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1993 J. Phys.: Condens. Matter 5 4759

(http://iopscience.iop.org/0953-8984/5/27/020)

J. Phys.: Condens. Matter 5 (1993) 4759–4766. Printed in the UK

The influence of annealing and x-irradiation on the optical anisotropy in incommensurate $(N(CH_3)_4)_2ZnCl_4$

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Received 30 September 1992, in final form 17 February 1993

Abstract. The optical activity, birefringence and the indicatrix rotation of a (001) sample of $(N(CH_3)_4)_2ZnCl_4$ are measured in the high-temperature, incommensurate and partly lock-in phases with a new high-accuracy null polarimeter. The optical properties are shown to be sensitive to the annealing and x-irradiation of a sample via the defect concentration changes. The results can be explained by consideration of a modulated gyration tensor in the incommensurate phase, using the idea of modulation wave distortions imposed by defects.

1. Introduction

In recent years, the physical properties of crystals with incommensurate (INC) phases have been investigated intensively (Cummins 1990). Much attention has been paid especially to the anisotropy of optical susceptibilities that are sensitive to INC modulation (Fousek 1991). Among the phenomena related to the optical anisotropy the optical activity (OA) in the INC phases represents, to our belief, one of the challenging problems from both theoretical and experimental viewpoints (see Ortega *et al* (1992) and Dijkstra *et al* (1992b), and references therein). This is because the OA of the INC materials should be symmetry restricted and its measurement is rather complicated. Saito *et al* (1985), Kobayashi *et al* (1986), Dijkstra and Janner (1990) and Dijkstra (1991) have measured the OA in INC $(N(CH_3)_4)_2ZnCl_4$ (TMA-Zn) with the HAUP technique (see Kobayashi *et al* (1986) and Moxon and Renshaw (1990)). Recently Dijkstra *et al* (1992b) have reported the temperature behaviour for all the components of gyration and linear birefringence (LB) in TMA-Zn. However, we suggest that more experimental data are still necessary for the following reasons. Firstly, essential discrepancies are seen in the results obtained by different workers. Secondly, in neither of the aforementioned papers have studies of the correlation between the OA magnitude and the external influences on a sample been dealt with.

In this paper we report detailed studies of the influence of annealing and x-irradiation on the OA in TMA-Zn. The results on LB and anomalous optical indicatrix rotation (IR) in the INC phase are also depicted. We measure the optical anisotropy parameters in the normal (N), INC and partly in the lock-in commensurate (C) phases. The temperatures of the phase transitions are $T_i \simeq 298$ K and $T_c \simeq 280$ K. The whole sequence of structural phases in TMA-Zn may be found anywhere (see, e.g., Dijkstra *et al* (1992b)).

The OA and LB in a freshly cut TMA-Zn are the subject of a brief communication (Kushnir *et al* 1992b); however, we present here these data for comparison.

0953-8984/93/274759+08$07.50

2. Experimental methods

2.1. General comments

The TMA-Zn single crystal was grown by the slow evaporation method from an aqueous solution of the $N(CH_3)_4Cl$ and $ZnCl_2$ salts taken in the appropriate stoichiometric ratio. After polishing, we obtained a (001) sample of good optical quality with a thickness of 2.81 mm.

Five polarimetric experiments designated as 1–5 were made in a heating regime (figure 1). In experiment 1 the as-grown crystal was dealt with. Then it was successively annealed before experiments 2, 3 and 4 for 3 h, 3 h and 14 h, respectively. Furthermore, specific weak 'annealing' took place in the N phase while the measurements continued in this phase (nearly 7 h in every experiment). Before experiment 5 the crystal was x-irradiated with Mo tube radiation (40 kV; 13 mA) for 50 min. The latter made it possible to create a small number of imperfections in a crystal without reducing its optical quality (Bziouet *et al* 1987). All measurements were taken immediately to avoid the atmospheric moisture acting on the sample surfaces. The quality of the latter had only slightly decreased during the experiments.

2.2. Polarimetry

We study the LB, linear dichroism (LD), OA and IR of TMA-Zn at 632.8 nm using the null polarimeter whose principles and design have been described by Kushnir *et al* (1992a). This polarimeter has been used to measure the OA in lead germanate (Vlokh *et al* 1992a). Here we present in brief the working principles of the method and illustrate the data processing which has some extra features when applied to INC TMA-Zn.

At each temperature we measure the linear dependences of the azimuth χ and the ellipticity ϵ of the transmitted light on the incident light azimuth θ lying in the vicinity of one of the principal axes of a crystal. Then the LB and LD may be derived on the basis of the relations

$$E = -\tfrac{1}{2}\sigma \qquad \cos\Delta = (\mathrm{d}\chi/\mathrm{d}\theta)/(1+\tfrac{1}{2}\sigma) \qquad \sin\Delta = (\mathrm{d}\epsilon/\mathrm{d}\theta)/(1+\tfrac{1}{2}\sigma) \tag{1}$$

with

$$\sigma = (\mathrm{d}\chi/\mathrm{d}\theta)^2 + (\mathrm{d}\epsilon/\mathrm{d}\theta)^2 - 1 \tag{2}$$

where E is the LD and Δ the phase retardation. The $\chi(\theta)$ and $\epsilon(\theta)$ dependences measured allow us to obtain a symmetry azimuth θ_0 ($\theta_0 = \chi_0$) and a characteristic ellipticity $\epsilon_0 = \epsilon(\theta_0)$:

$$\theta_0 = (k-p)\cot(\tfrac{1}{2}\Delta) + \delta\chi/(1-\cos\Delta) + \Delta\theta + \Delta\theta_0 \tag{3}$$

$$\epsilon_0 = 2k - p_0 + \delta\chi\cot(\tfrac{1}{2}\Delta) + \Delta\epsilon_0. \tag{4}$$

In (3) and (4), k denotes the eigenwave ellipticity, $\Delta\theta$ the IR, p, p_0 and $\delta\chi$ the effective imperfection parameters of the equipment (Kushnir *et al* 1992a), and

$$\Delta\theta_0 = (-E[(k-p)\sin\Delta + \delta\chi\cos\Delta]/(1-\cos\Delta)(1+E-\cos\Delta)) - k' \tag{5}$$

$$\Delta\epsilon_0 = -E[2(k-p) + \delta\chi\cot(\tfrac{1}{2}\Delta)]/(1+E-\cos\Delta) \tag{6}$$

where k' describes the circular dichroism (CD).

Here, we neglect the LD and CD terms in equations (3) and (4) (see also section 3.2) for the temperatures where Δ differs sufficiently from $\Delta = 2\pi m$ with an integer m. Like the studies of Kobayashi *et al* (1986) and Ortega *et al* (1992), the hypothesis is used that $k = 0$ in some high-temperature region of the investigated crystal. Good linear fitting of ϵ_0 to $\cot(\frac{1}{2}\Delta)$ with the mean square deviation close to the experimental error (about 1.4×10^{-5} rad) can confirm this, as the accidental situation $k =$ constant $\neq 0$ in the N phase is neglected. Thus p_0, $\delta\chi$ and therefore $k(T)$ can be extracted from the experimental data using (4).

Inserting relative readings θ' which are experimentally accessible instead of true azimuths θ (Kobayashi *et al* 1986, Kushnir *et al* 1992a), equation (3) becomes

$$\theta'_{\mathrm{ef}} = -p + (\theta'_{\mathrm{orig}} + \Delta\theta)\tan(\tfrac{1}{2}\Delta) \tag{7}$$

where θ'_{ef} is defined as

$$\theta'_{\mathrm{ef}} = \theta'_0 \tan(\tfrac{1}{2}\Delta) - \delta\chi / \sin\Delta \tag{8}$$

and $\theta'_0 = \theta_0 + \theta'_{\mathrm{orig}}$, with θ'_{orig} the value related to the zero symmetry azimuth ($\theta_0 = 0$). Using the experimental data θ'_0 for the N phase where $\Delta\theta = 0$ according to symmetry, one can fit θ'_{ef} to $\tan(\frac{1}{2}\Delta)$ and eliminate p and θ'_{orig} from (7). This enables one to examine an IR $\Delta\theta$ in the whole temperature range. It must be noted that the mean square deviation in the fitting was significantly larger (approximately 2.6×10^{-4} rad) than that for the ϵ_0 versus $\cot(\frac{1}{2}\Delta)$ fitting. Most probably, this was because the $\tan(\frac{1}{2}\Delta)$ values measured in the N phase of the TMA-Zn sample were far from zero.

3. Results

3.1. LD and LB

Dijkstra *et al* (1992b) have reported the LD in TMA-Zn to be zero for a light wavelength of 632.8 nm. The observed deviation of σ from unity confirms the conclusion that a small LD is present. It is scattered slightly asymmetrically around zero for different temperatures, showing no noticeable temperature dependence. The averages are $\bar{E} \simeq 4 \times 10^{-3}$ and $(\bar{E}^2)^{1/2} \simeq 10^{-2}$. These LD parameters are almost unaltered in all the experiments. Since the optical properties of TMA-Zn are measured outside the dichroic bands, the only reasonable source of LD is the anisotropic light scattering mainly at the crystal surfaces. Such effective dichroism has been described by Baturina *et al* (1985). Using the $(\bar{E}^2)^{1/2}$ value, we calculate the difference between the extinction coefficients as $\Delta\kappa = 3.6 \times 10^{-7}$, which is an order of magnitude larger than that of a high-quality hygroscopic $Tl_2Cd_2(SO_4)_3$ sample measured in the region of transparency (Baturina *et al* 1985).

The absolute magnitudes of LB are determined (figure 2) with $\sin\Delta$ and $\cos\Delta$ and previous knowledge of the existence of the LB inversion point in the INC phase of TMA-Zn. In experiments 3 and 4 the measurements were performed in the vicinity of another principal axis of the crystal. In general, our results are compatible with those of Dijkstra *et al* (1992b). One can see from figure 2 that the LB dependence in the N phase is not completely linear as a result of the order parameter fluctuations and defects (Fousek 1991). We detect with an accuracy of about 0.5 K the following positions of T_i in experiments 1, 2, 3, 4 and 5: 297.8 K, 296.9 K, 296.3 K, 295.6 K and 297.3 K, respectively. For

more reliable data, measurements high above T_i are required (Fousek 1991). It is known that annealing 'improves' the crystal structure whereas x-irradiation has the contrary effect. Thus T_i tends to become lower for a more perfect sample. The observed region $\Delta T_f \simeq 5$–7 K above T_i where precursor effects are obvious is not affected very much by annealing and x-irradiation. Note that Régis *et al* (1982) found ΔT_f to be nearly 15 K. In recent work, Vlokh *et al* (1991b) observed a slight dependence of T_i on x-irradiation, unlike T_c. Regarding T_c, our data are not detailed enough to ascertain the external influences.

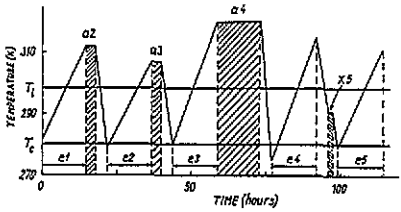

Figure 1. Representation of the sample temperature evolution. e1–e5 denote experiments 1–5, respectively, a2–a4 the anneals before experiments 2–4, respectively, and X5 the x-irradiation before experiment 5. The intervals between the experiments are not displayed.

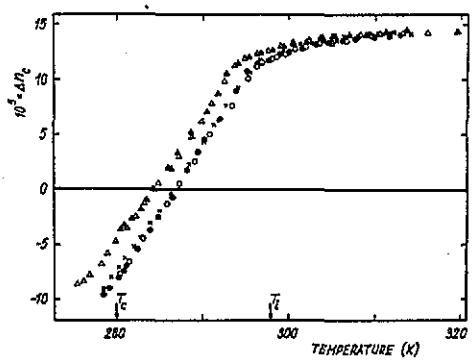

Figure 2. Temperature dependences of the LB Δn_c for TMA-Zn in experiments 1 (○), 2 (●), 3 (▲), 4 (△) and 5 (×).

The temperature T_0 where the LB goes through zero is influenced by both thermal cycling and x-irradiation. The maximum shift in T_0 is equal to 3 K. It has to be emphasized that we are able to measure the LB exactly at T_0, contrary to the HAUP method. Our T_0 obtained for a freshly cut sample (experiment 1) is in accordance with the data of Vlokh *et al* (1987).

3.2. IR

Processing θ_0' data in a manner described in section 2.2 gives the following results (figure 3). Small anomalous IRs $\Delta\theta$ are present in the INC phase, having cotangent-like divergences at T_{0i} and disappearing at temperatures far from T_{0i} in the N phase. To compare correctly the data for different experiments we plot $\Delta\theta$ against $\cot(\frac{1}{2}\Delta)$ (figure 3, inset). The slope moduli characterize the 'strength' of the divergences. They are 18.2×10^{-4} rad, 8.7×10^{-4} rad, 10.0×10^{-4} rad, 6.5×10^{-4} rad and 16.8×10^{-4} rad in experiments 1, 2, 3, 4 and 5, respectively. Thus, the IR around T_{0i} weakens on annealing and strengthens after x-irradiation. This excludes the origin of the singularity from the only LD. On the basis of the results on the LD and LB we conclude that the $\Delta\theta_0$ contribution to the maximum values calculated from (3) (approximately $\Delta\theta^{max} \simeq 5 \times 10^{-3}$ rad) is nearly 10% and decreases rapidly on going away from the temperatures T_{0i} (see equation (3)). The term $\Delta\epsilon_0$ contributes still less to k. Moreover, as the CD k' is typically 10^3 times less than LD, it is negligible in (5).

It is evident from the experiments that the IR depends on the defect concentration, similarly to the OA (see section 3.3). Although already reported for some centrosymmetric INC compounds (see Ortega *et al* (1992), and references therein), the IR seems to be a more controversial phenomenon than even the OA. A possible interpretation of the anomalous IR in TMA-Zn is suggested in section 4.

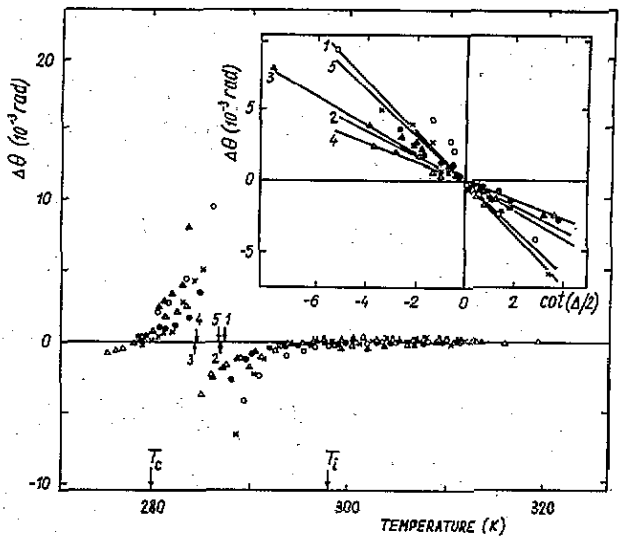

Figure 3. Temperature dependences of the IR $\Delta\theta$ around the c direction of TMA-Zn in experiments 1 (○), 2 (●), 3 (▲), 4 (△) and 5 (×). The arrows 1–5 indicate the temperatures T_{0i} of zero LB in experiments 1–5, respectively. The inset represents the fit of $\Delta\theta$ against $\cot(\frac{1}{2}\Delta)$.

3.3. OA

The eigenwave ellipticities derived in the experiments are shown in figure 4 as functions of temperature. They are divergent at T_{0i} despite the fact that the instrumental error $\delta\chi$ is eliminated reliably in the fitting procedure (see section 2.2). This implies that the gyration component g_{33} does not become zero when the LB does (figures 2 and 5). Our g_{33} in the as-grown crystal passes through zero only at nearly 1.5 K higher than T_c. The reasons for the difference from the data of Dijkstra *et al* (1992b) are not quite clear. This could originate from the peculiarities of the exact $k(T)$ behaviour around T_0 which is less accessible in experiments. So, zero g_{33} at T_0 found by Dijkstra *et al* (1992b) is a result of weakly pronounced $k(T)$ peak at T_0 (Dijkstra *et al* 1992a). It should be stressed that the characteristics of the $k(T)$ behaviour near T_{0i} vary in our experiments (figure 4), i.e. this phenomenon depends upon sample perfection.

The OA in TMA-Zn is in general non-zero in the INC phase and in the C phase within the temperature range measured. We can therefore expect the OA to have some mutual or close mechanisms in these phases rather than the OA in the INC phase to be a simple precursor effect for the lock-in phase; moreover the component g_{33} cannot be evoked by an electrogyration effect in the latter phase.

For the as-grown sample the maximum g_{33} in the INC phase is close to that found by Dijkstra *et al* (1992b). The sign of the gyration component is also the same. OA is present in the N phase as a precursor effect (see Kushnir *et al* (1992b) and section 3.1). The observed fluctuation region ΔT_f is compatible with that obtained from the LB measurements. Unlike the data of Dijkstra *et al* (1992b) our g_{33} clearly vanishes at higher temperatures in the N phase, thus providing a physically reasonable situation.

One can arrive at some important conclusions by comparing the results of experiments 1–5 (figure 5).. Annealing causes the OA to change its temperature behaviour, to decrease significantly and to vanish at lower temperatures. The OA for a strongly annealed sample (experiment 4) amounts to only 30% from its initial magnitude observed in experiment 1. Moreover the OA in experiment 4 is zero in the INC phase down to 6 K below T_i, and no precursor effect is visible in the N phase. On the contrary, x-irradiation induces a drastic increase in the OA magnitude together with the residual effect in the N phase ($\Delta T_f \simeq 3$ K; see

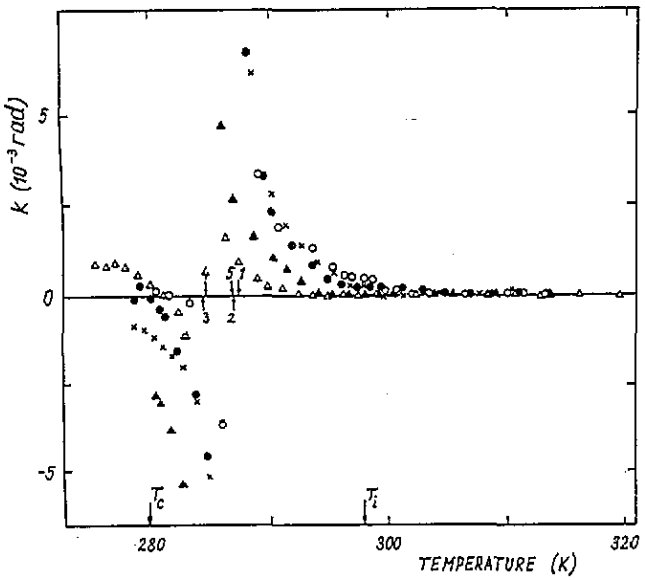

Figure 4. Temperature dependences of the eigenwave ellipticities k for TMA-Zn in experiments 1 (○), 2 (●), 3 (▲), 4 (△) and 5 (×).

experiment 5 in figure 5). Thus, one can see that the influence of defects on the OA is much greater than on the LB. Annealing and x-irradiation of a sample (i.e. defect concentration changes) not only produce a size effect on the OA but also alter its major characteristics.

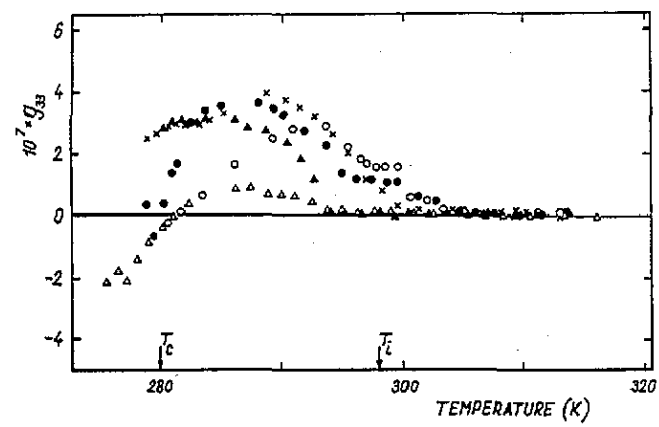

Figure 5. Temperature dependences of the gyration component g_{33} for TMA-Zn in experiments 1 (○), 2 (●), 3 (▲), 4 (△) and 5 (×).

4. Discussion

Among the theoretical treatments that explain the OA in the INC materials (see, e.g., Kobayashi (1991) and references therein) the most complete are those based on the idea of spatially dependent gyration and dielectric tensors (Meekes and Janner 1988). Dijkstra (1991) and Dijkstra *et al* (1992a) have shown that the modulation of the dielectric tensor gives rise to an OA even without accounting for the gyration tensor. It should be noted that the above-mentioned approach considers in fact a perfect (non-distorted) modulation wave. An INC crystal is treated as a sequence of whole identical unit cells with modulated

off-diagonal dielectric components ϵ_{ij} (Dijkstra 1991). A model describing a crystal with the gyration tensor modulated with a simple square-wave form is suggested by Vlokh *et al* (1991a, 1992b). It is non-gyrotropic until the modulation wave is regarded as being perfect but gives an IR (quasigyrotropic rotation). Distortions of the modulation wave (due to unipolarity and defects) cause the appearance of OA within the model and alter the IR. Thus, both the OA and the IR are the results of the inhomogeneity of a crystal on a semimacroscopic scale. If local perturbations of the modulation wave occur, then the eigenwave ellipticity and the quasigyrotropic rotation have cotangent-like singularities when the phase retardation goes through zero (generally, through the values $\Delta = 2\pi m$ (Vlokh *et al* 1992b)). This explains qualitatively the temperature dependences of k and $\Delta\theta$ which would both be forbidden, by simple symmetry considerations, in the INC phase of TMA-Zn. The model is also valid for the multidomain C phase. It is noteworthy that similar pecularities of the OA and the IR were observed experimentally by Vlokh *et al* (1992b) in the multidomain ferroelectric phase of lead germanate. Moreover, a weak singularity of the eigenwave ellipticity (maximum magnitude $k \simeq 4 \times 10^{-4}$ rad) was found by Ortega *et al* (1992) in the INC $(N(CH_3)_4)_2CuCl_4$ compound around the temperature where $\Delta = 2\pi m$ (4 K higher than T_i). It may probably be evoked by the above-mentioned mechanisms as a precursive effect for the INC phase.

The data presented in this paper indicate that the OA in the INC phases is very sensitive to defect concentration. In our view, the reason is the partial (local or extended) loss of the periodicity of structure along the modulation direction imposed by defects (cf the deperiodization effects considered by Bziouet *et al* (1987)). This results in corresponding distortions in the modulation of the gyration tensor and in changes in the OA.

5. Concluding remarks

The parameters of optical anisotropy (LB, OA and IR) of a TMA-Zn crystal are measured in the N, INC and C phases. Annealing and x-irradiation act significantly on the optical properties of the INC phase via the defect concentration variations. The results can be understood qualitatively from the viewpoint of a semimacroscopic spatial modulation of gyration and dielectric tensors in the inhomogeneous INC medium. The theories that regard the OA in INC phases to be a consequence of a perfect modulated structure are rather limited. Although these theories give rise to a macroscopic OA, it is questionable whether they can explain the observed gyration magnitude in the INC materials (Ortega *et al* 1992). On the other hand, just as the OA is restricted by the symmetry of the average structure of the INC phase, so it should be reasonable to consider the mechanisms for the OA that arise from the distortions of the ideal modulated structure due to the imperfections, defects, etc, present. Such mechanisms, which have been discussed partly by Vlokh *et al* (1991a, 1992b), may contribute essentially to the OA. The present studies confirm considerable enhancement of the OA because of the defect concentration increase.

A more detailed interpretation of the OA and the IR in a medium with modulated gyration and dielectric tensors will be the subject of a forthcoming paper.

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