Vol. **109** (2006) *ACTA PHYSICA POLONICA A* No. 6

The Stochastic Mode of the Modulated Structure in $[N(CH_3)_4]_2MeCl_4$ Dielectric Crystals

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(Received September 2, 2005; revised version February 2, 2006; in final form April 6, 2006)

Temperature behavior of the optical birefringence in the transitional regions of the incommensurate phase of $[N(CH_3)]CuCl_4$ was studied. Temperature dependencies of the modulated structure wave vector and of the specific heat in these regions were analyzed. The stochastic mode of the incommensurate modulated structure in $[N(CH_3)]MeCl_4$ (Me = Cu, Fe) dielectric crystals was discovered.

PACS numbers: 42.25.Lc, 61.44.Fw, 64.70.Rh, 78.20.Fm

1. Introduction

According to the theoretical approach [1], the physical models (for example: Frenkel–Kontorova model, ANNNI model et al.) can be described by the energy functional of the type

$$\Phi = 2\gamma\rho^2 S \int \mathrm{d}z \left[(1/2)(\partial\varphi/\partial z - k_0)^2 + \upsilon(1+\cos n\varphi)\right]. \tag{1}$$

These models reveal special behavior in the vicinity of the transition from the incommensurate phase into the commensurate one. In particular, some chaotic structures with the accidental distance between the solitons can exist together with the commensurate and the incommensurate phases. The solution of the energy minimization equation suggests that the stochastic trajectories are present together with the conventional plain trajectories. The stochastic trajectories correspond to the chaotic structures and the plain ones to the commensurate structures at the quite big values of the anisotropy potential (υ-value in (1)). Such structure consists of the commensurate structure fragments with different periods. The common period averaged over the whole chaotic set may be incommensurate with the period of the initial crystal. Thus, in the outlined systems the superstructure wave vector can change between the commensurate values ("devil's staircase") and in the stochastic mode. In the latter case, the wave vector can also assume irrational values. The chaotic phase corresponds to the solitons fixed on the crystal basic lattice in contrast to the incommensurate phase described by the unfixed soliton lattice. The shift of the soliton lattice requires the activation energy and, thus, the chaotic structure may be considered as the commensurate one. However, the chaotic phases are metastable differing from the commensurate phases in their ability to create the "devil's staircase".

Taking into account the factors mentioned above we consider that the dielectric crystals of the $[N(CH_3)]MeCl_4$ (Me = Cu, Fe) group deserve a detailed scientific investigation. The "viscous" interaction of the modulated structure with defects is realized in these crystals at the temperature change rate of $dT/dt \leq 180$ mK/h. When the value of interaction force between solitons approaches the value of the solitons–defects interaction value, the transition regions appear between metastable states. The metastable states are the temperature regions in the incommensurate phase where the wave vector localizes in the higher order values. Then the coexistence of the few spatially modulated waves in one crystallographic direction has been observed [2]. Multiwave modulations have been studied by X-ray diffraction in the paper [3]. The displayed difference wave vectors Δq relate to the superposition of the existing q-components of the modulation structure. The anomalous behavior of the optical birefringence in the conditions of the "viscous" interaction reported in [4] also relates to the same phenomenon. Under such circumstances it would be interesting to study the physical parameter behavior in the transition region in detail.

2. Experimental methods

The crystals have been grown by the evaporation of aqueous solutions of $N(CH_3)_4Cl$ and $MeCl_2$ (Me = Cu, Fe) salts taken in their stoichiometric ratios. The grown crystals have developed both good crystalline shape and optical quality.

The optical birefringence increment has been measured by the Senarmont method applying the automatized setup with a modulation of optical signal at the wavelength of $\lambda = 633$ nm. The temperature was measured and controlled with an accuracy of 0.01 K.

3. Results and discussion

The temperature dependencies of the optical birefringence increment in the conditions of "viscous" interaction for $[N(CH_3)_4]_2CuCl_4$ crystals are presented in Fig. 1. The anomalous change of $\delta(\Delta n_b)$ shows that the transitional region is

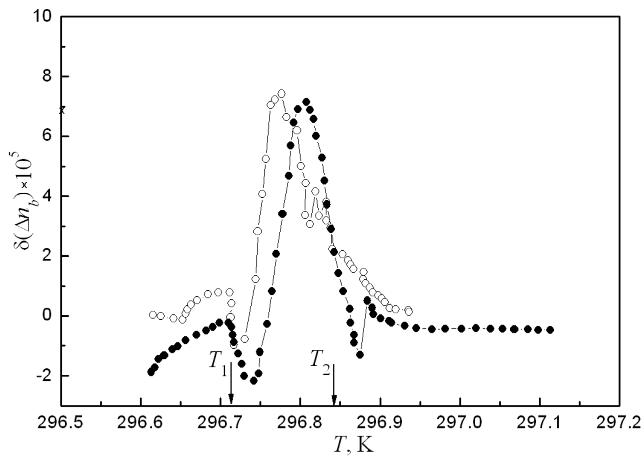

Fig. 1. Temperature dependence of the optical birefringence in the incommensurate phase of $[N(CH_3)_4]_2CuCl_4$. ○ — experimental curve, ● — theoretical curve (shifted), calculated according to Eq. (2).

located within the temperature range of $T_1 \div T_2 = 296.70 \div 296.85$ K. To explain the obtained behavior of the $\delta(\Delta n_b)$ let us use the approach elaborated in [4, 5]. In the conditions of the "viscous" interaction the optical birefringence increment in the direction perpendicular to the modulation axis is proportional to the spatial change of the order parameter phase. The defect density wave is considered to be an action of the spatially modulated electric field with the period close to the modulation structure period. Consequently,

$$\delta(\Delta n) \sim \frac{\partial \varphi}{\partial z} \sim \left[C + \frac{a_1 b E_0 \rho^{l-2} \cos(l\varphi - l_1 \varphi_1)}{h} \right]^{\frac{1}{2}}, \qquad (2)$$

where C denotes integrating constant, a_1 and b denote expansion coefficients, ρ and φ denote amplitude and phase of the order parameter of the commensurate structure, respectively, E_0 and φ_1 denote amplitude and phase of the defect density wave, l and l_1 correspond to the periods of the structure and defect density modulation, respectively. As it follows from Fig. 1 the theoretical curve fits the experimental data quite well. Therefore, the superposition of the two modulation waves is observed: the structure modulation wave with the wave vector q and the defect density wave with the wave vector q_1. The resulting modulation wave with the difference wave vector $\Delta q = q - q_1$ [7] makes the main contribution to the anomalous behavior of the optical birefringence.

The temperature change of the resulting wave vector has a dome-shaped character with the asymmetrical increasing and decreasing branches (Fig. 2). It testifies the continuous change of the Δq as in the incommensurate phase.

According to the theoretical paper [8], the complicated sequence of the commensurate (C_1) → incommensurate (I) → commensurate (C_2) phase transitions

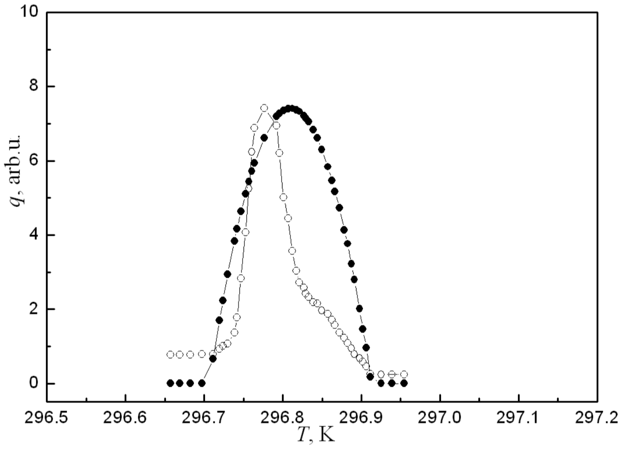

Fig. 2. Temperature dependence of the modulated structure wave vector in the transition region of $[N(CH_3)_4]_2CuCl_4$ crystal: ○ — experimental curve, ● — theoretical curve.

for A_2BX_4 group of crystals cannot be explained on the basis of the temperature change of the coefficient α from the thermodynamical potential

$$\Phi(z) = \alpha\rho^2 + \beta\rho^4 - \alpha'\rho'' \cos n\varphi - \sigma\rho^2\varphi_z + \delta\left(\rho^2\varphi_z^2 + \rho_z^2\right). \tag{3}$$

In this case, it was assumed that coefficient α' changes with temperature passing through zero, while $\alpha = \text{const}$. Phase transitions between the incommensurate phase and the commensurate phases (C_1 and C_2) occur at values $\alpha' = \alpha'_{C1}$ and $\alpha' = \alpha'_{C2}$, respectively. On the basis of the above assumption these transitions are continuous: expressions for ρ^2 are the same in all phases and the wave number q achieves maximum in the middle of the incommensurate phase and converts into zero in the transition points (Fig. 2, theoretical curve). As it can be seen, Fig. 2 reproduces the experimental temperature behavior of the resulting Δq vector in the transition region.

Such transitions are distinguished by the anomalies of the physical parameters (for example: specific heat c_p) [8]. The temperature dependence of the specific heat in the incommensurate phase is inverse to the corresponding temperature behavior of the incommensurate wave number q. It also passes through zero at transition points (Fig. 3a). Due to Ref. [9] the $\mathrm{d}(\delta(\Delta n))/\mathrm{d}t$ behaves similarly to the specific heat c_p. Then the corresponding temperature dependence of c_p calculated from the experimental data $\delta(\Delta n) \sim f(T)$ (Fig. 1) is presented in Fig. 3b. The obtained dependence $c_p \sim f(T)$ reproduces the theoretical curve in the temperature interval marked by arrows (Fig. 3). It should be noted that the temperature range of the incommensurate phase existence, according to the experimental c_p temperature behavior, is narrower than the theoretically obtained temperature range. To our mind, it is caused by the transition process from one metastable state to another.

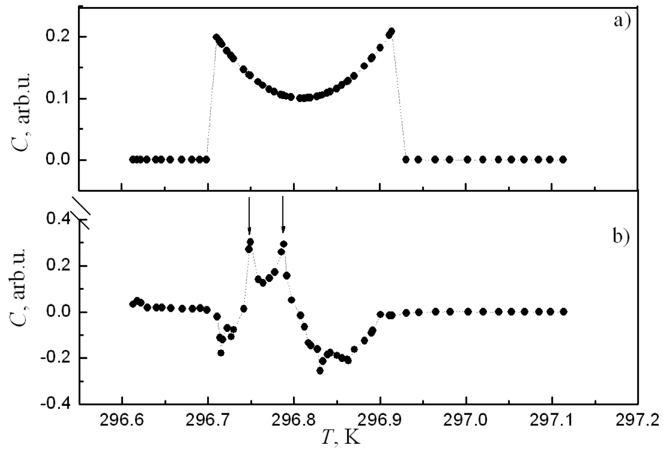

Fig. 3. Temperature dependence of the specific heat for $[N(CH_3)_4]_2CuCl_4$ crystals in the transition region: (a) calculated from [6], (b) obtained from the experimental dependence $\delta(\Delta n) \sim f(T)$.

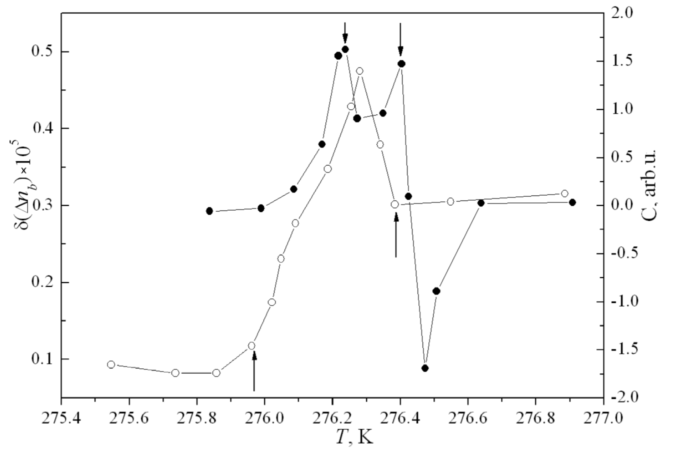

Fig. 4. Temperature dependencies ∘ — of the optical birefringence $\delta(\Delta n)$, • — specific heat for $[N(CH_3)_4]_2FeCl_4$ crystals in the transition regions, depending on power of interaction of modulated structure and defects. Arrows ↑ determine the temperature intervals of the transitional regions, ↓ the temperature intervals of the chaotic phase.

If the incommensurate phase appearing in the transitional region has a chaotic character, then the temperature range of its existence should be dependent on the solitons–defects interaction force. Otherwise, it should be dependent on the temperature range of the transition region.

Due to the experimental temperature dependencies of the optical birefringence and the specific heat (Fig. 4), the temperature interval of the chaotic phase existence increases with the increase in the transitional region temperature range. One can see that the temperature intervals of the transitional regions ($\Delta T = 0.18$ K, 0.48 K, 0.53 K) correspond to the incommensurate chaotic phase existence ranges ($\Delta T = 0.07$ K, 0.13 K, 0.24 K), respectively.

4. Conclusions

The transitional region should be considered as a region of the coexistence of the two modulation waves: structure modulation wave and defect density wave. Their superposition results in the difference wave vector Δq, which changes continuously with temperature. The region of the Δq change may be considered as a region of the chaotic phase existence. Following the temperature dependencies of Δq, c_p, $\delta(\Delta n)$ one can suppose that the chaotic phase is incommensurate.

It has been discovered for the first time that in the conditions of the "viscous" interaction of the modulated structure with defects in $[N(CH_3)_4]_2MeCl_4$ dielectric crystals the stochastic mode of the incommensurate modulated structure appears.

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