8 – 6.4 wt% $AgNO_2$ and 37.2 – 30.5 wt% $NaNO_2$. Since these values correspond to a molar composition of approximately 8.5:1 to 10.6:1 ($NaNO_2$: $AgNO_2$) when growing the $AgNa(NO_2)_2$ single crystal the solution becomes more and more depleted of $AgNO_2$. Consequently only a limited amount of $AgNa(NO_2)_2$ single crystal may be grown from a given solution. Furthermore while growing the crystal the crystal quality diminishes. These problems may be avoided by growing the crystal in a rather big amount of aqueous solution of $AgNO_2$ and $NaNO_2$[4]. Three crystals each of which had a mass of 5 – 6 g (about $28 \times 12 \times 10$ mm^3 in size) were simultaneously grown by slow cooling between 27.0 and 25.5 C from a solution of 2 l. At the beginning the rate of change of the temperature was 0.003 C per day. It was increased quadratically reaching a value of 0.013 C per day at the end of the growing process after two months. The seed crystals were moved in the solution.

The samples needed for the dielectric measurements were prepared from the single crystals with a wet thread saw using a nearly saturated aqueous solution of $NaNO_2$ as solvent. We obtained two plates with a thickness of about 1.2 mm (ferroelectric axis) and an area of about 3×5 mm^2. At first the surfaces of the plates were polished by rubbing the plates on a silk which was imprignated with a saturated $NaNO_2$ solution. The plates were finally polished by applying diamond powders with a grit size up to 0.25 μm. The electrodes were prepared by a silver paste (Du Pont No. 4922). The frequency and temperature dependent capacity of the plates was measured between 60 Hz and 100 kHz with a General Radio Bridge 1621 and between about -16 C and $+53$ C. Generally the temperature stability was about ± 0.01 C. In particular, very close to the transition point it was about ± 0.003 C.

III. Experimental Results and Discussion

The complex dielectric constant $\varepsilon(\omega)$ in the ferroelectric b direction can be represented in the entire temperature range by a Cole-Cole formula, i. e.

$$\varepsilon(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)/[1 + (i\,\omega\,\tau_\varepsilon)^{1-h}]\,. \quad (1)$$

By ε_s and ε_∞ we denote the static and high frequency values of the dielectric constant. The relaxation time is τ_ε and the parameter h describes the distribution of relaxation times. In Fig. 1 results are presented for one sample in a temperature range close to T_c which are of special interest. Generally in accordance with Ref. [1, 2] the following facts may be stated. In the entire temperature range the dispersion step of the dielectric constant is nearly of the single Debye relaxational type. A very small distribution parameter h of about 0.05 and 0.03 can be observed for the two samples respectively. It does not show a significant temperature dependence except for a small temperature intervall of about 1 C around T_c. At T_c h is in the order of 0.1. These results are in accordance with those of Gesi [1]. Thus, it can be concluded that the polarization dynamics of a perfect $AgNa(NO_2)_2$ single crystal are of the single Debye relaxational type. The observed small distribution of relaxation times near T_c may be caused by the influence of an inhomogeneous non-ferroelectric surface layer, by a radial temperature gradient over the sample volume, and by a distribution of transition points within the sample (inhomogeneous crystal [5]). Consequently, from the small distribution of relaxation times which is observed near T_c it cannot be concluded that the polarization dynamics in a perfect bulk crystal of $AgNa(NO_2)_2$ could be described by a distribution of relaxation times. From the observed small distribution angles it may be concluded that the crystals are of good quality . The high frequency dielectric constant ε_∞, which was measured explicitly at 2 MHz, has values between 5 and 6 and does not show any critical behaviour, too. On the other hand ε_s strongly depends on the temperature reaching a maximum value of about 10^4 and 0.4×10^4 for the two samples near T_c. These extremely high values, too, demonstrate the good quality of the samples. In particular there can only be a small influence of a non-ferroelectric dielectric surface layer, which limits the maximum value of ε_s near T_c. The influence of a surface layer on the critical dynamics near T_c has been discussed in Reference 2. According to Fig. 1 near T_c the critical dielectric relaxation frequency reaches the extremely small value of 400 Hz.

The temperature dependence of the relaxation strength is given by a Curie-Weiss law in the paraelectric phase. In the ferroelectric phase there are – close to T_c (Fig. 2) and far away from T_c (below 20 C) – deviations from a Curie-Weiss law, which consequently may be used only in a first approximation. In accordance with Ref. [1] the Curie constants are about $C_p = 4.5 \times 10^3$ K and $C_f = 4.9 \times 10^2$ K for the paraelectric and ferroelectric phases, respectively. The ratio C_p/T_c is of the order of 14, thus indicating that the transition is of the order-disorder type [6]. The fact that a very small difference $T_c - \Theta \cong 0.3$ C is observed (for the sample of Fig. 2) between the phase transition temperature T_c and the temperature Θ of the limit of stability of the paraelectric phase indicates a phase transition of the first order which is very close to a second order one. The ratio C_p/C_f of the Curie constants is 9.2 which is a value typical for a first order phase transition.

A homogeneous non-ferroelectric dielectric surface layer would influence the results of Fig. 2 in that way that all measuring points were shifted to higher values by a constant amount [2]. In fact this behaviour was observed for the other sample. Thus, the difference $T_c - \Theta$ of a perfect bulk crystal may have as a maximum the value of 0.3 C reported above. Consequently it seems to be likely that there is a first order phase transition which is very close to a second order one. However, the case that there is a second order phase transition which is very close to a first order one cannot be fully excluded.

On approaching T_c both from above and below the reciprocal relaxation time τ_ε^{-1} strongly decreases indicating the critical slowing down of the polarization reversal motion (Figure 3). In contrast to many other ferroelectric crystals the behaviour of τ_ε cannot be represented by a Curie-Weiss law. Thus, τ_ε and the relaxation strength do not show the same temperature dependence near T_c. At about $+25.6$ C τ_ε^{-1} reaches a maximum value and de-

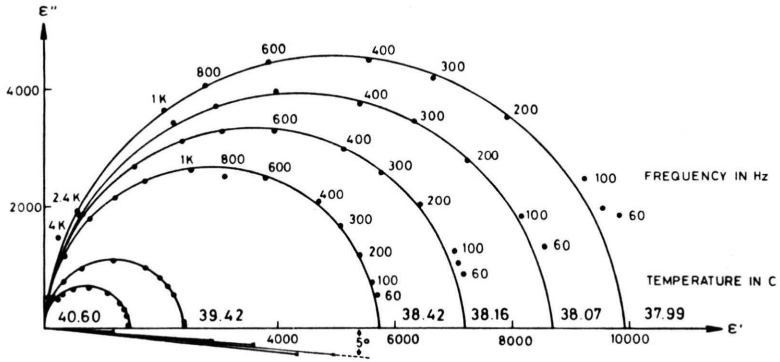

Fig. 1. Frequency and temperature dependence of the complex dielectric constant in the ferroelectric direction in the paraelectric phase near the transition point.

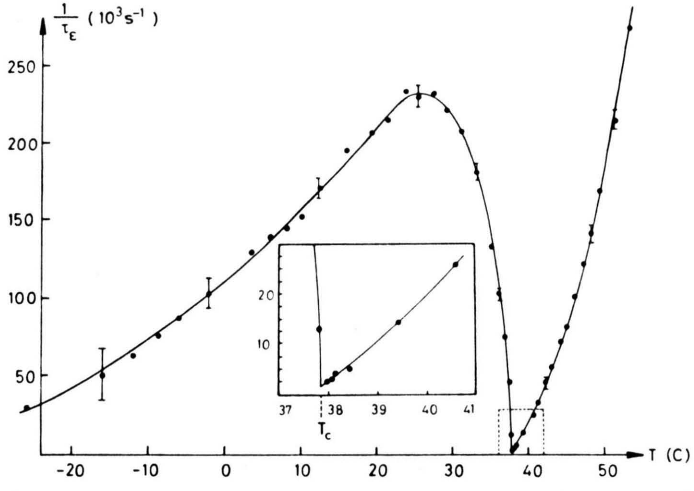

Fig. 3. Temperature dependence of the reciprocal relaxation time $\tau_\varepsilon{}^{-1}$ obtained from the results of Figure 1.

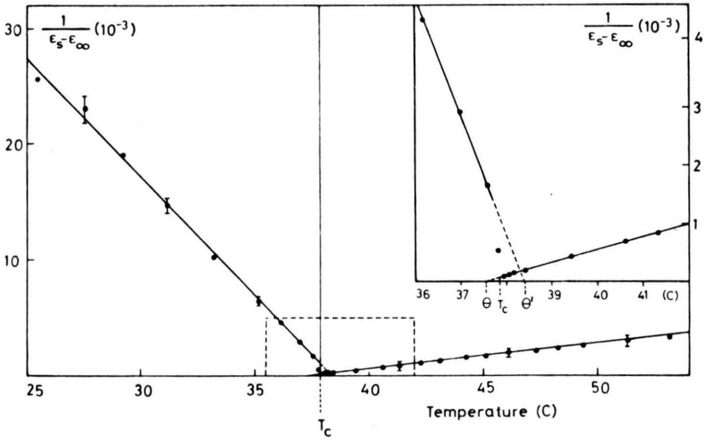

Fig. 2. Temperature dependence of the relaxation strength $\varepsilon_S - \varepsilon_\infty$ near T_c, obtained from the results of Figure 1.

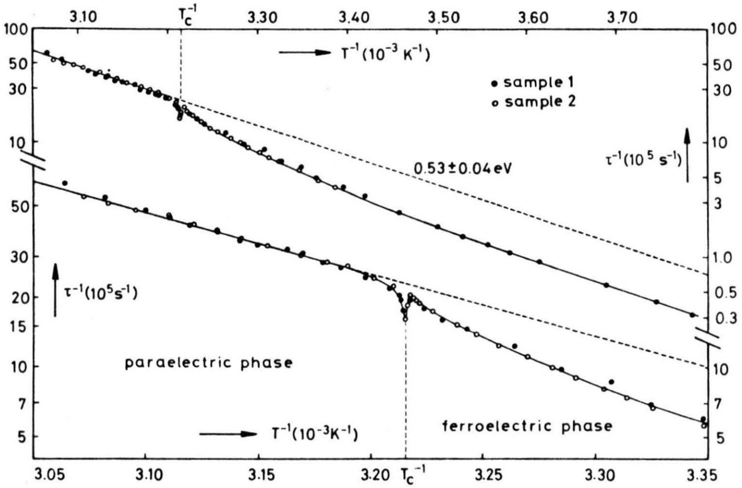

Fig. 4. Arrhenius plot of τ^{-1} for two samples.

creases at lower temperatures. So far, a behaviour of this type has not been observed in other ferroelectric crystals.

A molecular interpretation of these results may be achieved by assuming a dynamical Ising model in the random phase approximation for the motions of the electrical NO_2^--dipoles[2]. According to this model the relaxation time

$$\tau_0 = \tau_\varepsilon / (\varepsilon_s - \varepsilon_\infty) \qquad (2)$$

which may be determined from the experiment is directly related to the relaxation time $\tau = \tau_0 \, C_p / T$ of the non-interacting system of the electrical dipoles (as above C_p is the Curie constant of the paraelectric phase). This quantity should depend on the temperature according to a thermally activated process[2, 6]

$$\tau = \Gamma^{-1} \exp\{\Delta U / k\,T\} \qquad (3)$$

where ΔU is the activation energy for the motions of the dipoles. According to Fig. 4 the value of τ^{-1} obtained for the two samples coincide despite the fact that the corresponding values of τ_ε and $\varepsilon_s - \varepsilon_\infty$ show a difference. This fact clearly indicates that the molecular parameter τ can be determined from dielectric measurements which are performed on crystals with surface layers of different thickness. A phenomenological description of this behaviour was given in Reference[2]. There is a thermally activated process with an activation energy of 0.53 ± 0.04 eV in the paraelectric phase (Figure 4). Obviously in the ferroelectric phase and at T_c τ^{-1} differs from the values which are extrapolated from the paraelectric phase. Close to T_c in the paraelectric phase the temperature dependence of τ^{-1} deviates from the linear behaviour in Figure 4. Probably this is not a critical effect. It is rather very likely that, as in other ferroelectrics[9], this behaviour is a consequence of the increase of the distribution parameter h near T_c which may be caused either by a "critical" behaviour of the perfect bulk crystal or, more probably, by the inhomogeneities discussed above.

Far away from T_c in the ferroelectric phase the observed temperature dependence of τ^{-1} corresponds to the activation energy of the paraelectric phase. It seems to be likely that this observed behaviour of τ^{-1} in the ferroelectric phase is mainly due to an influence of the temperature dependent spontaneous polarization P_s. This quantity may influence τ in the following ways. In the ferroelectric phase the double well potential for the motions of the dipoles becomes more assymetric. The influence of this effect has been discussed in Reference[7, 8]. Since AgNa$(NO_2)_2$ is a non piezoelectric – i.e. electrostrictive – crystal in the paraelectric phase there appear spontaneous strains $e_{is}(T)$ in the ferroelectric phase which are proportional to P_s^2. Consequently the activation energy of the ferroelectric phase may be written as

$$\Delta U(T) = \Delta U + \sum_{i=1}^{6} \left.\frac{\partial(\Delta U)}{\partial e_i}\right|_{e_i=0} e_{i_s}(T) = \Delta U + c\,P_s^2 \qquad (4)$$

where, as above, ΔU is the activation energy of the paraelectric phase and c is a suitable constant.

From Eq. (4) it follows for the relaxation time $\tau(T)$ in the ferroelectric phase $(T \leqq T_c)$

$$\ln \tau(T) = \ln \tau_+(T) + c\,P_s^2 / k\,T \qquad (5)$$

where $\tau_+(T)$ is the relaxation time $\tau(T)$ of the paraelectric phase which has been extrapolated to the ferroelectric phase. According to Eq. (5) one would expect a temperature dependence of $\tau(T)$ in the ferroelectric phase which reflects the temperature dependence of the spontaneous polarization P_s. As demonstrated in Fig. 4 this behaviour is in accordance with the experimental facts. At low temperatures below about +10 C P_s is saturated[10]. In this region the activation energy should differ from the value of the paraelectric phase by the amount of $c\,P_s^2$. However this difference cannot be detected in Fig. 4 because

$$\ln\{\tau(T)/\tau_+(T)\} \cong 0.70 \ll 23 \cong \Delta U / k\,T \,.$$

In a previous work[7] it was proposed that a mechanical clamping of the crystal in the dielectric measurements may also give different temperature dependences of τ in the paraelectric and ferroelectric phases. However, since there is an extremely slow dielectric motion in AgNa$(NO_2)_2$ this effect does not influence the results.

IV. Conclusions

Finally the following facts may be stated:

1. In the entire temperature range the critical dielectric relaxation of the dielectric constant of AgNa$(NO_2)_2$ is nearly of the single relaxational type. From the observed small deviations it cannot be concluded that the ferroelectric polarization dynamics of a perfect bulk crystal differ from the monodispersive type.

2. In the paraelectric phase the relaxation strength $\varepsilon_S - \varepsilon_\infty$ shows a Curie-Weiss law, thus indicating that the mean field approximation can be applied to this substance. This also shows that $\varepsilon_S - \varepsilon_\infty$ is the critical parameter describing the phase transition. In the ferroelectric phase there are deviations from the Curie-Weiss law and, at present, it is not clear wether or not they may be accounted for by a phenomenological theoretical approach.

3. The reciprocal relaxation time τ_ε^{-1} shows a temperature dependence which, so far, was not observed in other ferroelectrics. The reason is that the activation energy for the motions of the electrical dipoles is extremely large.

4. The reciprocal relaxation time τ^{-1} of the non-interacting system of the electrical dipoles deviates in the ferroelectric phase from the values extrapolated from the paraelectric phase. This effect is caused by an influence of the spontaneous polarization. As a whole the critical dynamics can be described in accordance with phenomenological theories[6].

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