Phase Transitions in $[\text{N(CH}_3\text{)}_4]_2\text{ZnCl}_4$ and $[\text{N(CH}_3\text{)}_4]_2\text{CuCl}_4$ Crystals Related with the Incommensurate Modulation Existence

S. Sveleba$^{a,*}$, O. Semotyuk$^a$, I. Katerynchuk$^a$, I. Kunyo$^a$, I. Karpa$^a$ and Yu. Pankivskyi$^b$

$^a$Department of Nonlinear Optics, Lviv National Ivan Franko University
Tarnavskogo str. 107, Lviv, UA-79017, Ukraine
$^b$Department of Ecology, Ukrainian National University of Forestry
O. Kobylyanskiy str. 1, Lviv, UA-79005, Ukraine

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The continuous phase transitions are observed in the crystals with incommensurate phase. They are transitions of parent–incommensurate phases ($T_i$); transitions between metastable states; incommensurate–commensurate phases ($T_c$). It was set that phase transition between parent and incommensurate phase is a continuous second-order phase transition with a critical index $\beta = 0.5$. The transition between metastable states is a continuous phase transition through the intermediate temperature region — incommensurate phase. The wave vector changes with the temperature here and wave vector $q^\ast = q_1 - q_2$ appears, where $q_1, q_2$ denote commensurate values of incommensurability wave vector of neighboring metastable states. It was shown that the phase transition between incommensurate and commensurate phases is a continuous phase transition.

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1. Introduction

According to the group-theoretic method, the spatially modulated structure appearance in phenomenological analysis is concerned with the existence of the Lifshitz invariant in the thermodynamical expansion. Its presence is determined

$^*$corresponding author; e-mail: kno@electronics.wups.lviv.ua
by the instability in the parent phase. It is an implicit reflection of the limited resistance of this phase. X-ray, electron paramagnetic resonance, nuclear magnetic resonance, dielectrical, optical investigations [1, 2], phenomenological description of “devil’s staircase” [3], study of the pressure influence on incommensurate (IC) phase [4–6] introduce us to this problem.

There were a lot of attempts to clear up the nature of IC phase appearance. Today it is a fast developing branch of the condensed matter physics. It covers a whole range of the problems, concerned with the physics of disordered state, including IC phases in dielectrics, magnetics, conductors, nature of chaos and so on.

The \([\text{N(CH}_3\text{)}_4\text{]}_2\text{ZnCl}_4\) and \([\text{N(CH}_3\text{)}_4\text{]}_2\text{CuCl}_4\) are model objects for incommensurate structure investigations. Tetramethylammonium tetrachlorozincate, \([\text{N(CH}_3\text{)}_4\text{]}_2\text{ZnCl}_4\), undergoes successive phase transitions at and below room temperature [7]. This compound has attracted much interest because of its incommensurate–commensurate phase transition. The highest temperature phase P (parent) has the \(Pmcn\) symmetry. In this phase, a unit cell contains four formula units consisting of two nonequivalent kinds of tetramethylammonium ions, abbreviated TMA-1 and TMA-2 hereafter, and one kind of \(\text{ZnCl}_2\) ion. IC phase under \(T_i\) has a modulation wave vector \(q = 2c^*/5\), where \(c^*\) is the reciprocal cell in parent phase. Phase III under \(T_c\) is the commensurate phase with \(q = 2c^*/5\) and shows ferroelectricity along the \(a\)-axis. Phase IV is ferroelastic with \(q = c^*/3\), which is followed by two low-temperature phases V \(q = 0\) and VI \(q = c^*/3\). Under atmospheric pressure, the transition temperatures are \(T_i = 296.6\), \(T_c = 280\), \(T_3 = 275\), \(T_3 = 168\) and \(T_5 = 155\) K, respectively, on cooling.

The microscopic models of the phase transitions in the IC phase are based on the concepts introduced by Bak [8] and Aubry [9]. The existence of the competitive short-range order forces in the structure is considered to be a reason for the IC modulation appearance in the dielectric crystals. A general idea about this competition can be obtained from the model of linear sequence of atoms [10], where each atom moves in the potential with two minima and interacts with neighboring atoms by harmonic forces.

In the case of \(\text{A}_2\text{MeX}_4\) crystals the situation is as follows. Each tetrahedral group (T-group) in the parent phase has two states with different directions of turnings around \(c\)-axis [11]. Therefore, the orientation states with two minima potential correspond to each group. In this case one can introduce the local variable \(\sigma_i = \pm 1\) [12]. The results of structural investigations confirm that turnings of T-groups around the orthogonal axes \(c\) in each layer take place in one direction. However, between layers they can turn in both directions. That is why one can consider the incommensurately modulated structure model as an alternation of arrows, characterizing the turnings of T-groups in each layer. For example ↑↓, ↑↑↓.
Therefore, one can imagine the incommensurate superstructure as a set of T-group rotation angles of different amplitude in the sequence of layers. The period of such structure increases in accordance with the proximity of incommensurability wave number $q_\delta$ to the rational value. In the soliton mode, when the force of interaction between solitons and defects approximate to the soliton–soliton interaction force one can consider the incommensurate phase as a temperature sequence of the long-periodic commensurate regions (metastable states) separated by the transition regions. The transition between neighboring metastable states passes through the intermediate by temperature region of several modulation waves coexistence. The symmetry point groups of metastable states are the subgroups of the parent phase. Under these conditions they are not the subgroups of each other and can coincide. In the [N(CH$_3$)$_4$]$_2$ZnCl$_4$ crystals the metastable states are ferroelectric (with the presence of spontaneous polarization along a-axes — $P_a$ or along b-axes — $P_b$) and ferroelastic phases. As it was mentioned in [13] the metastable state reveals both commensurate and incommensurate phase properties. The transition from one metastable state into another passes through the intermediate by temperature region, where at least two modulation waves coexist [14]. These results give some special characteristics to the phase transition type and behavior of physical parameters in the vicinity of this phase transition.

The similar transition between metastable states is observed in the Josephson effect systems [15]. This transition occurs by the participation of more than one flux and reveals hysteresis of the physical parameters (non-reverse dependence).

Numerous experiments [11] performed by different methods for different crystals of A$_2$BX$_4$ group demonstrate the deviation from “classical” values of the critical indices which describe the order’s parameter behavior in the vicinity of the parent–incommensurate phase transition. The obtained values were compared with the corresponding theoretical values for the three-dimensional XY-model [16]. In Ref. [17] it was shown that in critical region the value of birefringence (difference between refractive indices) $\Delta n$ does not carry information about the critical index of order’s parameter $\beta$ ($\rho = \rho_0 (T_i - T)^{2\beta}$), $\rho$ is the amplitude of order parameter, $\rho_0$ constant), but it is determined by the expansion term $\sim c \tau ^ {1-\alpha} (\alpha$ — critical index of specific heat, $\tau = (T_i - T)/T_i$) and higher degrees of $\tau$. The expression for optical birefringence increment (increment of refractive indices difference) $\delta(\Delta n) \sim |\tau|^{2\beta}$ is valid only out of the critical region followed by the region of small correction.

Due to the investigations of the crystals with different defect concentration in the vicinity of $T_i$ the temperature dependences of birefringences $\Delta n_a$, $\Delta n_b$, $\Delta n_c$ corresponding to light expansion along a, b, c axes are essentially non-linear and values of $d(\delta(\Delta n))/dT$ have wide peaks. The same features have been observed at studying of the specific heat and thermal expansion [11]. As it was shown in [3] the correlated motion of T-groups contributes to spontaneous birefringence increment $\delta(\Delta n)$ which reflects in non-linear dependence of $\delta(\Delta n) \sim f(T)$ in wide
temperature range $T_i \approx 345$ K. At higher temperatures the mentioned dependence should be linear.

Due to Ref. [18] the metastable states display themselves in the regions with stable value of $\delta(\Delta n)$ on the temperature birefringence dependence. However, the transition regions show themselves in S-like anomalous behavior of $\delta(\Delta n)$. Besides, the non-monotonous (anomalous) behavior of the optical indicatrix rotation (rotation of the refractive index ellipsoid) was observed in IC phase [19]. The experimental study of the small-angle light scattering [20] and theoretical analysis of the symmetry properties of incommensurate phases [21] indicate such temperature behavior of the optical indicatrix rotation.

The optical indicatrix rotation has been observed in the set of experimental works [22–24]. However, the authors did not take into account that the incommensurate phase symmetry point group coincides with the point group of the high-temperature parent phase which forbids appearance of the optical indicatrix rotation. Therefore, the results reported in [22–24] do not agree with the well-known statement of the macroscopic crystallophysics that the symmetry of crystal tensor properties is determined by its symmetry point group [25, 26].

Thus, the symmetry point groups of the metastable states (long-periodic phases in IC phase) do not coincide with the symmetry point group of the parent phase [21]. However, they are the subgroups of the parent phase symmetry point group. Therefore, under given conditions one can expect the optical indicatrix rotation, especially, its non-monotonous temperature dependence [22]. The symmetry groups of commensurate phases are not the subgroups of each other and can coincide. It was predicted that they are the symmetry subgroups of the symmetry group of some prophase according to its two-dimensional representation which allows the Lifshitz gradient invariant. Under such consideration it would be interesting to investigate temperature properties of $\delta(\Delta n)$ and rotation of the optical indicatrix ($\varphi$) in the incommensurate and parent phases. As objects of investigations the $\left[N(CH_3)_4\right]_2\text{ZnCl}_4$ and $\left[N(CH_3)_4\right]_2\text{CuCl}_4$ dielectric crystals were chosen. They are typical representatives of $A_2BX_4$ family. These crystals are model objects in research of the physical parameters in the incommensurate phase. For example, their optical birefringence was studied by the sequence of authors [27–29]. The linear optical birefringence and the rotation of the optical indicatrix of $\left[N(CH_3)_4\right]_2\text{ZnCl}_4$ and $\left[N(CH_3)_4\right]_2\text{CuCl}_4$ crystals are studied in the vicinity of phase transitions limiting the incommensurate phase from both sides.

2. Experimental

The crystals have been grown by evaporation of aqueous solutions of $[N(CH_3)_4]\text{Cl}$ and ZnCl$_2$ salts taken in their stoichiometric ratios. The grown crystals have developed both good crystalline shape and optical quality. The 1.0–3 mm thick $\left[N(CH_3)_4\right]_2\text{ZnCl}_4$ crystal samples were used.
The measurement of the $\delta(\Delta n)$ was performed applying the standard Senarmont method with a modulation of main light beam using the automatized setup \[30\] in condition of light propagation along crystallographic axes.

The helium–neon laser (wavelength $\lambda = 632.8$ nm, power 20 mW) was used. The sample was placed into the cryostat that was a part of the automatic temperature control device. The temperature was measured by the copper–constantan thermocouple with an accuracy of $\approx 0.05$ K.

The accuracy of the $\delta(\Delta n)$ determination was estimated as $5 \times 10^{-7}$. The residual intensity ($I_r$) was determined as minimum value of main light beam intensity in the Senarmont method.

Due to the necessity of taking into the account the correlated motion of T-groups \[31\] the alignment of the optical system was performed in the parent phase (in the vicinity of $T = 370$ K, where T-group correlated motion is absent). Its influence was subtracted in the calculations of the incommensurate phase parameters.

The T-group correlated motion exists in narrow temperature interval (about 0.1 K) and the change of the physical parameter is small ($\delta(\Delta n) \approx 10^{-5}$) so the temperature was set with step less than $\Delta T = 0.01$ K. The birefringence was measured with an accuracy not worse than $10^{-7}$.

The measurement of the optical indicatrix rotation angle was performed using the following method. At first, the experimental setup was graded in the measurement range for every crystal sample. It was reached by the measurement of dependence of light intensity from the optical indicatrix rotation (angle of the simultaneous rotation of the crossed analyzer and polarizer around the crystallographical axes). The obtained dependence was extrapolated by the second-order polynomial.

Then the $I_r \sim f(T)$ dependence was measured. Further, it was transformed into the optical indicatrix rotation dependence $\varphi \sim f(T)$ applying the polynomial coefficients.

The temperature change rate was 3 K/h. The physical parameters measurement rates were: 1 point per minute for birefringence and 6 points per second for light intensity.

3. Experimental results

3.1. Transition from parent into IC phase

Temperature dependence of linear optical birefringence increment $\delta(\Delta n)$ for $[\text{N(CH}_3)_4]_2\text{ZnCl}_4$ crystal in incommensurate phase and in range of the parent phase where the T-group correlated motion exists is shown in Fig. 1. At the temperature of $T^* = 345$ K the deviation from linear dependence of $\delta(\Delta n_c) \approx f(T)$ (index c is the direction of axis, where measurement took place) is observed. This non-linearity takes place down to phase transition into incommensurate phase. We have extrapolated linear contribution to IC phase temperatures and subtracted
it from the total $\delta(\Delta n_c)$ and obtained the spontaneous birefringence increment $\delta_s(\Delta n_c) \sim f(T)$ dependence in IC phase. The $\delta(\Delta n_c) \sim f(T)$ dependence in current phase has been replotted in ln–ln scale in the vicinity of $T_i$ from the side of incommensurate phase is linear with the slope $2\beta = 1.0 \pm 0.01$ (see Fig. 2). The obtained value of $\beta$ correlates well with value of 0.5 predicted by Landau theory for second order phase transitions. It differs from $\beta$ value obtained in [17, 32–34].

Fig. 1. Temperature dependence of the optical birefringence $\delta(\Delta n_c)$ and residual intensity $I_r$ of $\left[N\left(CH_3\right)_4\right]_2ZnCl_4$ crystal annealed in the temperature range of 340–360 K.

Fig. 2. Temperature dependence of the spontaneous increment of the optical birefringence in the double logarithm scale.
According to the $\beta$ calculation method, this difference is caused by exclusion of the T-group correlated motion contribution in $\delta(\Delta n_c)$. However, according to [35], T-group correlated motion shows itself in the optical indicatrix rotation. The temperature behavior of the residual intensity confirms the presence of the optical indicatrix rotation in the incommensurate phase (Fig. 1).

Therefore, the transition at $T_i$ is the second-order phase transition described by the critical index $\beta = 0.5$.

### 3.2. The optical indicatrix rotation $\varphi$

The temperature dependence of the optical indicatrix rotation for $c$-cuts of $[N(CH_3)_4]_2\text{ZnCl}_4$ crystal is shown in Fig. 3. As one can see, the rotation of the optical indicatrix takes a non-linear value already in the parent phase in the temperature range of T-group correlated motion existence. The indicatrix rotation change rate increases with temperature approaching the transition into IC phase and in the temperature region of IC modulation origin. It is known that defects and impurities cause an increase in temperature intervals of metastable commensurate states existence. The last one causes an increase in the optical indicatrix rotation because in commensurate regions the order parameter appears. For current crystal the spontaneous deformation or spontaneous polarization can be the order parameter. The sample annealing in the parent phase causes the spatial redistribution and decrease in sample defectiveness. Thus, the annealing in temperature range of T-group correlated motion absence ($T > T^*$) essentially decreases the optical indicatrix rotation in the T-group correlated motion region as well as in IC phase (Fig. 3b).

![Graph showing temperature dependence of the optical indicatrix rotation](image-url)

Fig. 3. Temperature dependences of the optical indicatrix rotation for $c$-cut of $[N(CH_3)_4]_2\text{ZnCl}_4$ crystals: $a$ — fresh sample; $b$ — after annealing during $t = 1 \text{ h}$ at $T = 370 \text{ K}$. 
Therefore, the incommensurate structure origins at phase transition from
the parent into IC phase. Such origin process consists of merging of the T-group
correlated motion spatial regions.

3.3. The transition between commensurate phases

According to the X-ray diffraction data, in [N(CH$_3$)$_4$]$_2$ZnCl$_4$ crystal at slow
heating ($dT/dt = 3$ K/h) at the transition from the commensurate ferroelastic
phase $C_2$ ($q = 1/3$) ($T > T_3 = 275$ K) in the vicinity of phase transition
$T_2 = T_c$ [31] two satellite reflexes $q_1 = 0.4$ and $q_2 = 0.425$ appear simultaneously.
They correspond to commensurate phase ($T_3 = 275 \div T_2 = 280$ K) and IC phase
($T_2 = T_c = 280$ K $\div T_1 = T_i = 296.6$ K) respectively [36]. In the vicinity of
the phase transition from ferroelectric into ferroelastic phase ($T_3 = 275$ K) the
temperature range of simultaneous existence of two X-ray reflexes has also been
found. They correspond to the wave vectors of two neighboring commensurate
phases — ferroelectric and ferroelastic [36]. Such phase “coexistence” should be
accompanied by the appearance of the resulted reflex corresponding to the wave
vector $q = q_1 \pm q_2$, which was also observed in the X-ray diffraction picture for
other crystals [37]. Therefore, one cannot consider these phase transitions as the
first order type transitions with the jump of the physical parameters. The appearance
of reflex with $q = q_1 \pm q_2$ confirms the continuous character of such
transitions and existing of the set of commensurate phases and metastable states
with symmetry point group as the subgroup of the parent phase [38].

To clarify the type of phase transition from ferroelectric into ferroelastic
phase at $T_3$ the $\delta(\Delta n) \sim f(T)$ for [N(CH$_3$)$_4$]$_2$ZnCl$_4$ crystals was studied at slow
temperature change rate.

The appearance of the metastable states in IC phase was experimentally
detected and theoretically confirmed in the numerous works [39–41]. Near the
IC–commensurate phase transition the IC phase is considered as sequence of the
commensurate long-periodic phases (metastable states). The transition from one
commensurate phase into another crossed the intermediate temperature transition
region of their “coexistence”. Such regions can be essentially widened by decreasing
the temperature change rate $dT/dt$ [42]. In this case such phase coexistence reflects in S-like anomalies on the temperature dependences of $\delta(\Delta n)$ [43]. Such
anomaly shape is caused by the superposition of the existing waves of modulation
and the appearance of the resulting wave vector $q = q_1 \pm q_2$ [37].

The experimental temperature dependence of $\delta(\Delta n_0)$ in the vicinity of phase transition at $dT/dt = 3$ K/h at cooling run is shown in Fig. 4. As one can see,
the dependence is continuous with an S-like birefringence behavior. As it was
mentioned above, in the vicinity of phase transition at $T_3$ the “coexistence” of the
neighboring phases with $q_2 = 1/3$ and $q_1 = 2/5$ is observed. It is followed by
the appearance of the modulation wave with difference value of the wave vector.
According to Fig. 5, the S-like $\delta(\Delta n_0)$ behavior confirms the existence of such modulation wave.
As one can see from Fig. 4, current transition between two commensurate phases is not followed by the optical birefringence jump which indicates the first-order phase transition. Thus, this phase transition can be classified as the continuous phase transition, possibly, of the second order. However, such temperature behavior of $\delta(\Delta n_b)$ does not allow to classify it as the second-order phase transition.

The temperature dependences of $\delta(\Delta n_b)$ in the vicinity of $T_3$, measured during heating and cooling runs are shown in Fig. 5. As one can see, there is no jump of birefringence on any of runs, but the specific S-like shape is observed.
in both cases. One should also note the presence of temperature hysteresis in birefringence behavior at this phase transition.

3.4. The transition between metastable states

It is known that in [N(CH\textsubscript{3})\textsubscript{4}\textsubscript{2}CuCl\textsubscript{2}]\textsubscript{2} crystals birefringence in the incommensurate phase behaves monotonously with temperature. However, it is characterized by the changes of the slope that confirms the non-monotonous behavior of the incommensurability parameter ($\delta$) in the vicinity of $293 \div T_i$. Due to Ref. [44] temperature behavior of $\delta$ is non-monotonous in this interval. Therefore, the structural experimental results of $\delta$ [44] were used as a source for this work.

There were calculated values of wave vector localization in the incommensurate phase. The values of $\delta$ in the vicinities of $T_c$ and $T_i$ were used as defined points for calculation. Besides, the investigations of $\delta (\Delta n)$ [45] were taken into account. The temperature points of wave vector localization with the accuracy of the second digit after comma agree with the calculated from structural investigations values of wave vector localizations on the commensurate values of higher order [44]. Let us note that the smaller value of $n$ ($q = n/m$) the better agreement of calculated and experimental values of $q$.

Fig. 6. Temperature dependence of the birefringence along $a$-axis in the conditions of viscous interaction (at $dT/dt = 60$ mK/h) in the case of [N(CH\textsubscript{3})\textsubscript{4}\textsubscript{2}CuCl\textsubscript{2}] crystal.

The temperature dependence of $\delta (\Delta n)$ is depicted in Fig. 6. One can see that at heating the crystal passes through the sequence of metastable states, characterized by the wave vector values of $q = 50/147$, $33/97$, $49/144$ (Fig. 7). Those states are divided by transition temperature regions, where $\delta (\Delta n)$ takes S-like form. Due to [46] the anomalous behavior is explained by the superposition wave vector. The values of this difference wave vector was obtained from [44]. It is equal to $q^{*'} = q_1 - q_2 = 0.000071$, $q^{*''} = q_3 - q_2 = 0.000070$ and is in good agreement with the results obtained from the birefringence.
Fig. 7. Temperature dependeces of the birefringence and wave vector in the chaotic phase of \([\text{N(CH}_3\text{)}_4]_2\text{CuCl}_4\) crystal.

Fig. 8. Temperature dependence of the specific heat in the transition region (value of \(\frac{d(\Delta n)}{dT}\)), obtained from experimental dependence of \(\delta(\Delta n) \sim f(T)\) (Fig. 1) in the case of \([\text{N(CH}_3\text{)}_4]_2\text{CuCl}_4\) crystal.

The transition by temperature region is considered as the region of the chaotic–incommensurate phase [46]. The temperature behavior of the specific heat \(c_p \sim \frac{d(\delta(\Delta n))}{dT}\) has been calculated (Fig. 8). As it was noted in [46] the temperature interval of the chaotic phase existence the specific heat behaves in the same character as in [38]. Namely, in the metastable state the specific heat takes constant value. On the other hand in the transition regions it has a shape of the parabolic temperature dependence. In the points of entry and exit from the transition region the value of the specific heat increases endlessly.
Under conditions of “viscous” interaction of IC structure with defects [46] the transition from one metastable state to another crosses the transition region [43, 46]. In this region the two waves of modulation (defects’ density wave and modulation wave) coexist. As the result of their superposition, the modulation wave with wave vector $q^* = q_1 \pm q_2$ appears [37]. The temperature behavior of the resulting wave vector confirms that the transition region should be considered as the temperature range of IC phase existence. The temperature behavior of the resulting modulation wave vector and specific heat confirms that the transition from one metastable state into another crosses the IC phase. The temperature entry and exit points of this IC region are the phase transitions.

The temperature dependence of the optical indicatrix rotation ($\varphi$) and time dynamics of the temperature behavior in the sample are shown in Fig. 9. In the aim to enlarge the temperature intervals of metastable states and transition regions the investigations of $[\text{N(CH}_3\text{)}_4]\text{CuCl}_4$ with the impurity of Ni$^+$ was performed.

Fig. 9. Time dependences of the optical indicatrix rotation and sample temperature in the incommensurate phase of $b$-cut of $[\text{N(CH}_3\text{)}_4]\text{CuCl}_4\text{Ni}$ crystal.

The $\varphi$ has anomalous behavior in the temperature entry and exit points of the transition region ($T_1$, $T_2$). One can also see anomalies on the time dependence of temperature in these temperature points. Therefore, the phase transition with calorification occurs.

4. Discussion

Let us use the thermodynamical description for $A_2BX_4$ class of crystals. As it was shown in [38] the sequence of phase transitions in $[\text{N(CH}_3\text{)}_4]\text{ZnCl}_4$ can be described on the basis of thermodynamical potential of the parent phase, because the symmetry groups of metastable phases are the subgroups of the parent phase.
In general, the thermodynamical potential $F(z)$ can be expressed as

$$F(z) = \alpha \rho^2 + \beta \rho^4 + \alpha \rho^n \cos n\varphi - \sigma \rho^2 - \frac{\partial \varphi}{\partial z} + \delta \left( \frac{\partial \rho}{\partial z} \right)^2 + \rho^2 \left( \frac{\partial \varphi}{\partial z} \right)^2$$

$\alpha, \beta > 0, \alpha' > 0, \sigma, \delta > 0$ expansion coefficients; $n$ — integer; $\rho$ and $\varphi$ amplitude and phase of order parameter; $z$ — crystallographical direction corresponding to the IC modulation existence.

The phase transitions occur, when coefficient $\alpha$ at the anisotropic term changes with temperature passing through zero, while $\alpha$ has insignificant changes. In the simplest case one can assume that $\alpha$ is practically constant.

Accordingly, the phase transitions into commensurate phases ($C_1$ and $C_2$) occur at values $\alpha = \alpha'_{C_1}$ and $\alpha = \alpha'_{C_2}$ respectively.

At the absence of electrical field $E_j = 0$ the solutions of the thermodynamical potential (1), corresponding to two commensurate phases $C_1$ and $C_2$ are

$$\cos n\varphi = \frac{\alpha'}{|\alpha'|}, \quad \rho^2 = -\frac{\alpha}{2\beta}, \quad F = \frac{\alpha^2}{4\beta} \left( 1 + \frac{|\alpha'|}{\beta} \rho^{n-4} \right),$$

where $|\alpha'| \rho^n \ll |\alpha| \rho^2$. The last inequality is the condition of weak anisotropy in the space of order parameter. It means that the anisotropic invariant in the thermodynamic potential is relatively smaller in comparison with the isotropic invariant.

The solutions for IC phase can be obtained at the constant amplitude approach $\partial \rho/\partial z = 0$ [38], which is correct under conditions of weak anisotropy. There are the solutions

$$\varphi(x) = \varphi_0 + \frac{2}{n} am \left( \frac{n}{2} px \right), \quad \cos n\varphi_0 = -\frac{\alpha'}{|\alpha'|}, \quad \rho^2 = -\frac{\alpha}{2\beta},$$

$$F = F_0 - 2|\alpha'| \rho^n \frac{\kappa^2}{K^2}, \quad \frac{\kappa^2}{K^2} = \frac{|\alpha'|}{\alpha_0} \rho^{n-2}, \quad \alpha_0 = \frac{\pi^2}{8} \alpha_0,$$

$$\alpha_0 = \frac{\sigma^2}{4\delta} = \delta q_0^2, \quad p = q_0 \pi/2 \frac{E}{E_k}, \quad q = q_0 \left( \frac{\pi/2}{E_k} \right)^2, \quad -\kappa^2 = 1 - \kappa'^2,$$

where $q$ — wave number, $q_0$ — wave number of modulated structure, $k$ — wave vector, $0 \leq k \leq 1$; $F_0$ thermodynamical potential in the commensurate phase; $am(X, k)$ denotes elliptic Jacobi amplitude, $K(k)$ and $E(k)$ are full elliptic integrals of the first and the second order; $q$ denotes wave number, which characterizes the periodicity of the functions $\eta(x) = \rho \cos \varphi(x)$, $\xi(x) = \rho \sin \varphi(x)$ — two-component order parameter. The validity limits of the solution are determined from conditions $k = 1$; $\alpha'_{C_{1,2}} = \pm \alpha_0 \rho^{2-n}$.

Phase transitions between the IC phase and commensurate phases $C_1$ and $C_2$ occur at values $\alpha' = \alpha'_{C_1}$ and $\alpha' = \alpha'_{C_2}$, respectively. Under considered approach these phase transitions are continuous: expressions for $\rho^2$ are the same in all phases, the wave number $q$ takes zero value in the transition points. Such
transitions differ essentially from usual second-order phase transitions. That is why they were called the continuous [38].

Let us note that the amplitude of incommensurate superstructure is constant, but the wave number changes non-monotonously, taking the zero value in the transitions points at $\alpha' = \alpha'_{\text{C}_{1,2}}$. It reaches its maximum $q_0$ in the middle of IC phase at $\alpha' = 0$.

5. Conclusions

The crystals that possess the incommensurate phase in some temperature regions are characterized by three phase transitions in its vicinity. The phase transition from parent into incommensurate phase is a second-order phase transition which is characterized by the critical index $\beta = 0.5$.

In the crystals with the IC phase the phase transition from one commensurate phase into another passes through the transition temperature region of the “coexistence” of these phases. The “coexistence” is followed by the superposition of the existing modulation waves (the defects’ density wave with the period, equal to the period of the first modulation and next going by temperature modulation wave). As the result, the modulation wave with wave vector $q^* = q_1 - q_2$ appears. The last modulation wave makes the main contribution to the temperature behavior of $\delta(\Delta n)$ in the transition region.

In the crystals with IC phase the phase transition from one commensurate phase into another is continuous, which is reflected in corresponding behavior of the physical parameters. It is accompanied by temperature hysteresis of $\delta(\Delta n)$. The insignificant difference between temperature dependences of birefringence at heating and cooling is caused by the different dynamics of the soliton structure.

The transition region between metastable states is separated by the continuous phase transitions.

References


