The ferroelectric low-temperature phase of single crystals of the substituted diacetylene 1,6-bis(2,4-dinitrophenoxy)-2,4-hexadiyne (DNP)

The ferroelectric low-temperature phase of single crystals of the substituted diacetylene 1,6-bis(2,4-dinitrophenoxy)-2,4-hexadiyne (DNP)

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Abstract. Dielectric and pyroelectric properties of single crystals of 1,6-bis(2,4-dinitrophenoxy)-2,4-hexadiyne (DNP) were measured parallel to the polar b axis. Poling experiments with static electric field strengths of up to 33 kV cm^{-1} prove that, at least for parts of the crystals, the direction of the spontaneous polarization can be reversed, implying a distribution of transition temperatures. The maximum polarization measured reveals values up to 2.4×10^{-7} C cm^{-2} at 10 K, which is in very good agreement with x-ray studies. Within a Landau theory of phase transitions for ferroelectric materials, the experimental curves of the spontaneous polarization seem to behave tricritically in the polar phase below 46 K. Owing to the distribution of transition temperatures, the order of the phase transition cannot be determined from permittivity experiments. The influence of a small static electric field on the electric susceptibility is discussed as well.

1. Introduction

Diacetylenes R$_1$—C≡C—C≡C—R$_2$ are special in that they form macroscopic monomer single crystals, which can be converted into macroscopic polymer single crystals by means of a solid-state polymerization if the substituents R$_1$ and R$_2$ are chosen appropriately [1]. This reaction, which has been investigated in considerable detail, is accompanied by a crankshaft type of motion of the monomer molecule around its centre of mass (figure 1). Owing to the softness of these librations, it is a promising approach to take substituents with permanent electric dipole moments in order to yield interesting dielectric, pyroelectric or even ferroelectric organic crystals. In this way, different polar (poly)diacetylenes have been successfully synthesized [2–4].

The symmetrically substituted diacetylene 1,6-bis(2,4-dinitrophenoxy)-2,4-hexadiyne (DNP) (figure 2), is the only diacetylene that is supposedly ferroelectric [5, 6]. Each substituent group carries a permanent electric dipole moment of about 3 D or 1×10^{-29} C m. DNP is known to undergo a phase transition from a non-polar high-temperature phase (space group $P2_1/n$) to a polar low-temperature phase (space group $P2_1$) at 46 K [6, 7] where there is a non-zero net dipole moment per molecule. Above 46 K, the dipole moments per molecule cancel each other. Owing to the peculiarity of thermal, but not x-ray, polymerization, x-ray studies can be done for both
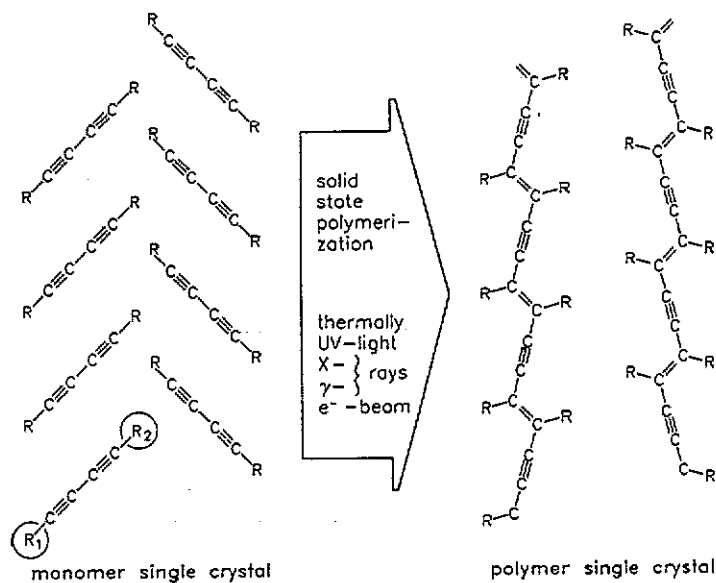
Figure 1. Scheme of the topotactic solid-state polymerization of diacetylene crystals with side groups R_1 and R_2.

monomer and polymer. So, x-ray and ^1H nuclear magnetic resonance (NMR) studies showed that both the phenyl rings are slanted against each other by an angle of 5.1° in the polar phase and the molecule is twisted around its diacetylene backbone [7, 8]. Thus the suppression of the phase transition with increasing degree of polymerization observed earlier [5, 6] is understood very well as the polymerization hinders the torsion of the monomer unit.
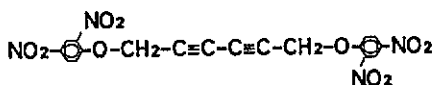

Figure 2. Diacetylene monomer molecule of DNP.

So far, it is still open whether the phase transition at 46 K is one to a ferroelectric or a pyroelectric low-temperature phase. Here we will discuss poling experiments proving it to be indeed a ferroelectric transition. Furthermore, the measurements of the spontaneous polarization parallel to the polar *b* axis of the DNP crystal give rise to the assumption that we have to deal with a so-called tricritical transition within the Landau theory of ferroelectrics. The reason for an obvious disagreement between theory and the behaviour of the electric susceptibility and its dependence on the static electric field will be discussed as well.

2. Experimental part

The synthesis and crystal growth are described in detail in the literature [6, 9]. Single crystals of DNP monomer were appropriately cut with a razor blade, kept under technical vacuum for about 20 h and then electroded as parallel-plate capacitors with silver paint and gold wire of a diameter of 50 μm. The geometry of the samples was

determined under a microscope. The typical size amounted to 0.5–3 mm^2 in area and 0.2–1 mm in thickness.

The spontaneous polarization, being identical to the surface charge density as long as the electric field vanishes, was measured with a commercial electrometer (Keithley EM 617). The dielectric permittivities were determined with a commercial capacitance bridge (GenRad Digibridge 1689M) at a frequency of 1 kHz mainly. During the temperature-dependent measurements the sample temperature was controlled with an Oxford Instruments cryostat. The absolute error amounts to ±0.5 K.

3. Spontaneous polarization of the polar low-temperature phase

3.1. *Without external electric field*

Figure 3 shows the temperature dependence of the spontaneous polarization parallel to the polar *b* axis for different single crystals of DNP monomer. When normalized to the respective maximum value at the lowest temperature, all curves show a very similar behaviour, so that one order parameter should be sufficient for a description within the Landau theory of phase transitions. The maximum value of the spontaneous polarization at about 10 K was 2.4×10^{-7} C cm^{-2}, corresponding to an angle of 5.9° between the phenyl rings of the DNP substituents, which is in very good agreement with 5.1° from x-ray studies at 5 K [7].
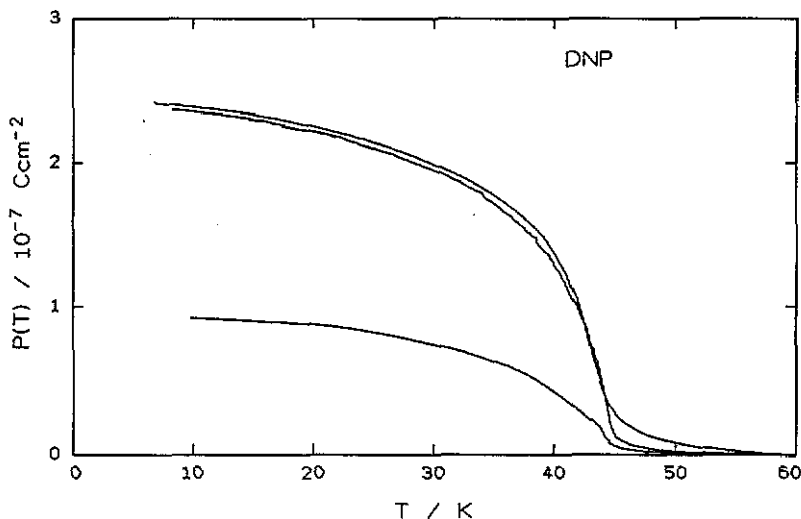

Figure 3. Temperature dependence of the spontaneous polarization parallel to the polar *b* axis for different single crystals of DNP monomer.

3.2. *Poling experiments*

In order to prove the ferroelectricity of the polar low-temperature phase, the orientation of the spontaneous polarization must invert under the action of a (strong) static electric field that is applied parallel and antiparallel, respectively, to the polar *b* axis. For experimental reasons, like small sample area, sparking or breakthrough, electric

fields of a sufficient strength could not be applied to the small DNP single crystals. Therefore, the electric field was applied already in the high-temperature phase and during cooling through the phase transition.

In the following the electric field was always applied during cooling. The spontaneous polarization was determined then on heating without an external electric field. The respective curves are shown in figure 4. In the first run, the value of the spontaneous polarization for the unpoled sample was determined by cooling it from room temperature to about 10 K and then heated up to about 120 K without an external electric field (figure 4, curve I). At this temperature, the sample is 'far above' the transition point. Then, an electric field of 33 kV cm^{-1} was applied during cooling the sample again to about 10 K. Curve II in figure 4 shows the spontaneous polarization measured afterwards when heating the sample. After poling with an electric field of 33 kV cm^{-1} of opposite direction, we got curve III in figure 4 when heating the sample.
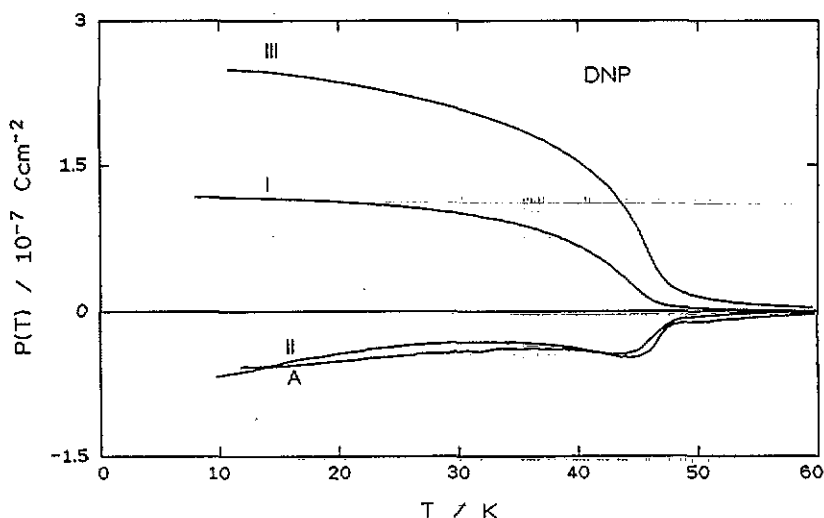

Figure 4. Temperature dependence of the spontaneous polarization parallel to the polar b axis after applying an external electric field of 33 kV cm^{-1} in different orientation (see text).

From former experiments the transition temperature is known to change to lower values if a sample is thermally cycled several times [6]. The maximum value of the spontaneous polarization drops as well. This is due to cracks and therefore due to an increasing number of defects. After the poling procedure, however, the absolute value of the low-temperature polarization nearly doubled and the transition region was shifted to a higher temperature when comparing curves I and III (figure 4). This supports the assumption that within the same sample there must be a distribution of transition temperatures. The difference of curves III and I in figure 4 can be used to estimate that part of the spontaneous polarization that can be poled by applying the electric field. Subtracting such a contribution from curve I yields curve A of figure 4, which is in close agreement with the experimental curve II in figure 4.

Thus, the ferroelectricity of the low-temperature phase is established, as the spontaneous polarization can be reversed by an external electric field, at least in parts of the sample.

The distribution of transition temperatures might be due to regions of different strain, which are inevitable as in all monomer samples there is always a small amount of polymer ($< 5\%$). The phase transition is connected with a torsion of the diacetylene backbone —$C{\equiv}C$—$C{\equiv}C$—, which is suppressed in polymer molecules. Besides, there is aways a mismatch due to the different lattice parameters for monomer and polymer crystals. In addition, real crystals contain imperfections that lead to different volumes for intramolecular motions. According to figure 4, apparently only those regions of a crystal can be poled which are distinguished by the higher transition temperatures, i.e. by a smaller degree of imperfections.

4. Description of the phase transition within Landau's theory of ferroelectrics

The simplest approach to a theoretical description of a ferroelectric phase transition is Landau's theory of ferroelectrics [10]. Because of the temperature dependence of the spontaneous polarization (figure 3 and [6]), DNP is considered as ferroelectric with only one polar axis, which coincides with the crystallographic b axis. In this case, the phenomenological approach of Landau's theory deals with the free enthalpy G as an expansion in even powers of the order parameter, here being identical to the spontaneous polarization P:

$$G = G_0 + \tfrac{1}{2}a P^2 + \tfrac{1}{4}b P^4 + \tfrac{1}{6}c P^6. \tag{1}$$

Usually the validity of this equation is assumed in the vicinity of the transition point T_c. Here G_0 is the free enthalpy at zero polarization and depends on temperature and pressure as do the coefficients a, b and c. Usually, $a(T)$ is taken as a linear function of $T - T_c$ to guarantee stable equilibrium positions for $T < T_c$, i.e. in the ordered phase. Here, the only restriction for $a(T)$ shall be the change of sign at T_c as usual. The coefficients b and c are not strongly dependent on temperature. Then, the equilibrium value of P can be determined by demanding it to be stable:

$$\partial G/\partial P = 0 \qquad \text{and} \qquad \partial^2 G/\partial P^2 > 0. \tag{2}$$

There are different orders of phase transitions. Generally speaking, a phase transition of nth order is accompanied by a discontinuity of the nth derivative of G. For example, the variables of state change steplike at T_c for a first-order transition. As this is not the case in our experiments, first-order transitions will not be considered here.

On the other hand, the sign of the coefficient b is an important quantity. For b negative, we must take the expansion of equation (1) to sixth degree ($c > 0$) to obtain the polarization in the ordered phase. For b positive, it is sufficient to take into account a fourth-order expansion and we get a second-order transition. And for b zero, equation (1) gives a so-called tricritical phase transition describing a borderline case between a first-order and a second-order phase transition. However, it is quite different compared to a phase transition of first order: for symmetry reasons the transition from the unordered to the ordered phase is accompanied by small lattice distortions. For $b = 0$ equation (2) leads to

$$P(T) = 0 \qquad \text{for } T > T_c$$
$$P(T) = \pm[-a(T)/c]^{1/4} \qquad \text{for } T < T_c \tag{3}$$

and

$$\partial^2 G/\partial P^2 = 1/\epsilon_0 \chi_{ferro}(T) = a(T) > 0 \qquad \text{for } T > T_c$$
$$\partial^2 G/\partial P^2 = 1/\epsilon_0 \chi_{ferro}(T) = a(T) + 5cP^4(T) = -4a(T) > 0 \qquad \text{for } T < T_c.$$
$$(4)$$

Here χ_{ferro} is that part of the electric susceptibility which essentially describes the phase transition. Assuming Curie–Weiss laws for both regions

$$\epsilon_0 \chi_{ferro}(T) = C_>/(T - T_c) \qquad \text{for } T > T_c$$
$$\epsilon_0 \chi_{ferro}(T) = C_</(T_c - T) \qquad \text{for } T < T_c$$
$$(5)$$

the Curie–Weiss constants $C_>$ and $C_<$ for the high-temperature and the low-temperature region, respectively, behave like

$$C_>/C_< = 4 \tag{6}$$

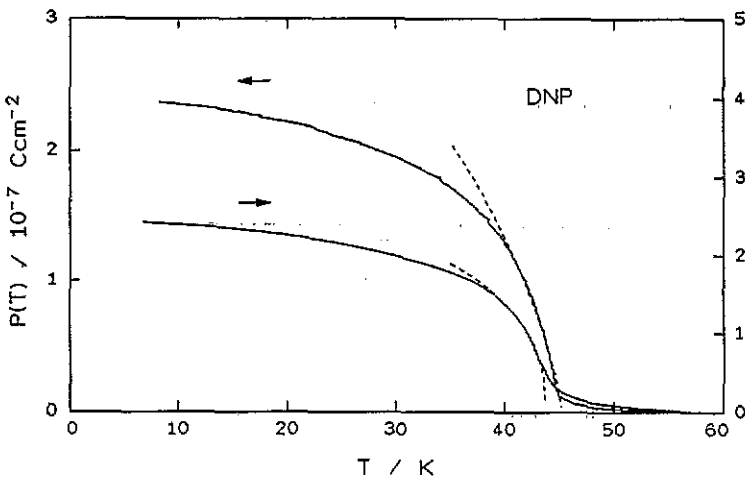in the case of a tricritical phase transition.

Figure 5. Experimental and fitted curves of the spontaneous polarization. The fits correspond to equation (8) ($T_c = 43.8$ K and $T_c = 46.6$ K, respectively). The arrows point to the appropriate vertical scale.

5. Comparison of experiment and theory

5.1. The spontaneous polarization

The fits to the experimental curves of P were determined numerically. In figures 5 and 6, two of them are shown for the coefficient $a(T)$ taken in the usual manner (the so-called Devonshire theory) as
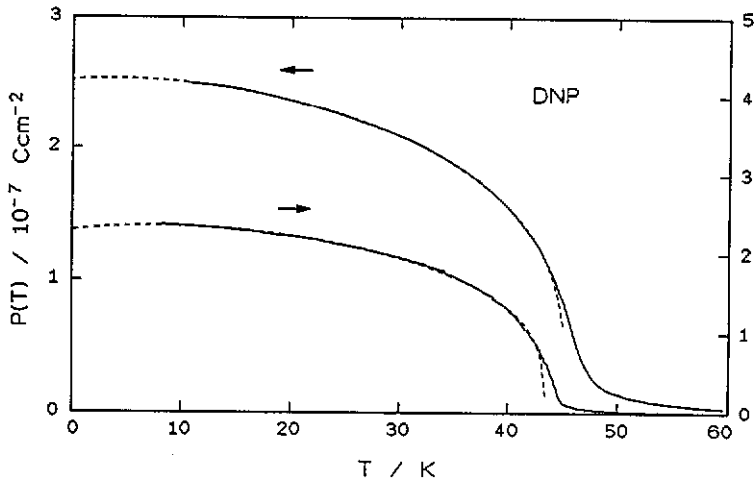
$$a(T) = a_0(T - T_c) \tag{7}$$

Figure 6. Experimental and fitted curves of the spontaneous polarization. The first correspond to equation (10) ($T_c = 43.4$ K and $T_c = 45.3$ K, respectively). The arrows point to the appropriate vertical scale.

which ends up in

$$P(T) = \pm P_0(1 - T/T_c)^{1/4}. \tag{8}$$

Surprisingly, there is very good agreement between the experimental results and the respective fits in a very large temperature regime when using

$$a(T) = a_0(T - T_c) + a_1(T - T_c)^3. \tag{9}$$

In figure 6 two experimental curves and the respective fits are given. The spontaneous polarization can then be written as

$$P(T) = \pm P_0[1 - T/T_c + \alpha(1 - T/T_c)^3]^{1/4}. \tag{10}$$

As a result of the fits to all experimental curves, we find

$$\alpha = -0.55 \pm 0.10. \tag{11}$$

(For temperatures $T < T_c$ each value of $a(T)$ must guarantee a minimum value of G, which also means that $a(T) < 0$ must be fulfilled. For all numerical values of P_0, T_c and α, this condition is fulfilled. It must be borne in mind, however, that equation (9) is the result of finding the best suitable fits to experiment and not of expanding Landau's theory.)

5.2. The electric susceptibility

The physical quantity being measured to get $\chi_{\text{ferro}}(T)$ is the dielectric permittivity $\epsilon_r(T)$. So, some assumptions are necessary to determine the ferroelectric part $\chi_{\text{ferro}}(T)$. 'Far above' the ferroelectric transition $\chi_{\text{ferro}}(T)$ is assumed to be negligible [10]. The contribution $\chi_{\text{el}}(T)$ to $\chi(T)$ which is not covered by $\chi_{\text{ferro}}(T)$, may

only weakly depend on temperature in the vicinity of the phase transition, so that it can be neglected there. These prerequisites lead to

$$\chi(T) \equiv \epsilon_r(T) - 1 = \chi_{el}(T) + \chi_{ferro}(T). \tag{12}$$

Defining the room-temperature value of $\epsilon_r(T)$ as ϵ_∞ one gets

$$\chi_{ferro}(T) = \epsilon_r(T) - \epsilon_\infty. \tag{13}$$

Then, the inverse of $\chi_{ferro}(T)$ leads directly to the experimental values of equation (6) by determining the slopes at the transition temperature. We must bear in mind, however, that the derived relations for a ferroelectric phase transition are valid for a single-domain ferroelectric only. In our 'real' crystals, there are several domains, as is seen from the poling experiments. The motion of the domain walls gives the predominant contribution to the low-frequency dielectric susceptibility in the ferroelectric phase. Therefore, we will discuss experiments with and without an external static electric field being applied during cooling.

Finally, we must take into account that experimental data may strongly depend on crystal quality: both the temperature dependence and the maximum value of $\epsilon_r(T)$ are known to depend on sample quality [6]. A good measure for the sample quality is how much larger $\epsilon_r(T_c)$ is than $\epsilon_r(T_{room})$. In addition, the 'peak' of ϵ_r versus T at T_c is broadened for 'relatively poor' crystals compared to the curves of 'relatively good' crystals.

5.2.1. Without external electric field. Figure 7 shows the temperature dependence of both $\epsilon_r(T)$ and the inverse of $\chi_{ferro}(T)$ for DNP samples of rather good quality. Note that we deal with organic crystals that show values of up to 150 for ϵ_r, being 19 times larger than the room-temperature value. Then, the slopes of either side of the phase transition yield

$$\begin{aligned} \epsilon_0/C_> &= 1.11 \times 10^{-2} \text{ K}^{-1} \qquad \text{for } T > T_c \\ \epsilon_0/C_< &= -2.65 \times 10^{-3} \text{ K}^{-1} \qquad \text{for } T < T_c \end{aligned} \tag{14}$$

so that we get

$$C_> / C_< = (4.2)^{-1} = 0.24 \tag{15}$$

as a typical value for good crystals.

Figure 8 shows the respective curves for a sample rich in defects. Here, the maximum value of $\epsilon_r(T)$ at T_c is only 10 times larger than at room temperature. The slopes of either side of the phase transition give

$$C_> / C_< = (3.1)^{-1} = 0.32 \tag{16}$$

which is a typical value for crystals rich in defects.

Comparing the values of equations (15) and (16) for the ratios of the Curie–Weiss constants with the theoretical value of 4 for a tricritical transition, apparently the order of the phase transition cannot be determined from the permittivity experiments whereas this is possible from the polarization experiments. The reasons for this
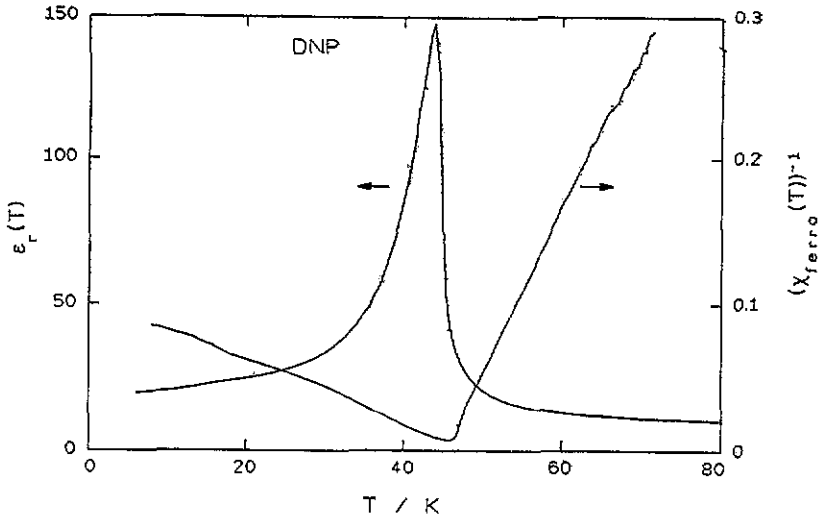
Figure 7. Temperature dependence of the low-frequency electric permittivity (left axis) and the inverse of the ferroelectric part of the susceptibility (right axis) for a monomer DNP crystal of reasonably good quality. The arrows point to the respective axes.
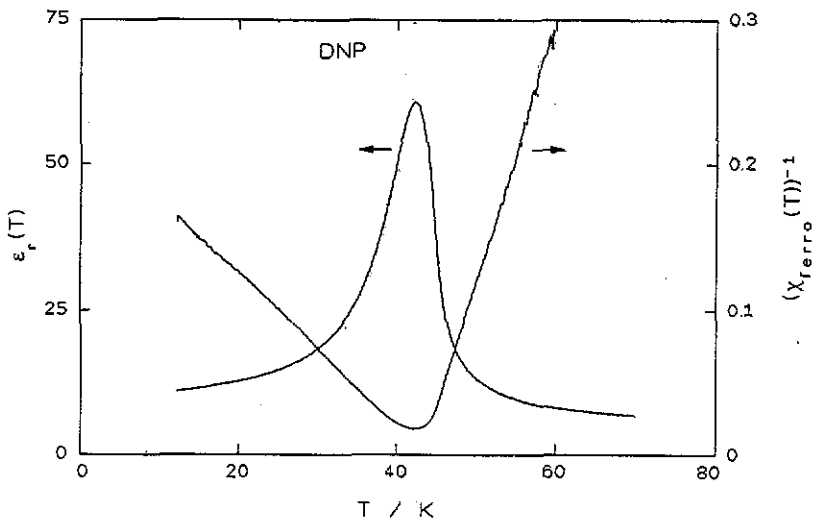

Figure 8. Temperature dependence of the low-frequency electric permittivity (left axis) and the inverse of the ferroelectric part of the susceptibility (right axis) for a relatively poor DNP monomer crystal. The arrows point to the respective axes.

discrepancy may be the following. (i) Domain-wall motion increases the value of the low-frequency dielectric constant and thus the value of the apparent Curie–Weiss constant $C_<$ of our samples substantially. This explanation is supported by the results at microwave frequencies where much smaller values of $\epsilon_r(T)$ were observed in the low-temperature phase [11]. (ii) As discussed before, there is a distribution of transition temperatures in real crystals. So, one could imagine that some parts of a sample undergo the phase transition at higher temperatures than others do, leading to a smearing and broadening of the transition curve, explaining why also for good crystals the $\epsilon_r(T)$ curve is not very narrow.

5.2.2. The influence of a small static electric field. The electric permittivity was measured during a temperature cycle from 290 K to 10 K and then to 100 K without an external field. Then $\epsilon_r(T)$ was measured under the influence of a static electric field of 0.8 kV cm^{-1} in strength. (This field strength amounts to roughly 3% of the poling field strength for the spontaneous polarization.) In the first case, the ratio of the Curie–Weiss constants gives 0.25 (indicating a relatively good crystal quality), and it changes to 0.29 when the electric field is applied. In order to exclude the possibility that this change is caused by induced cracks and thus simply due to repeating a temperature cycle for the same crystal, $\epsilon_r(T)$ was measured again without applying an electric field. The ratio of the Curie–Weiss constants was determined to be 0.25 again, so that its change is indeed due to the electric field. Besides, the width of $\epsilon_r(T)$ is slightly smaller than under zero-field conditions. In the low-temperature phase, the $\epsilon_r(T)$ curve is steeper in the case of applying the electric field than of zero field when approaching the lower temperature limit. In each case, however, the value of $\epsilon_r(T)$ at the lowest measured temperature is approximately the same. This dependence on a small static electric field indicates the influence of domain walls on the permittivity measurements in the low-temperature phase. Thus our experimental results for the ratios of the Curie–Weiss constants should not be compared with equation (6).

5.3. Frequency dependence of the electric susceptibility

For frequencies up to 100 kHz, the shape of the $\epsilon_r(T)$ curves does not depend on frequency and the ratio of the Curie–Weiss constants is hardly influenced. The maximum value of $\epsilon_r(T)$ only slightly decreases with increasing frequency, as expected.

At a microwave frequency of 10.3 GHz the ratio of the Curie–Weiss constants amounts to 17 typically, which was taken as an indication of a ferroelectric phase transition of weakly first order [11]. The microwave values of ϵ_r for $T < T_c$ are much smaller than the results for the low-frequency regime, as can be explained by the influence of the domain wall motion. Not only are the measuring techniques for low-frequency and microwaves different, but also the samples investigated in [11] were much smaller than those used for our experiments. However, the interpretation of the phase transition is not dramatically different in [11] and in this contribution since a tricritical transition as described above represents a borderline case between phase transitions of first and second order.

6. Conclusions

We were able to prove that the polar low-temperature phase of DNP monomer crystals is ferroelectric. The phase transition is accompanied by a maximum of the electric permittivity up to values as high as 150, which is a very high value for an organic crystal. The spontaneous polarization of the low-temperature phase reveals values of up to 2.4×10^{-7} C cm^{-2} at 10 K. Applying static electric fields of field strengths up to 33 kV cm^{-1}, the reversal of the orientation of the spontaneous polarization is possible at least for parts of the crystals that are relatively free of crystal defects. Such defects are also the origin of a distribution of transition temperatures. The higher it is, the fewer defects the poled region should have. The occurring 'under-ground' for temperatures slightly above the transition temperature can now be explained easily by this distribution of transition temperatures.

The fits to the experimental curves of the spontaneous polarization indicate that the phase transition might be a tricritical one within Landau's theory of ferroelectrics. A tricritical transition is connected with so-called soft modes, the existence of which should be seen in optical experiments with special emphasis on the temperature dependence. Owing to the distribution of transition temperatures, the experimental data of the electric permittivity cannot be compared with the theoretical value for the ratio of the Curie–Weiss constants of either side of the phase transition. This is the more so as for the reported low-frequency investigations in larger crystals the contributions of domain walls must also be taken into account as is shown by the influence of a static electric field on $\epsilon_r(T)$ measurements.

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