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Optical birefringence in the incommensurate phase of $\{N(CH_3)_4\}_2ZnCl_4$

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Résumé. — La biréfringence du tétraméthyl tétrachlorozincate d'ammonium $\{N(CH_3)_4\}_2ZnCl_4$ a été mesurée entre 35 °C et 0 °C. Au-dessous de T_0 , elle obéit à une loi de puissance en fonction de la température, dont l'exposant $0,87 \pm 0,02$ est identifié à $2 - \alpha - \Phi$. La transition de blocage présente une hystérésis de l'ordre de 0,25°. Ces données sont comparées aux prédictions de la théorie de Mashiyama.

Abstract. — The optical birefringence of $\{N(CH_3)_4\}_2ZnCl_4$ has been measured. Below T_0 , the exponent of its temperature dependence is identified to $2 - \alpha - \Phi = 0,87 \pm 0,02$. The lock-in transition is observed, exhibiting an hysteresis of about 0.25°. These data are compared with the predictions of Mashiyama's theory.

Tetramethylammonium tetrachlorozincate $\{N(CH_3)_4\}_2ZnCl_4$ (abbreviated hereafter as TMA-Zn) exhibits five successive structural phase transitions between 150 K and 300 K.

The space group determination of each phase and the study of the incommensurate modulation have been carried out simultaneously and independently by Japanese [1] and French [2, 3] groups.

The high temperature phase (I) (above about 297 K) is a paraelectric orthorhombic phase and belongs to the $P_{nam}(D_{2h}^{16})$ group ($a = 12.276 \text{ \AA}$, $b = 15.541 \text{ \AA}$, $c = 8.998 \text{ \AA}$). Between $T_0 \simeq 297 \text{ K}$ and $T_i \simeq 281 \text{ K}$ (phase II) the structure becomes incommensurate with $q_b \simeq 0.42 a$ near T_0 . In phase III (P_{na2_1}), the wave vector of the distortion locks at $q_{com} = 0.40 a^*$ and a spontaneous polarization parallel to the **b** axis appears. The phase IV, below $T_c \simeq 277.8 \text{ K}$, is monoclinic ($P_{2_1/n,1,1}$), with $q'_{com} = \frac{1}{3} a^*$.

Our birefringence measurements were carried out in the (a, c) plane, between 300 K and 273 K. The resolution obtained by this method gives interesting information on the critical regime.

The birefringence change $\Delta n = \delta n_a - \delta n_c$ occurring at a structural phase transition is directly related to the normal coordinates of the soft modes, as demonstrated in [4]. So Δn is to first order, proportional to the square of the primary order parameter, Q (except in the case of a ferrodistortive phase transition). This relation was shown to hold in the case of incommensurate phase transitions (BaMnF_4 [5], $\text{CS}(\text{ND}_2)_2$ [6]). Another approach involves the linear approximation : $\Delta n \propto \sum_i c_i x_i$, where the x_i are the components of infinitesimal strains ($i = 1 \dots 6$).

In the case of TMA-Zn, elementary symmetry considerations show that invariants of the form x_i^2 and $x_i \cdot Q Q^*$ are allowed in the development of the Landau free energy [7]. The minimization with respect to the x_i gives

$$x_i \propto |Q|^2 \quad \text{or} \quad \Delta n \propto \left(\frac{T_0 - T}{T_0} \right)^{2\beta},$$

neglecting the fluctuations.

However, in the case of transitions involving a n -dimensional soft-mode [8], the order parameter symmetry will generally allow additional symmetry breaking interactions. In such cases, a temperature dependence

$$\Delta n \propto \left(\frac{T_0 - T}{T_0} \right)^{\tilde{\beta}} \quad \text{with} \quad \tilde{\beta} = 2 - \alpha - \Phi$$

has been predicted, with the help of renormalization group calculations [9].

The linear birefringence has been measured at $6328 \text{ \AA}$ with a modulation technique [6], allowing a detection of $\delta \Delta n$ as low as 10^{-7} to be obtained. The temperature precision was about 2 mK. The rate of the temperature shift was about 0.2 mK/s. Figure 1 shows the evolution of Δn with

Fig. 1. — Temperature dependence of the experimental birefringence of TMA-Zn in the a c plane (increasing temperature).

temperature. The disordered-incommensurate phase transition at T_0 seems to be second order, without any measurable hysteresis.

However, at T_0 , the experimental curve shows a kink, indicating a small discontinuity of $\partial \Delta n / \partial T$, and two different regimes below and above T_0 . Far above T_0 in the disordered phase, the birefringence has a linear dependence with temperature.

The spontaneous change of birefringence below T_0 is then deduced from the experimental curve by subtracting the extrapolated linear contribution. The following power law is found :

$$\Delta n - \Delta n_0 \propto \left(\frac{296.97 - T}{296.97} \right)^{0.87 \pm 0.02}$$

between $2 \times 10^{-4} < t < 1.8 \times 10^{-2}$ (Fig. 2). The same procedure as in [5] is used to choose the best value of T_0 and of the exponent.

This value, 0.87 ± 0.02 is significantly different from a Landau exponent : $2\beta = 1$, and also from the value calculated by R.G. techniques [10] : $2\beta = 0.70$ for the $d = 3, n = 2$ class to which TMA-Zn is expected to belong. The temperature dependence of the intensity of first order satellites gives $2\beta \simeq 0.76$ [3].

Our exponent is nearer to $\tilde{\beta} = 2 - \alpha - \Phi = 0.845$ ($\Phi = 1.175$ [11]; $\alpha = -0.02$ [12]). This result may be an indication that the strains accompanying the phase transition have a specific critical behaviour, different from $|t|^{2\beta}$ [9]. But in such a case, the nature of the cross-over is unclear.

Fig. 2. — Log-log plot of the birefringence *versus* the reduced temperature below T_0 . The slope is 0.87 ± 0.02 .

It is generally admitted that the onset of the incommensurate modulation occurs in TMA-Zn without any change of the crystal symmetry. However this is not exactly the case, at least on a microscopic scale (the incommensurate structure develops along a two-fold screw axis, so in principle it destroys the C_2 symmetry).

If no symmetry change occurs at the transition, the expected critical behaviour for Δn would be, by analogy with magnetic systems [8], proportional to $|t|^{1-\alpha}$ below and above T_0 , so the experimental signal would be a smooth — S — shaped curve without any kink. It is then suggested that the birefringence tail above T_0 is due to short range correlations. Below T_0 , Δn is proportional to the symmetry breaking operator and obeys the law $|t|^{2-\alpha-\phi}$.

In the lower region of the incommensurate phase II, there is a small temperature range (286-281.5 K) in which $\Delta n(T)$ becomes surprisingly linear. This behaviour, also observed in the case of $\text{CS}(\text{ND}_2)_2$, corresponds to the abrupt change in q_0 value, and certainly also to the discommensurations regime of the incommensurate phase, but is still quantitatively unexplained. The lock-in phase transition occurs at $T_i = 281.25$ K in decreasing temperature ($T_i = 281.50$ K in increasing temperature) and appears as a step, with a small « global » hysteresis (Fig. 3). Within experimental accuracy, Δn does not obey the logarithmic law in $\text{Log}^{-1}(T - T_i)$ as predicted by several authors [13]. Below T_i the system is in the ferroelectric phase (III) and Δn is a linear function of T , as in a perfect crystal. The first order transition to the monoclinic phase IV occurs at $T_c = 277.8$ K (increasing temperature) with an hysteresis of about 1.2° .

Finally, the experimental birefringence is also compared to the numerical calculations of $|Q|^2$, performed in the framework of the Landau theory by Mashiyama [7] (Fig. 4). Though the fit is not good in the critical region (near T_0 , this theory predicts a linear dependence in T), it however

Fig. 3. — Birefringence at the lock-in phase transition in increasing and decreasing temperature.

Fig. 4. — Comparison between the experimental Δn (dots), the power law $|t|^{0.87}$ (continuous line), and $|Q|^2$ calculated by Mashiyama (dashed line).

qualitatively explains the variation of the birefringence in the succession of the I, II, III, IV phases, and the discontinuities observed at T_i and T_c . This indicates that, outside the critical region, the proportionality between Δn and $|Q|^2$ can be considered as an useful approximation.

This fit could probably be improved by adjusting some of the ten parameters of Mashiyama theory. However, a more accurate theoretical treatment is needed, especially to explain the linear behaviour of Δn in the lower range of the incommensurate phase II.

As a conclusion, following [8], our results seem to indicate that the birefringence varies as a secondary order parameter in the case of TMA-Zn. This is different from the case of BaMnF_4 [5], where it seems to be proportional to the square of the primary order parameter. A comparison of experimental critical indices measured in different incommensurate crystals will give useful information on the nature of the symmetry breaking operators involved in these phase transitions.

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