# Theoretical Approach to Constructing Temperature-Pressure Phase Diagrams for TMA-Family Crystals

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The main theoretical concepts of phenomenological approach to constructing temperature - pressure phase diagrams for TMA - family crystals are presented. The phase diagram is calculated successfully for $\{N(CH_3)_4\}_2CuCl_4$.

*Keywords*: Phase diagram; Devil's staircase; incommensurate phase

A theoretical method is developed for a constructing the temperature-pressure (T-P) phase diagrams of different crystals of tetramethylammonium tetrahalogenometalic compounds, $\{N(CH_3)_4\}_2MX_4$, where M and X are divalent metals and halogens, respectively (see, e.g. reviews [1-3]). The method is based on the phenomenological description of a Devil's staircase [4]. We assume that all phases, observed on the T-P phase diagram in experiment for each crystal, are produced by a single soft optical branch of the normal vibration spectrum of the crystal. This branch in TMA-crystals has, in some range of parameters, two minima: the first at the center and the second at an arbitrary point of the Brillouin zone (Fig. 1). Due to this special feature, the TMA crystals differ from other crystals with the same space group $D_{2h}^{16}$ of the initial phase C, such as, e.g., $K_2SeO_4$, $SC(NH_2)_2$, BCCD, the soft optical branch for which has only one minimum. As a result, a triple point of a new type, called the Lifshitz-type (LT) point, appears on the T-P phase diagrams. This point was previously predicted theoretically [5]. The LT-point can be observed in the T-P phase diagram at a given wave number $q=q_{TL}$. At $q<q_{TL}$ the C-$C_{0/1}$ phase transition occurs, ($C_{0/1}$ is the commensurate phase with $q=0$, i.e., it is equi-translational with the C phase). At $q>q_{TL}$ the C-IC phase transition occurs (IC is the incommensurate phase). Thus, the LT-point separates the transitions from the C phase to the $C_{0/1}$ and IC phases. The Lifshitz (L) point separates the same transitions [6]. But the L-point can be observed on the T-P phase diagrams at $q=0$. Therefore a specific feature of the T-P phase diagrams for the TMA-crystals is just the absence of the L-point.

We use two theoretical approaches for description of the sequence of phase transitions

through the IC phase: C-IC-$C_{0/1}$ and C-IC-$C_{m/l}$ ($C_{m/l}$ is the commensurate phase with $q=q_{m/l}=m/l$). In the first approach (the $SC(NH_2)_2$ crystal is an example), expressions of thermodynamic potentials for the IC and $C_{0/1}$ phases are known. In the second approach ($K_2SeO_4$ is an example), expressions of thermodynamic potentials for the IC and $C_{m/l}$ phases are known. The requirement for the two expressions for the IC phase to coincide permits to write down the thermodynamic potentials for all phases with consistent coefficients. We use the single harmonic approximation for the IC phase, and a condition of weak anisotropy for the $C_{m/l}$ phases (the anisotropic invariants in the potential are assumed to be small in comparison with isotropic invariants). The space groups of all commensurate phases in TMA-CuCl are presented in Table 1.

By equating the thermodynamic potentials of different phases we obtain expressions for the boundaries between these phases expressed in terms of coefficients of the potentials. (The equations for the thermodynamic potentials and boundaries between different phases can be found in refs. 10, 11). The two coefficients, denoted as D and A, are small and their dependencies on T and P are essential. Therefore the initial theoretical phase diagram is constructed in the D-A plane. We assume that the dependences of D and A on T and P are linear. The width of the area of existence of every $C_{m/l}$ phase is determined by setting a value of only one dimensionless coefficient. Thus coefficients, the values of $q_{TL}$, and also positions and orientations of the T and P axes in the D-A phase diagram are chosen on the condition of better agreement between theoretical and experimental T-P phase diagrams.

The theoretical T-P phase diagram is constructed on the basis of the initial D-A diagram with the T and P axes chosen on it. It is impossible to give here results, which were obtained, for different crystals. We choose as an example the crystal TMA-CuCl. Figure 2 shows the experimental T-P phase diagram combined from diagrams presented in Refs. 7-9. Figure 3 shows the initial theoretical phase diagram in the D-A plane. (We chose the following parameters Q = 0.5, $Q_L^2 = 0.2$, $A_\gamma = A_3 = 0.6$, $A_8 = 1.5$, see Refs. 10, 11). Figure 4 shows the theoretical T-P phase diagram constructed on the base of the D-A diagram. Comparing Figs. 2 and 4 one can see a fairly good agreement between experimental and theoretical T-P phase diagrams, especially if account is taken of all approximations and assumptions made in constructing the theoretical diagrams. Approximately the same agreement has been also achieved for different crystals of the TMA-family: ZnCl [10], MnCl [11], CuBr [12], and ZnI [13].

These results demonstrate that the theoretical approach presented in this paper can be considered to be adequate to the experimental data.

Two of the authors (G. A. K and D. G. S.) gratefully acknowledge the financial support of the Russian Fund of Fundamental Research (Grant Ns. 02-00-17746).

**References**


[1] J. D. Axe, M. Iizumi and G. Shirane: *Incommensurate Phases in Dielectric*s 2, edited by R. Blinc and A. P. Levanyuk (North-Holland, 1986, Amsterdam) Ch. 10.

[2] K. Gesi: *Ferroelectrics* **66** (1986) 269.

[3] H. Z. Cummins: *Phys. Reports* **185** (1990) 211.

[4] D. G. Sannikov: *Zh. Eksp. Teor. Fiz.* **96** (1989) 2198, [*Sov. Phys. JETP* **69** (1989) 1244].

[5] T. A. Aslanyan and A. P. Levanyuk: *Fiz. Toerd. Tela* (Leningrad) **20** (1978) 804, [*Sov. Phys. Solid State* **20** (1978) 466].

[6] R. M. Hornreich, M. Lubau and S. Strikuran: *Phys. Rev. Lett.* **35** (1975) 1678.

[7] S. Shimamura, H. Terauchi, N. Hamaya and Y. Fujii: *Phys. Rev*. B **54** (1996) 6915.

[8] K. Gesi: *J. Phys. Soc. Jpn.* **65** (1996) 1963.

[9] K. Gesi: *Kristallografya* **44** (1999) 89, [*Crystallogr, Rep*. **44** (1999) 84].

[10] D. G. Sannikov, G. A. Kessenikh and H. Mashiyama: *J. Phys. Soc. Jpn*. **69** (2000) 130.

[11] D. G. Sannikov, G. A. Kessenikh and H. Mashiyama: *J. Phys. Soc. Jpn*. **71** (2002) No.6 (in press).

[12] D. G. Sannikov and H. Mashiyama: *J. Phys. Soc. Jpn*. **71** (2002) No.7 (in press).

[13] D. G. Sannikov and H. Mashiyama: *J. Phys. Soc. Jpn.* (in preparation).


Table 1. The space groups of all commensurate $C_{m/l}$ phases, with $q=q_{m/l}$=m/l, which can be produced by a single soft optical branch in TMA-CuCl crystal (Pmcn $D_{2h}^{16}$, $k_z=qc$*).

| 0/1 | | m_/l_ | $m_+/l_-$ | $m_-/l_+$ |
|---|---|---|---|---|
| | $c_1$ | $P2_1cn$ $C_{2v}^9$ (x) | $P112_1/n$ $C_{2h}^5$ (xy) | $Pc2_1n$ $C_{2v}^9$ (y) |
| $B_{1g}$(xy) $P112_1/n$ $C_{2h}^5$ | $c_2$ | $P12_1/c1$ $C_{2h}^5$ (zx) | $P2_12_12_1$ $D_2^4$ (xyz) | $P2_1/c11$ $C_{2h}^5$ (yz) |
| | $c_3$ | P1c1 $C_s^2$ | $P112_1$ $C_2^2$ | Pc11 $C_s^2$ |

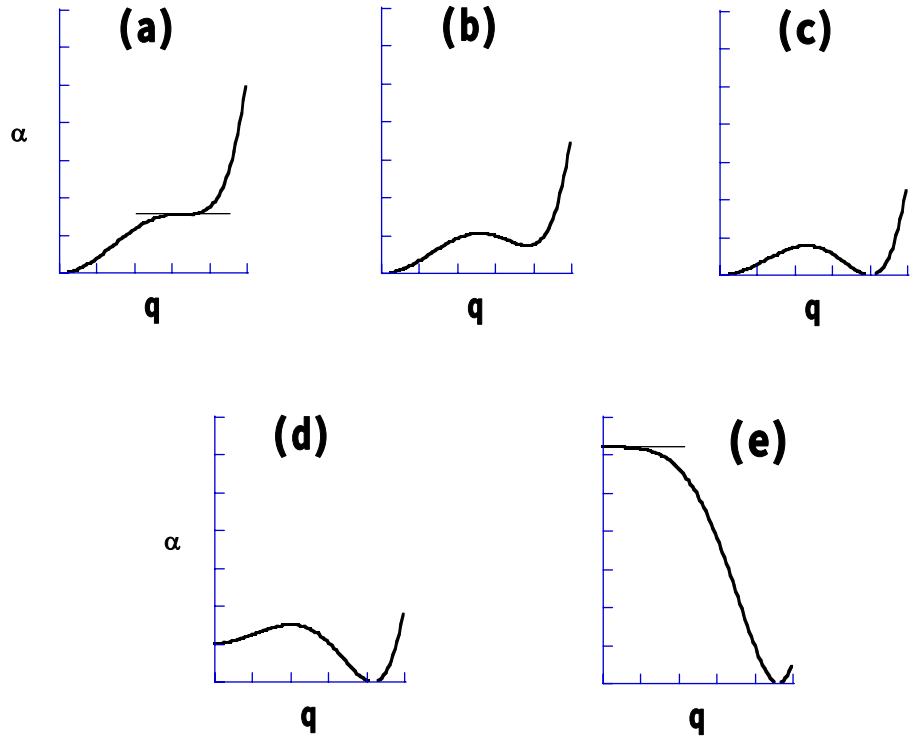


Figure 1. The dependence of elastic coefficient α of the soft optical branch on $q$ at temperatures of phase transitions from the C phase to the $C_{0/1}$ phase (a, b) and to the IC phase (d, e). These transitions meet at the LT point (c). The variables A and B are coordinates of the minimum at an arbitrary point of the Brillouin zone. At $B^2=(2/3)q_{TL}^2$ the minimum at $q$=0 disappears (it becomes maximum, e). The value $B=q_{TL}$ corresponds to the LT point (c).

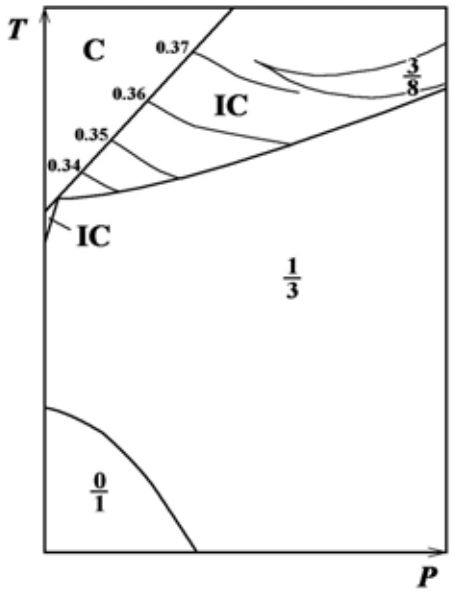


Figure 2. The experimental T-P phase diagram for TMA-CuCl obtained from Refs. 7-9.

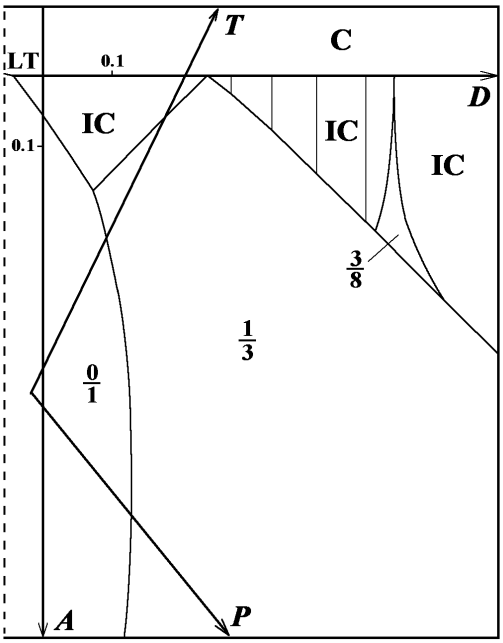


Figure 3. The oinitial theoretical D-A phase diagram plotted for TMA-CuCl.

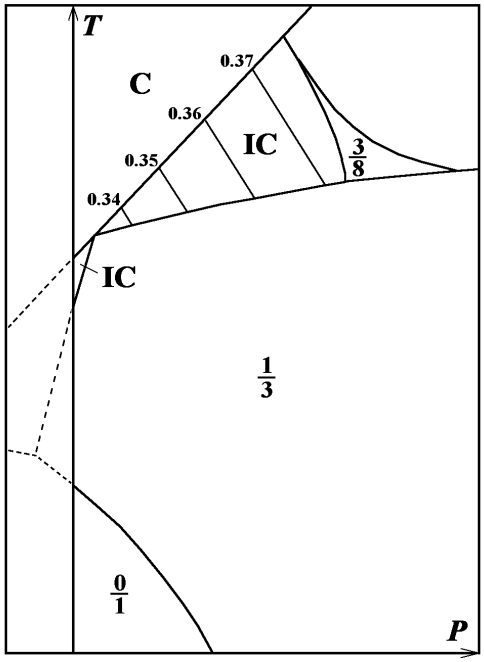


Figure 4. The theoretical T-P phase diagram plotted on the bases of Fig. 3 for TMA-CuCl. Extensions of some boundaries into the range of negative P are shown by dashed lines.