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## Optical study of the phase transitions in $[N(CD_3)_4]_2ZnCl_4$ and $[N(CH_3)_4]_2CoCl_4$

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**Abstract.** The birefringence study of the phase transitions in  $[N(CD_3)_4]_2ZnCl_4$  (abbreviated as d-TMA-Zn) and  $[N(CH_3)_4]_2CoCl_4$  (TMA-Co) in the temperature region 265–310 K is reported. For the d-TMA-Zn the effect of uniaxial stress was also investigated. Observation of the domain structure in the ferroelastic phase IV of TMA-Co below 277 K confirmed that as in d-TMA-Zn the domain walls are oriented parallel to the incommensurate wavevector, in agreement with the requirement of mechanical compatibility.

### 1. Introduction

Phase transitions in the crystals of the tetramethyl ammonium chloride compounds  $[N(CH_3)_4]_2BCl_4$ , where B = Zn, Co, Fe or Mn and their deuterated analogues have been studied by many authors (see the reviews by Gesi (1986), Perret *et al* (1987), Cummins (1990) and references therein). Shimizu *et al* (1980) and Gesi (1986) have suggested a unified  $p$ - $T$  phase diagram which applies for any member of this family if the axes are suitably shifted and rescaled. In table 1 the phase transitions in d-TMA-Zn and TMA-Co are shown. Non-deuterated TMA-Zn is included in the table for comparison. Note that the exchange of Zn by Co has only a small effect but the deuteration of TMA-Zn alters the transitions significantly.

As can be seen from table 1, there are large differences in the behaviour of d-TMA-Zn crystals obtained from different sources. The 'French' crystals (Marion *et al* 1984) exhibit a ferroelastic phase with space group  $P2_1/c11$  and  $q_0 = c^*/2$  which has been observed only with applied hydrostatic stress in the 'Japanese' crystals (Mashiyama *et al* 1981) of d-TMA-Zn. Izumi and Gesi (1983) attributed this phase transition to the  $P2_1/c11$ , phase to the existence of residual internal stresses.

While the optical properties of TMA-Zn have been studied by several authors (Regis *et al* 1982, Vlokh *et al* 1983) much less data are available for d-TMA-Zn or TMA-Co. Regis *et al* (1982) tried to analyse the birefringence  $\Delta n_{zz}$  in TMA-Zn in order to obtain the temperature dependence of the order parameter. The observed blurring of the

**Table 1.** Phases, space groups and critical wavevectors of TMA-Co (Cummins 1990), h-TMA-Zn (Cummins 1990), d-TMA-Zn<sup>1</sup> (Mashiyama *et al* 1981) and d-TMA-Zn<sup>2</sup> (Marion *et al* 1984).

TMA-Co	h-TMA-Zn	d-TMA-Zn <sup>1</sup>	d-TMA-Zn <sup>2</sup>
I Pmcn(Z = 4) $T_{c1} = 293$ K	Pmcn(Z = 4) $T_{c1} = 296$ K	I Pmcn(Z = 4) $T_{c1} = 300$ K	Pmcn(Z = 4) $T_{c1} = 298$ K
II INC $T_{c1} = 281$ K	INC $T_{c1} = 280$ K	II INC $q_0 = (2/5 + \delta)c^*$ $T_{c2} = 285$ K	INC $T_{c1} = 279.5$ K
III $P2_1cn$ ferroelectric $T_{c2} = 279$ K	$P2_1cn$	III' INC or incomplete $3/7c^*$ phase	$P2_12_12_1$ $3/7c^*$ $T_{c2} = 277.5$ K
II' INC $q_0 = (2/5 - \delta)c^*$ $T_{c2} = 277$ K	— $T_{c2} = 275$ K	III'' — $T_{c1} = 276$ K	$P2_1/c11$ $c^*/2$ $T_{c3} = 271.6$ K
IV $P112_1/n$ $c^*/3$ $T_{c3} = 192$ K	$P112_1/n$ $c^*/3$ $T_{c3} = 168$ K	$P112_1/n$ $c^*/3$	$P112_1/n$ $c^*/3$
V $P12_1/c1$ (Z = 4) $q_0 = 0$ $T_{c4} = 122$ K	$P12_1/c1$ (Z = 4) $q_0 = 0$ $T_{c4} = 155$ K	—	—
VI $P2_12_12_1$ $c^*/3$	$P2_12_12_1$ $c^*/3$		

transition, however, makes such procedures rather questionable (Ivanov *et al* 1989, 1990). We shall also consider this problem for the example of TMA-Co. As we have already mentioned, much interest was previously devoted to the study of the  $p$ - $T$  phase diagrams of the TMA compounds. However, data on the effect of a uniaxial stress are missing in most cases. We therefore also report some preliminary results on measurements of birefringence and of dielectric constants of d-TMA-Zn with uniaxial stress applied. We used  $X_4$  (i.e. the stress along the (011) direction), which according to Mashiyama *et al* (1981) should stabilize the phase with  $k = c^*/2$  and  $X_5$  stress respectively.

The last problem studied in the present work is related to the mechanism of the structural change from the incommensurate to the commensurate ferroelastic phase which occurs in both of our compounds. Saint-Gregoire *et al* (1989) observed that in d-TMA-Zn the ferroelastic domain walls are rotated by  $90^\circ$  from the position perpendicular to the incommensurate wavevector  $k$ . Because a similar situation can also be expected in TMA-Co for symmetry reasons (mechanical compatibility) we have also investigated the domains in this material under the polarizing microscope.

## 2. Experimental procedure

### 2.1. Crystal growth

TMA-Co single crystals were grown at  $303 \pm 0.003$  K by controlled evaporation from the stoichiometric aqueous solution resulting in deep blue crystals of several  $\text{cm}^3$ . The

crystals were of good optical quality with some small inclusions of water. To obtain single domain samples the plates (0.5–1 mm thick) used for the measurements have been controlled by the polarizing microscope (Zeiss Axiophot).

For d-TMA-Zn it is known (Mashiyama *et al* 1981, Marion *et al* 1981, 1984) that in some samples a phase with  $k = c^*/2$  exists between the phase with  $k = 3/7c^*$  and the ferroelastic phase, probably due to some residual internal stress. This phase has also been observed in other samples from the same source as ours (Marion *et al* 1981, 1984). Although the crystals used for this study were six years old, this phase occurs in all our samples.

## 2.2. Experimental set-up

The birefringence was measured with a Babinet Soleil compensator using the modulation technique with a resolution of about  $\lambda/1000$ . As a light source we used either a helium–neon laser or a high pressure mercury lamp with a 405 nm filter (for TMA-Co).

The home-made liquid nitrogen cryostat allowed us to apply uniaxial stress to the samples. The temperature was changed continuously at a rate of 0.1–1 K min<sup>-1</sup>. The samples for measurements under stress had dimensions of about  $2 \times 2 \times 4.5$  mm<sup>3</sup> and the stress was applied along the longest edge to ensure good homogeneity of the stress field in the middle part of the sample. Semi-transparent Au–Pd electrodes evaporated on the sample faces made it possible to measure the birefringence and the dielectric constant simultaneously. The domain structure and the rotation of the indicatrix in TMA-Co were investigated with a Zeiss Axiophot polarizing microscope equipped with a temperature controlled stage (Linkam).

## 3. Results and discussion

### 3.1. d-TMA-Zn

The temperature dependences of the birefringence components  $\Delta n_{ij} = n_i - n_j$ ,  $i, j = x, y, z$  of d-TMA-Zn are shown in figure 1.

The curves are quite similar to the one in non-deuterated TMA-Zn (Regis *et al* 1982, Vlokh *et al* 1983). In the low-temperature region, however the phase with  $k = c^*/2$  is surprisingly well pronounced. The width of this phase was decreasing from one temperature cycle to the following one. The maximal width was about 6 K (see first and second run on  $\Delta n_{xy}$ ), the minimal one slightly above 2 K after about 10 cycles (shown in  $\Delta n_{yz}$  of figure 1), where it stabilizes without further decrease. This behaviour indicates, that the  $k = c^*/2$  phase not present in other crystals of d-TMA-Zn is connected with residual internal stresses (Mashiyama *et al* 1981, Marion *et al* 1984) caused probably by some kind of crystal defects which were effective even in our (six year old) samples.

The appearance of the phase with  $k = 3/7c^*$  is practically invisible in our  $\Delta n_{ij}$  curves. Only on some detailed  $\Delta n_{ij}(T)$  curves was a very small kink observed at about 280 K. As we have mentioned above, the  $p$ - $T$  phase diagram of d-TMA-Zn has been studied several times (Gesi 1986, Marion *et al* 1984). It was shown that a ferroelectric phase can be induced by a hydrostatic pressure in d-TMA-Zn (Marion *et al* 1984). Mashiyama and Gesi (1981) have reported that the  $X_4$  stress can induce the  $k = c^*/2$  phase in the samples, where it is otherwise absent. To complete these data we have also measured the temperature dependence of the birefringence and of the dielectric constant at 100 kHz

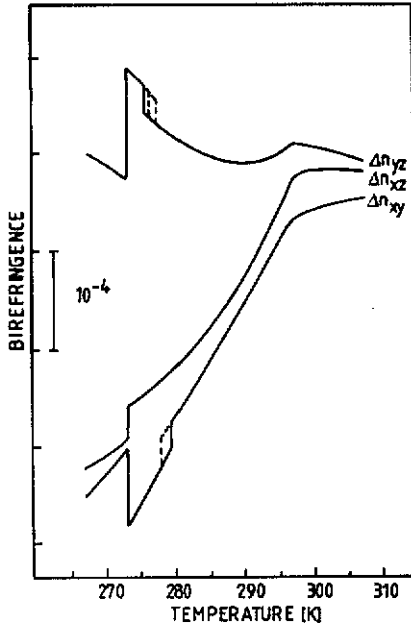


Figure 1. Temperature dependence of the linear birefringence of d-TMA-Zn.

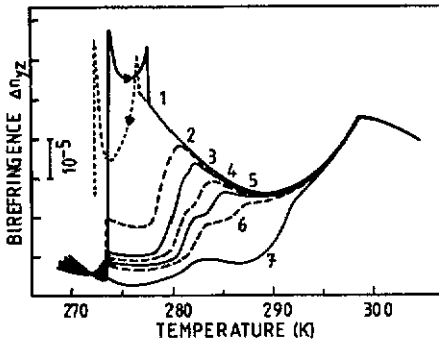


Figure 2. Temperature dependence of the linear birefringence  $\Delta n_{yz}$  of d-TMA-Zn at various uniaxial stresses  $X_4$ . The curves denote: 1, 0.04 MPa; 2, 0.21 MPa; 3, 0.43 MPa; 4, 0.64 MPa; 5, 0.81 MPa; 6, 1.27 MPa; 7, 2.98 MPa.

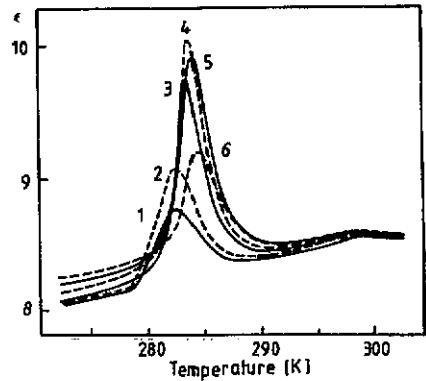


Figure 3. Temperature dependence of the dielectric constant  $\epsilon$  of d-TMA-Zn at various uniaxial stresses  $X_4$ . The curves denote: 1, 0.04 MPa; 2, 0.43 MPa; 3, 0.64 MPa; 4, 0.81 MPa; 5, 1.27 MPa; 6, 2.98 MPa.

with uniaxial stress applied. We used  $X_4$  and  $X_5$  stresses. In both cases the dielectric constant was measured along the light propagation direction to include the interesting  $\epsilon_x$  component (see the inserts in the corresponding figures).

The results are summarised in figures 2–5.

In figure 2 we can see, that while the transitions at 273 and 298 K are only slightly influenced by  $X_4$ , the transition into the  $k = c^*/2$  phase shifts to higher temperatures. When it reaches the temperature of the maximum of  $\epsilon_x$  (corresponding to the limits of

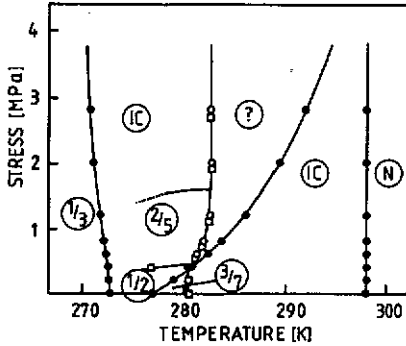


Figure 4. Stress-temperature phase diagram of d-TMA-Zn.

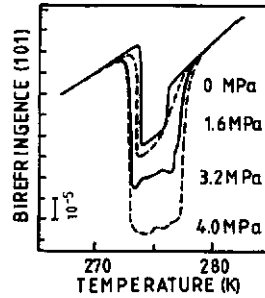


Figure 5. Temperature dependence of the linear birefringence  $\Delta n_{(101)}$  of d-TMA-Zn at various uniaxial stresses  $X_5$ .

the  $k = 3/7c^*$  phase) it splits into (at least) two transitions (figure 2). The first one continues to move upwards, unlike the second one, the temperature of which no longer changes with stress. At the same time the anomaly of  $\epsilon_x$  quickly increases and moves to slightly higher temperatures (see figure 3). The dielectric anomaly is largest at about  $X_4$  equal to 0.8 MPa and then starts to decrease again. Quite similar behaviour has been observed in d-TMA-Zn and also in other TMA compounds under hydrostatic pressure and it was assigned to the appearance of the pressure-induced ferroelectric phase (Marion *et al* 1984, Gesi 1982, Hasebe *et al* 1982) with  $k = 2/5c^*$ . In figure 4 the  $X_4$ - $T$  phase diagram compatible with our data is suggested. Some details of the diagram, however, need further investigation. We have applied  $X_5$  stress to another sample. Here  $\epsilon$  was measured in the (101) direction, which also contained the  $\epsilon_x$  component. No influence of  $X_5$  stress on the dielectric constant appeared. The  $\Delta n$  data (figure 5), however, show that  $X_5$  also stabilizes the  $k = c^*/2$  phase, but probably does not influence the other phases. Here the stress has been applied after several temperature cycles in order to stabilize the minimal width of the  $k = c^*/2$  phase (see above).

Unfortunately no samples were left with which to study the effect of  $X_6$ .

### 3.2. TMA-Co

In figure 6 the temperature dependences of the birefringence of TMA-Co are shown. They again correspond quite well to the  $\Delta n_{ij}$  of TMA-Zn. The only difference is a re-entrance of the incommensurate phase below the ferroelectric one in TMA-Co and is demonstrated in the insert where  $\Delta n_{yz}$  for both compounds above 277 K are plotted in detail. As in TMA-Zn and other TMA compounds we can observe an apparent blurring of the C-IC phase transition. Birefringence is often used to determine the temperature dependence of the order parameter (Fousek and Petzelt 1979, Kroupa *et al* 1982), but blurring of the transition complicates the procedure seriously. In TMA-Zn Regis *et al* (1982) analysed the birefringence data without taking this problem into account. Because this question seems to be important for all TMA-crystals we shall now briefly deal with it for the example of TMA-Co.

In the literature the blurring of the transition is commonly considered to be an effect of the order parameter fluctuations (Ivanov *et al* 1989, 1990) or of defects (Levanyuk *et*

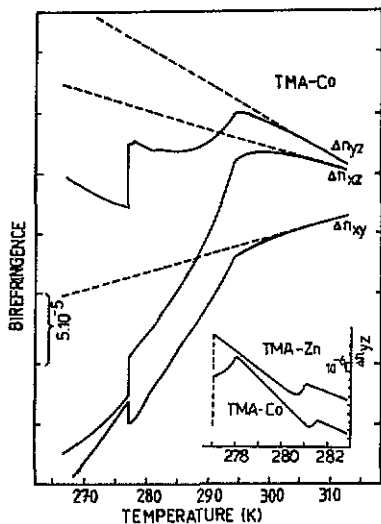


Figure 6. Temperature dependence of the linear birefringence of TMA-Co. In the insert  $\Delta n_{yz}$  of TMA-Zn and TMA-Co are given to show the additional anomaly in TMA-Co due to the additional incommensurate phase II' in TMA-Co.

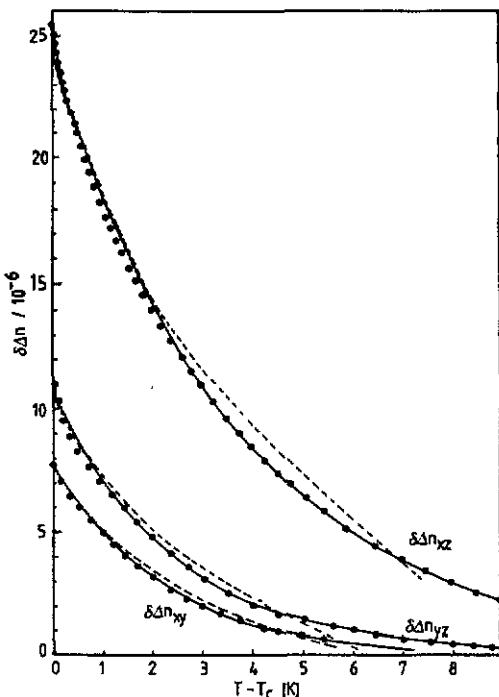


Figure 7. Anomalous parts of the components of the linear birefringence after subtraction of the linear part above  $T_{I1}$  of TMA-Co. The data are denoted as follows: ●, experimental data; ---, Ornstein-Zernike fit according to equation (1a); —, phenomenological fit according to equation (2).

al 1979). Both effects have been theoretically discussed either in the critical scaling region close to the phase transition, where the specific heat critical exponent  $\alpha$  (and not the exponent of the order parameter) determines the behaviour of  $\Delta n_{ij}$ , or in the region relatively far (but not too far) from  $T_T$ , where small corrections to the Landau behaviour are sufficient to describe the  $\Delta n_{ij}(T)$  dependences. In the case of TMA-Co the precise specific heat measurements of Gomez-Cuevas et al (1981) revealed that the critical behaviour is observed in a temperature region  $T - T_{I1} < 0.06$  K only. We can therefore conclude that the critical fluctuations are not responsible for the observed blurring of our  $\Delta n_{ij}$ . Therefore it is not reasonable to look for a critical exponent describing the  $\Delta n \approx \eta^2$  data in the wide temperature region below  $T_{I1}$ , as was done by Regis et al (1982).

In the non-critical region the corrections to the Landau behaviour have recently been discussed by Ivanov et al (1989, 1990), where the first corrections  $\Delta \eta_{k=0}$  to the mean field order parameter  $\eta_0$  obtained in the frame of the Landau theory have been calculated. In the presence of fluctuations they obtain:

$$\begin{aligned} \Delta n &\propto \sum_k \langle \Delta \eta_k \Delta \eta_{-k} \rangle = (T/V) \sum_k \chi(k) \\ &= (TK_{at}/2\pi^2 D) \{ 1 - [\tan^{-1}(K_{at} r_c^+) / K_{at} r_c^+] \} \quad T > T_{tr}. \end{aligned} \tag{1a}$$

Here  $K_{at}$  is a cut-off wavevector due to the continuous-media approximation, and  $r_c^+$  is the correlation length in the high-temperature phase.

In the ordered phase:

$$\Delta n \propto \langle \eta_{k=0}^2 \rangle + \sum \langle \Delta \eta_k \Delta \eta_{-k} \rangle \quad T < T_u. \quad (1b)$$

In figure 7 the spontaneous parts  $\delta \Delta n_{ij}$  of the birefringence components after subtraction of the linear part above  $T_{il}$  are plotted (full circles). The broken curve represents the behaviour according to (1a). The best fit has been obtained with  $K_{at} r_{c0}^+ \approx 100$ . We see that it only fits the experiment satisfactorily in a limited temperature range. This is not, however, inconsistent with the theoretical predictions (Ivanov *et al* 1990). As a matter of interest we can add that as in other incommensurate crystals which we have investigated, the blurring of the N-IC transition above  $T_l$  can be described quite well by a simple empirical relation

$$\delta \Delta n_{ij} = A_{ij} \exp\{-k_{ij}(T - T_{il})\} \quad (2)$$

(see the full line in figure 7) with the parameters

$$\begin{array}{lll} A_{xy} = 0.78 \times 10^{-5} & A_{xz} = 2.4 \times 10^{-5} & A_{yz} = 1.04 \times 10^{-5} \\ k_{xy} = 0.45 \text{ K}^{-1} & k_{xz} = 0.26 \text{ K}^{-1} & k_{yz} = 0.4 \text{ K}^{-1}. \end{array}$$

Below the transition temperature where the non-zero order parameter appears, the situation becomes much more complex because generally it is not possible to separate contributions arising from the order parameter and from defects or fluctuations, in a simple way. The theory, however, shows that in the first approximation the contributions from defects or from fluctuations are qualitatively the same as those above the transition but with opposite sign (Ivanov *et al* 1990).

The last question we have studied is connected with the domain structure of the ferroelastic phase of TMA-Co. On cooling through the IC phase no domains are seen, but at  $T_{c2} = 277 \text{ K}$  a dense system of lamellar domains is created in the sample. The density of the domains quickly decreases on cooling and soon only several larger domains remain which stay stable through the whole ferroelastic phase  $P112/n$  down to  $-90^\circ \text{C}$ . The domains are clearly observable on  $c$  plates, with domain walls parallel to  $b$  or  $a$  directions. Usually only one of these two possibilities (more frequently parallel to  $a$ ) occurs, but in some cases both systems were observed during the nucleation process.

We have also measured the angle between two extinction positions in polarized light in two different domains as a function of temperature. The behaviour is similar to the temperature dependence of the deviation of the monoclinic angle from  $90^\circ$  (Hasebe *et al* 1982), a linear variation in the monoclinic phase V followed by a small jump at  $T_{c3}$ .

#### 4. Summary

We have measured the temperature dependence of the linear birefringence of  $[N(CH_3)_4]_2CoCl_4$  and  $[N(CD_3)_4]_2ZnCl_4$  in the temperature region 265–310 K. The deviation in the linear birefringence from the regular part  $\Delta n_0$  above the normal-incommensurate phase transition can be described by the well known Ornstein–Zernicke function in a limited temperature range only. It turned out that the birefringence-tail above  $T_{il}$  can be described quite well by an exponential temperature dependence.



Below the transition temperature where the non-zero order parameter occurs the situation is much more complex.

A detailed analysis of the temperature dependence of the linear birefringence above and below  $T_{i1}$  will be the subject of a following paper.

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