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CALCULATION OF THE PHASE STATE OF THE $[N(CH_3)_4]_2CUCL_4$ CRYSTALS

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Abstract: The calculation of the spatial changes of the amplitude and phase of the order parameter was performed in the Python environment with the use of the Skipy and JiTCODE libraries.

In $[N(CH_3)_4]_2CuCl_4$ crystals, there is an incommensurate phase I_1 at the small values of the magnitude of long-range interaction (T<0.6) and an incommensurate phase I_2 at T≥1.0. This is the same incommensurate phase, although the behavior of the amplitude and phase functions in it is different under the different conditions mentioned above. At T = 0.6 ÷ 1.0, the coexistence of these two phases is observed which is manifested in the absence of anomalous changes of q during the transition from the sinusoidal mode of IC modulation to the soliton regime.

Keywords: Lyapunov's exponents; the incommensurate superstructure; surface energy, backward differentiation formula (BDF) method, Python.

In the group of $[N(CH_3)_4]_2MeCl_4$ crystals, the $[N(CH_3)_4]_2CuCl_4$ crystals deserve special attention, since the results of theoretical studies [1] and experimental studies [2] indicate the appearance of a commensurate ferroelectric region in an incommensurate phase (IC). The density of the thermodynamic potential of the $[N(CH_3)_4]_2CuCl_4$ crystals can be written as follows:

$$\begin{aligned}\Phi(z)&=\alpha\rho^2+\beta\rho^4-\gamma'\rho^6cos(6\varphi)-\\&-\nu\rho^2\partial\varphi/\partial z+\delta[(\partial\rho/\partial z)^2+\\&+\rho^2(\partial\varphi/\partial z)^2]+a\sigma\rho^3sin(3\varphi)+\\&+bE\rho^3cos(3\varphi)-\sigma^2/2c-E^2/2\chi\end{aligned}\quad, \qquad (1)$$

where ρ and φ are the amplitude and phase of a two-component parameter of order η, ξ; $\sigma=\sigma_{xz}$ is shear stress; $E=E_x$ is an electric field. The shear deformation $u=u_{xz}$ and the polarization $P=P_x$ are determined from (1) with the use of the relations $u=-\partial\Phi/\partial\sigma$, $P=-\partial\Phi/\partial E$. In addition to the initial phase C_0, potential (1) corresponds to two other commensurate phases: C_1 being stable at $\gamma'>0$, with spontaneous value of u, and C_2 which is stable at $\gamma'<0$, with spontaneous value of P (σ=0, E=0). The IC phase is described by the constant amplitude approximation $\partial\rho/\partial z=0$. It is assumed that only one coefficient α depends on T: $\alpha=\alpha_T(T-\Theta)$, and the coefficients β, γ', δ, c, $\chi>0$.

Under normal conditions, only the ferroelastic commensurate phase is observed in the crystal $[N(CH_3)_4]_2CuCl_4$ with the following sequence of phases: initial – paraphase – (T_i=297K) – IC – (T_c = 291K) – commensurate-ferroelastic phase.

The result corresponding to the potential (1) for the phase diagram in the $T-E_x$ plane was described in [1] and is shown in Fig. 1. The field E_x induces a new commensurate C_2 polar phase $C_{2v}^9-P2_1cn$. The IC phase (indicated by the letter I in the figure) is the same, but its structure is different (I_1 and I_2) in different areas of the phase diagram. To analyze the solutions of expression (1), let us introduce the following notation:

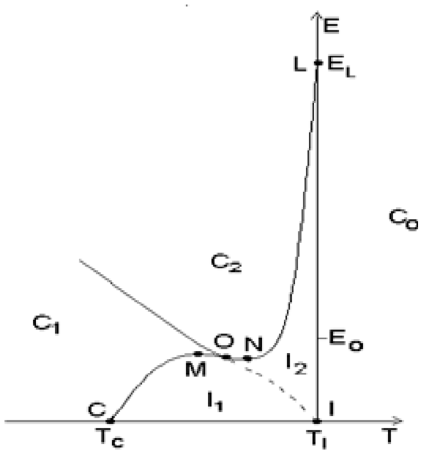
$$\begin{aligned}&E_0=\left(8\alpha_0\beta\varepsilon/b^2\right)^{1/2},E_L=E_0/\left(2\varepsilon\right)^{1/2},\\&\alpha_0=\nu^2/4\delta,\ \varepsilon=(\gamma'\alpha_0/2\beta^2)^{1/2}\end{aligned}\quad. \qquad (2)$$

The value of E_0 is chosen so that $|E|=E_0$ at the point O (see Fig. 1a).

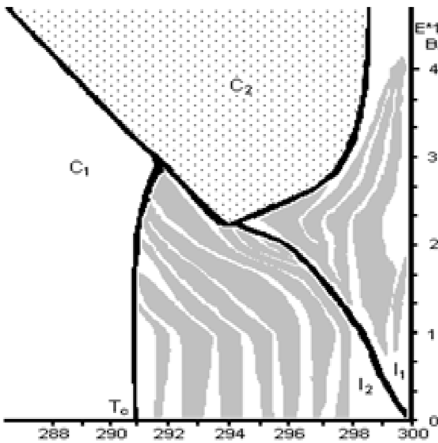
At $\alpha=\alpha_0$, there is a phase transition C_0-I of the second order. The transition temperature $T_i=\Theta+\alpha_0/\alpha_r$ does not depend on E. The dimensionless parameter ε characterizes the anisotropy in the space η, ξ.

The question arises as to whether the appearance of ferroelectricity is already inherent in the peculiarities of the structure of a given crystal, and hence in the peculiarities of the processes of nucleation of an incommensurate superstructure. For this purpose, the magnitude of the wave vector (q) of the incommensurate superstructure was calculated from the spatial modulation of the amplitude of the order parameter and Lyapunov's exponents.

In these systems (expression (1)), the incommensurate superstructure appears due to the presence of the Lifshitz invariant in the thermodynamic potential. For these systems, the amplitude and phase of the order parameter in polar coordinates are described by two second-order differential equations [3]:



a)



b)

Fig. 1. Phase diagram on the $T - E_x$ coordinates, where C_0 is an output phase, C_1 and C_2 are commensurate phases in dimensionless coordinates α_g/α_0 and $|E|/E_0$, obtained in [1] (a); phase diagram in $T - E_x$ coordinates obtained experimentally (b) [2].

$$R'' - R^3 + \left(1 - \varphi'^2 + T\varphi'\right)R - \\ -R^{n-1}K\left(\cos n\varphi + 1\right) = 0, \quad (3)$$

$$\varphi'' + 2\frac{R'}{R}(\varphi' - \frac{T}{2}) + R^{n-2}K\sin n\varphi = 0\,, \quad (4)$$

where $T = \frac{\sigma}{(\gamma r)^{\frac{1}{2}}}$, $K = 2^{-\frac{n}{2}} r^{\frac{n}{2}-2} n\omega u^{1-\frac{n}{2}}$ are dimensionless parameters, n is an integer characterizing the symmetry of the potential, and dimensionless variables

$$\eta = \left(\frac{r}{2u}\right)^{1/2} R,\ z = \left(\frac{\gamma}{r}\right)^{1/2} \xi\,.$$

The calculation of the spatial changes of the amplitude and phase of the order parameter was performed in the Python environment using the Skipy and JiTCODE libraries according to the method described in [4]. According to expressions (3) and (4), as noted in [5], the parameter T describes a long-range interaction and the parameter K is anisotropic, which is determined by the Dzyaloshinski invariant.

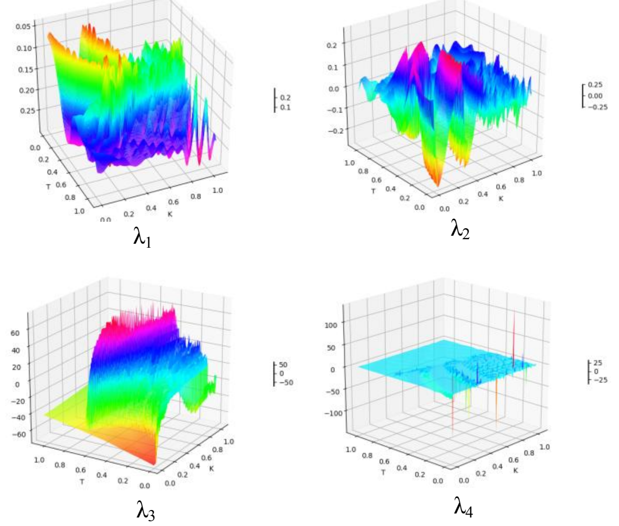
The obtained spectrum of Lyapunov's exponents is shown in Fig. 2 when changing the parameters T and K in the interval 0.0–1.0.

According to Fig. 1, the first Lyapunov's exponent is the positive one, the second takes both negative and positive values with a slight deviation of its value. The third and fourth indicators are negative. It should be noted that the first, second and fourth Lyapunov's exponents are abnormal in nature with a pronounced periodicity. At K and T <1, this system is characterized by one positive value of the Lyapunov's exponent and three negative ones. The third exponent takes a negative value, the modulo of which significantly exceeds other exponents. Therefore, the sum of all Lyapunov's exponents is a negative value, so the system has an attractor.

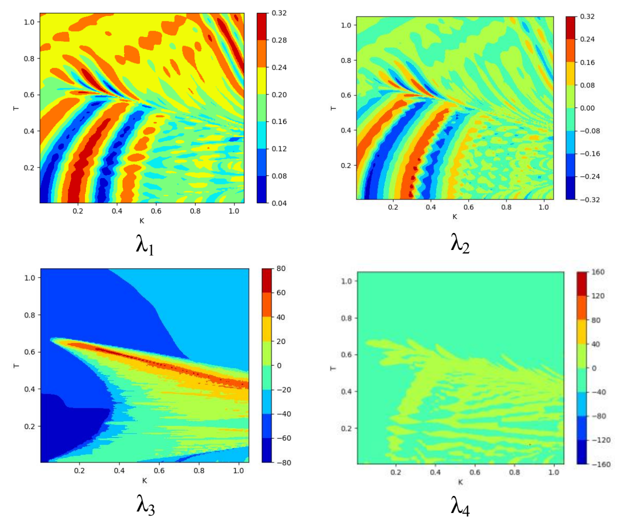
It should also be noted that the third Lyapunov's exponent is anomalous at T <0.6 and K <1. This is indicated in particular by the spectrum of λ_3. The presence of an anomalous periodic nature of the behavior of λ_1, λ_2 is indicated by the spectra of their quantities (Fig. 2).

The map of the spectrum of Lyapunov's exponents is characterized by an implicit line, which divides it into two regions with different behavior of the values of the exponents. This is especially evident for amplitude and phase function. The nature of the behavior of the Lyapunov's exponents (especially λ_3 and λ_4) indicate that structurally these regions of the IC superstructure are different, although they belong to the same IC phase. That is, the amplitude and the phase functions in these two areas are different.

Let us consider the change of the incommensurate wave vector in the range from 0 to 1.2. This range was chosen for T and K changes according to [6], where the dependence of Lyapunov's exponents showed a transition to a chaotic state ($K \geq 1.2$). It should also be noted that in [7], the value of the parameter T for the phase IC was chosen equal to 1 for reasons of realizing the minimum effective potential. At small values of the parameters T and K, as noted in [8], the transition to an undeveloped chaotic state was observed. This range of parameters T and K was associated with the origin of the superstructure. The phase diagram of the dependence of the magnitude of the IC modulation wave vector on the parameters T and K is shown in Fig.3. In the process of nucleation of the superstructure caused by the growth of long-range interaction (parameter T) there is an increase in the magnitude of the wave vector of the superstructure due to a decrease in the wavelength of the modulation.



a)

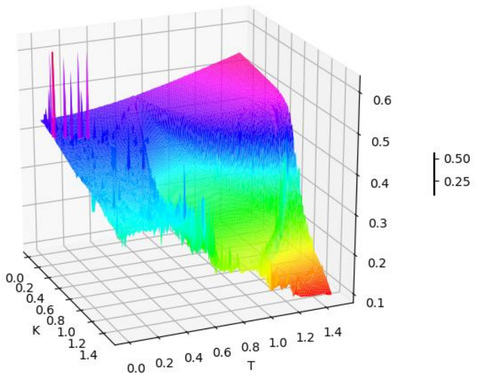


b)

Fig. 2. Dependence of Lyapunov's exponents (a), the spectrum of their values (b) when the parameters T and K were changed in the interval 0.0÷1.0.

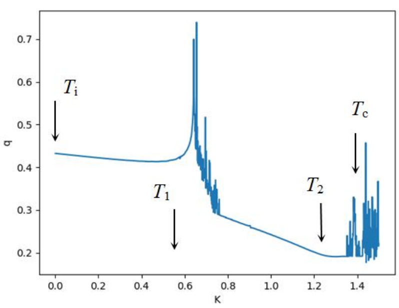
Such behavior of q indicates that in the spatial regions of the correlated motion of tetrahedral groups the modulation wavelength is smaller than in the formation of the IC superstructure. Under these conditions, considering the increase in the value of the anisotropic interaction (parameter K), the region of occurring the chaotic undeveloped state with sharp peaks of the q value exists in a rather narrow range of parameters T, K (Fig. 4).

A further change of T and K is characterized by a monotonic increase in q at constant K and increasing T, and a monotonic decrease in q at a constant T and increasing K. As it is known [9], in the IC phase anisotropic interaction K decreases, indicating the increase in the modulation wavelength. In our case, there is also an increase in the wavelength of IC modulation (decrease in the value of q) (Fig. 3, Fig. 4).



n=3

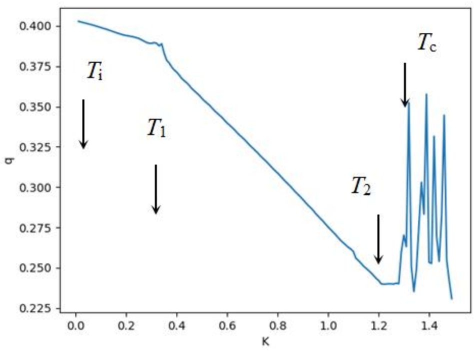
Fig. 3. Dependence of the wave vector (q) of incommensurate modulation on the magnitude of the long-range interaction T and the anisotropic interaction K, which is described by the Dzyaloshinsky invariant.



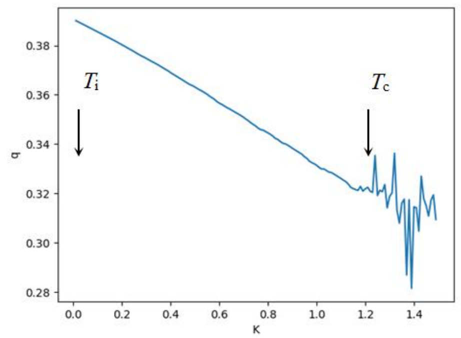
T=1.0

Fig. 4. Evolution of the wave vector of the incommensurate superstructure from the value of the anisotropic interaction K at a constant value of T=1.0, n=3, where T_i is the temperature of transition to the incommensurate phase; T_1 is the transition to the soliton mode of the superstructure; T_2 is the transition to stochastic mode of the superstructure; T_s is a phase transition to the commensurate phase.

According to Fig. 3, it should be noted that under the condition of a linear increase in the values of T and K, a range of their values at which an increase in the value of T is accompanied by a decrease in the value of the wave vector of the superstructure can be traced. That is, according to the authors, the IC superstructure changes from sinusoidal to soliton mode due to the increase in the number of IC modulation harmonics, which causes a decrease in T and an increase in K. Further changes in K and T cause chaotic behavior of q, indicating the transition to the stochastic mode of the IC superstructure with the emergence of a chaotic phase. Therefore, summarizing the results mentioned above, the parameters T and K responsible for the long-range and anisotropic interaction, respectively, well describe the behavior of the wave vector of IC modulation and its modes.



T=0.6



T=0.3

Fig. 5. Evolution of the wave vector of incommensurate superstructure from the K value and constant value of T, n = 3, where T_i is the temperature of transition to the incommensurate phase; T_1 is the transition to the soliton mode of the superstructure; T_2 is the transition to stochastic mode of the superstructure; T_s is a phase transition to the commensurate phase.

In the first approximation, we can assume that according to Fig. 3 the range of changing *T* from 0 to 0.6 corresponds to the first incommensurate phase I_1, where chaotic states are manifested, namely, a sharp change in the value of *q*. With increasing long-range interaction and, hence, the parameter T>0.6, the existence of the second incommensurate phase I_2 is observed, being characterized by all modes of the incommensurate superstructure. This fact is confirmed in particular by studies of harmonics of the IC modulation. Figure 5 shows the evolution of the wave vector of the incommensurate superstructure from the value of the anisotropic interaction *K* at a constant value of *T*, which corresponds to the condition of coexistence of two phases (*T*=0.6) and only phase I_1 (T=0.3). In contrast to phase I_2, phase I_1 does not show a change in the mode of existence of the incommensurate superstructure with increasing anisotropic interaction.

Therefore, in $[N(CH_3)_4]_2CuCl_4$ crystals at small values of the magnitude of the long-range interaction (*T*<0.6) there is the incommensurate phase I_1 at the small values of the magnitude of long-range interaction (*T*<0.6) and the incommensurate phase I_2 at *T*≥1.0. This is the same incommensurate phase, although the behavior of the amplitude and phase functions in it is different under the different conditions mentioned above. At *T* = 0.6 ÷ 1.0, the coexistence of these two phases is observed which is manifested in the absence of anomalous changes of q during the transition from the sinusoidal mode of IC modulation to the soliton regime.

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РОЗРАХУНОК ФАЗНИХ СТАНІВ КРИСТАЛІВ $[N(CH_3)_4]2CUCL_4$

Сергій Свелеба, Іван Катеринчук, Іван Куньо, Іван Карпа, Остап Семотюк, Володимир Бригілевич

Розрахунок просторових змін станів амплітуди й фази параметрів було виконано у середовищі Python з використанням бібліотек Skipy та JiTCODE.

У криталах $[N(CH_3)_4]_2CuCl_4$ існує неспіврозмірна фаза I_1 при малих значеннях величини дальньої взаємодії (T<0.6) та неспіврозмірна фаза I_2 при T≥1.0. Це та ж сама неспіврозмірна фаза, хоча поведінка амплітудних та фазових функцій у ней відрізняється за різних умов, згаданих вище. При T = 0.6 ÷ 1.0, спостерігається співіснування цих двох фаз, що проявляється у відсутності аномальних змін q під час переходу від синусоїдного режиму модуляції неспіврозмірної фази до режиму солітона.

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