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Phase diagrams of incommensurate ferroelectric NH_4HSeO_4: phenomenological treatment

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The phenomenological analysis of the pressure-temperature ($P-T$) phase diagram of NH_4HSeO_4 crystals is presented. It is shown that the disagreement between the experimental results and the theory may be removed assuming that the coefficient of the Landau free-energy expansion κ at the gradient term $(\mathrm{d}q/\mathrm{d}z)(\mathrm{d}q^*/\mathrm{d}z)$ changes the sign in the experimental range of pressures. According to the present model the triple point observed in NH_4HSeO_4 at $P_\mathrm{K} \approx$ 455 MPa, $T_\mathrm{K} \approx$ 236 K may be considered as artificial points which result from the limitation of experimental resolution. Therefore, even above P_K there still exist two very close (unresolved) lines of the incommensurate phase transitions.

Key words: *phase diagram, critical point, incommensurate phase*

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External effects (electric field, mechanical stress, hydrostatic pressure, etc) essentially distort the structure of incommensurate (IC) phases. In many cases they lead to the appearance of a triple point in phase diagrams. Two lines of the IC phase transitions (refered usually as normal (N)-IC and IC-commensurate (C) transition, respectively) merge in this point into one line of direct transitions from N- to C-phase. The similar point has been revealed recently in the pressure-temperature (P-T) phase diagram of the improper incommensurate ferroelectric NH_4HSeO_4 [1]. In these crystals the phase transformation from N- to C-phase is associated with a two-component order parameter (q_1, q_2) and Lifshitz invariant $\mathrm{i}\delta(q_1\mathrm{d}q_2/\mathrm{d}z - q_2\mathrm{d}q_1/\mathrm{d}z)$ is allowed by the symmetry. In the plane wave approximation it gives the linear (with respect to wavevector k) contribution to the soft mode dispersion near a commensurate point k_C:

$$\omega^2(k) = \alpha + 2\delta(k - k_\mathrm{C}) + \kappa(k - k_\mathrm{C})^2. \tag{1}$$

The minimum $\omega^2(k)$, thus, corresponds to the point $k_i = k_0 - k_\mathrm{C} = -\delta/\kappa$. Therefore if just only $\delta \neq 0$, the direct second order phase transition N-C phase is impossible. Accordingly, on the phase diagram only two types of polycritical points are expected to occur:

(i) The condition $\alpha = \delta = 0$ defines the isolated point of direct second order phase transition from N- to C-phase in $\alpha - \delta$ phase plane. Such a point appears in the intersection of two lines of phase transitions into IC-phase, i.e. it is the tetracritical point [2].

(ii) In principal, a direct first order phase transition from N- to C-phase is possible. The corresponding phase diagram has been considered by Sannikov [3]. The direct first order N-C transition appears at $\alpha = a_{\rm nc}$ for $\beta < 0$ if $\alpha_{\rm nc} = \beta^2/4\gamma > \alpha_i$ (where β and γ are the free-energy coefficients at forth- and sixth-order terms, respectively), thus, the condition $\alpha_{\rm nc} = \alpha_i$ defines the coordinates of the triple point in the phase diagram. This point, however differs from the Lifshitz point, since the wavevector of the IC-modulation, as well as the angle between the tangents to the lines of IC phase transitions are finite in the triple point. Instead of this, only the lines of the first order transitions $\alpha_{\rm nc}(\sigma)$ and $\alpha_{\rm ic}(\sigma)$ $(\sigma = \beta^2/4\gamma - \delta^2/2\kappa)$ have a common tangent in the triple point.

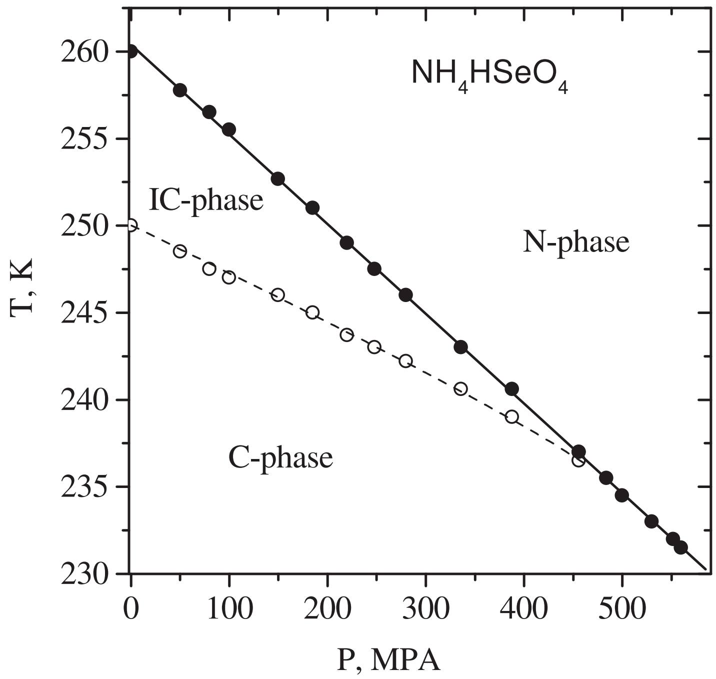

Figure 1. The pressure-temperature phase diagram of NH_4HSeO_4 crystals [1].

It seems that none of these polycritical points have been revealed in $P-T$ phase diagram of NH_4HSeO_4 (figure 1) [1]. In particular, above $P_{\rm K} \approx 455$ MPa the direct phase transition from N- to C-phase is observed. However, the magnitude of the jump of the elastic constant at the first order phase transition from the IC- to C-phase ($T = T_{\rm C}$) critically decreases approaching $P_{\rm K}$ [1], whereas the lines of N-C and IC-C phase transitions do not have a common tangent in the triple point $(P_{\rm K}, T_{\rm K})$ (figure 1). In fact, this contradicts to the prediction of the theory [3].

Considering the phase diagrams in the IC-systems I authors [2,3] have restricted the free energy expansion by the first order gradient terms of the order parameter. In this case only two types of the polycritical points are expected, which correspond to the tetracritical or triple points. Within these theories it was assumed that coefficient κ at the gradient term $(\mathrm{d}q_1/\mathrm{d}z)(\mathrm{d}q_2/\mathrm{d}z)$ is positive and not dependent on the external effects. Obviously such an assumption restricts the behaviour of IC–systems and results in a reduction of a number of possible types of polycritical points in their phase diagrams. In fact, there are no physical reasons for such a restriction and the coefficient κ for some real systems may change the sign at the experimental range of the applied pressures P. In order to stabilize the Landau free energy we must then include additional higher order gradient terms into the expansion. The corresponding phase diagram in $\alpha - \kappa$ phase plane has been recently considered[4] regarding TMATC-Cu crystals. It appears later that the application of this model exactly to this crystals is not quite successful. According to the recent X-ray results [5] the observed polycritical point in TMATC-Cu is indeed tetracritical point but not the triple point as it was assumed in our previous work [4]. Nevertheless, the appearance of the phase diagram described in this work is quite possible in other crystals. It seems that one of such crystals is NH_4HSeO_4. At least up to now there is no experimental evidence that the observed polycritical point in the P-T diagram of these crystals is a tetracritical point. In this case the application of the modified phenomenological model is inevitable.

Let us consider the free-energy expansion for NH_4HSeO_4 which contains a sixth-order ($n = 6$) anisotropic invariant [6]:

$$\begin{aligned} F &= \int_{-L/2}^{L/2} \phi(z)\mathrm{d}z, \\ \phi(z) &= \frac{\alpha}{2}qq^* + \frac{\beta}{4}(qq^*)^2 + \frac{\gamma_1}{6}(qq^*)^3 - \frac{\gamma_2}{12}(q^6 + q^{*6}) + \frac{\mathrm{i}\delta}{2}\left(q^*\frac{\mathrm{d}q}{\mathrm{d}z} - q\frac{\mathrm{d}q^*}{\mathrm{d}z}\right) \\ &+ \frac{\kappa}{2}\frac{\mathrm{d}q}{\mathrm{d}z}\frac{\mathrm{d}q^*}{\mathrm{d}z} - \frac{\mathrm{i}\mu}{2}\left(q^*\frac{\mathrm{d}^3q}{\mathrm{d}z^3} - q\frac{\mathrm{d}^3q^*}{\mathrm{d}z^3}\right) + \frac{\lambda}{2}\frac{\mathrm{d}^2q}{\mathrm{d}z^2}\frac{\mathrm{d}^2q^*}{\mathrm{d}z^2} - \mathrm{i}f(q^3 - q^{*3})P_0 \\ &+ \frac{1}{2\chi_o}P_0^2, \end{aligned} \tag{2}$$

where $\alpha = A_0(T - T_0)$ and $\beta, \delta, \gamma_1, \gamma_2, \mu$ and λ are assumed to be positive. One must remember that in the case of NH_4HSeO_4 crystal, the IC-phase appears in the region $T_\mathrm{c} = 252$ K $< T < T_\mathrm{i} = 262$ K with the wavevector of IC modulation $k_0 = c^*(1/3 - \xi)$, where $\xi \approx 0.019$ [7]. The free energy density functional $\phi(z)$ in equation (2) differs from [3,6] only by the presence of the two last terms, which contain third and second order derivatives of the inhomogeneous two-component order parameter $(q(z), q^*(z))$. For simplicity here we consider only one gradient invariant (μ-term) which produces the contribution to the free energy proportional to $(k - k_\mathrm{C})^3$ (see below). Indeed, the free energy is stabilized by λ-term. Kind and Muralt [8] have used the similar free energy expansion to explain the sequence of the phase transitions in $(NH_3C_3H_7)_2MnCl_4$. A trivial minimization procedure applied to equation (2) leads us to the following expressions for the free energy in the IC- and C-phases:

$$\begin{aligned}
F_{\mathrm{IC}} &= \frac{\alpha_k}{2}q_k q_k^* + \frac{\beta}{4}(q_k q_k^*)^2 + \frac{\gamma_1}{6}(q_k q_k^*)^3 - \frac{\gamma_2}{2}(q_k^5 Q_{K''} + q_k^{*5}Q_{K''}^*) \\
&\quad + \frac{\alpha_Q(K'')}{2}Q_{K''}Q_{K''}^* - \mathrm{i}f(q_k^3 P_{K'} - q_k^{*3}P_{K'}^*) + \frac{1}{\chi_o(K')}P_{K'}P_{K'}^*, \\
&\quad \alpha_k = \alpha + 2\delta(k-k_{\mathrm{C}}) + \kappa(k-k_{\mathrm{C}})^2 + 2\mu(k-k_{\mathrm{C}})^3 + \lambda(k-k_{\mathrm{C}})^4, \\
&\quad q_k = q\mathrm{e}^{\mathrm{i}(k-k_{\mathrm{c}})z},\ q_k^* = q^*\mathrm{e}^{-\mathrm{i}(k-k_{\mathrm{c}})z},\ K' = c^* - 3k,\ K'' = 2c^* - 5k; \qquad (3)
\end{aligned}$$

$$\begin{aligned}
F_{\mathrm{C}} &= \frac{\alpha}{2}qq^* + \frac{\beta}{4}(qq^*)^2 + \frac{\gamma_1'}{6}(qq^*)^3 - \frac{\gamma_2'}{12}(q^6 + q^{*6}), \\
&\quad q = r\mathrm{e}^{\mathrm{i}\psi},\ q^* = r\mathrm{e}^{-\mathrm{i}\psi}, \\
&\quad \gamma_1' = \gamma_1 - 6\chi_o f^2,\ \gamma_2' = \gamma_2 + 6\chi_o f^2,\quad \psi = (2m+1)\pi/6,\ m = 0,1,2... \qquad (4)
\end{aligned}$$

The N-IC transition occurs at $\alpha_i = A_0(T - T_i) = \alpha_k(k_i) = 0$. The equilibrium value of the incommensurate wavevector $k_i = |k_0 - k_{\mathrm{C}}| = \xi_i c^*$ at this second order phase transition corresponds to the absolute minimum of α_k in equation (3), therefore it should be found from the condition:

$$\partial\alpha_k/\partial k = \delta + \kappa(k-k_{\mathrm{C}}) + 3\mu(k-k_{\mathrm{C}})^2 + 2\lambda(k-k_{\mathrm{C}})^3 = 0. \qquad (5)$$

The analytical solution of equation (5) is rather complicated, therefore we solved it numerically for the case of NH_4HSeO_4 crystals. It is convenient to use the normalized coupling constants $\delta' = \delta c^*$, $\kappa' = \kappa c^{*2}$, $\mu' = \mu c^{*3}$ and $\lambda' = \lambda c^{*4}$ presenting thus the incommensurate modulation by the dimensionless wave number ξ. Their magnitude has been found in order to adjust the experimental value $\xi_i \approx 0.019$ for NH_4HSeO_4 at $P = 0.1$ MPa [7]. An interesting case occurs when the coefficient κ' changes in the limits $-\kappa_m' \leqslant \kappa' \leqslant \kappa_m'$, which are defined by the conditions $|\kappa_m'| \approx \lambda'\xi_m^2$ and $|\kappa_m'| \gg \delta'/\xi_m$; here ξ_m is the equilibrium value of the wave number ξ at $\kappa' = -\kappa_m'$. The corresponding dependences $\alpha_i(\kappa') = A_0(T - T_i)$ and $\xi_i(\kappa')$ are presented in figure 2. As the parameter κ' arises to its certain value, the wave number $\xi_i(\kappa')$ initially decreases rapidly and then gradually tends to zero; indeed it approaches zero-value at $\kappa' \to \infty$.

The phase transition point $\alpha_{\mathrm{ic}} = A_0(T - T_{\mathrm{c}})$ from IC- to C-phase cannot be exactly determined since it usually depends on a chosen approximation. In the simple soliton model, that is a second order, transition never occurs in a real crystal. The inclusion of just only the mechanisms of the soliton-defects or soliton-lattice interaction makes this transition discontinuous [9]. Accordingly, the magnitude of α_{ic} can be approximately estimated using the condition $F_{\mathrm{IC}}(\alpha_{\mathrm{ic}}) = F_{\mathrm{C}}(\alpha_{\mathrm{ic}})$. Indeed the free-energy expansion for the IC-phase (see equation (3)) can be reduced to a more suitable form. The forth and the fifth terms in equation (3) are of the order of $(qq^*)^5$ and thus they can be neglected. Then eliminating the polarization $P_{K'}$ from equation (3) one obtains:

$$F_{\mathrm{IC}} = \frac{\alpha_k}{2}q_k q_k^* + \frac{\beta}{4}(q_k q_k^*)^2 + \frac{\gamma_1'}{6}(q_k q_k^*)^3, \qquad (6)$$

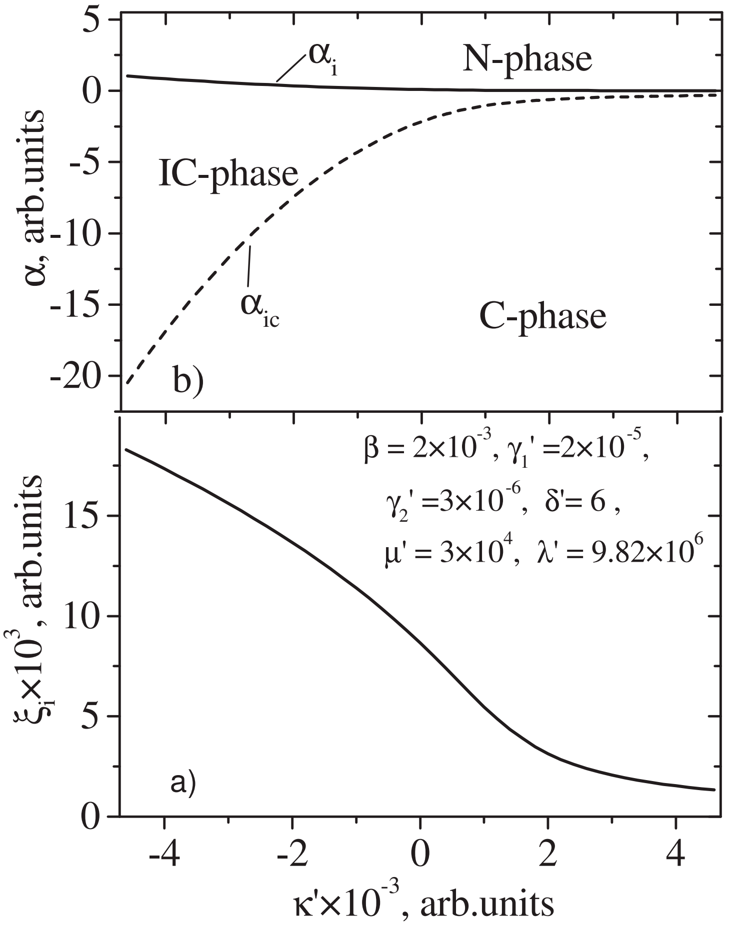

Figure 2. The calculated equilibrium wavenumber ξ_i of the incommensurate wave on the α_i-line (a) and calculated phase diagrams in the $\alpha - \kappa'$ coordinate plane (b). The values of the free-energy coefficients have been found in order to adjust the experimental values $\xi_i = 0.019$ [7] and $\alpha_{\rm ic}/\alpha_i \approx 20$ [1] for NH_4HSeO_4 at $P =$ 0.1 MPa.

where γ_1' is defined by equation (4). The values of the free energy coefficients γ_1', γ_2' and β have been chosen to adjust the ratio $\alpha_{\rm ic}/\alpha_i \approx 20$ which follows from the experiment for NH_4HSeO_4 crystals [1]. Obviously in this case $\gamma_1' \gg \gamma_2'$. The line $\alpha_{\rm ic}(\kappa')$ was calculated numerically (figure 2) for the given set of parameters. As κ' arises both the lines of N-IC and IC-C phase transitions approach and merge at $\kappa' \to \infty$. It is evident, that in the infinity these lines have a common tangent, whereas the wavevector of IC-modulation $k_i = \xi_i c^*$ approaches a zero value.

The unusual phase diagram considered above does not contain any finite triple point, which seems to be observed in the experiment (figure 1). The appearance of this point can be attributed to the limitation of experimental resolution. There is always a certain limit up to which both N-IC and IC-C lines can be observed separately. It immediately becomes obvious if we present the phase diagrams in the $P - T$ coordinate plane (figure 3), which has been obtained assuming that the free energy coefficients $\beta, \gamma_1', \gamma_2', \lambda', \delta', \mu'$ are nearly pressure independent. Some justification for

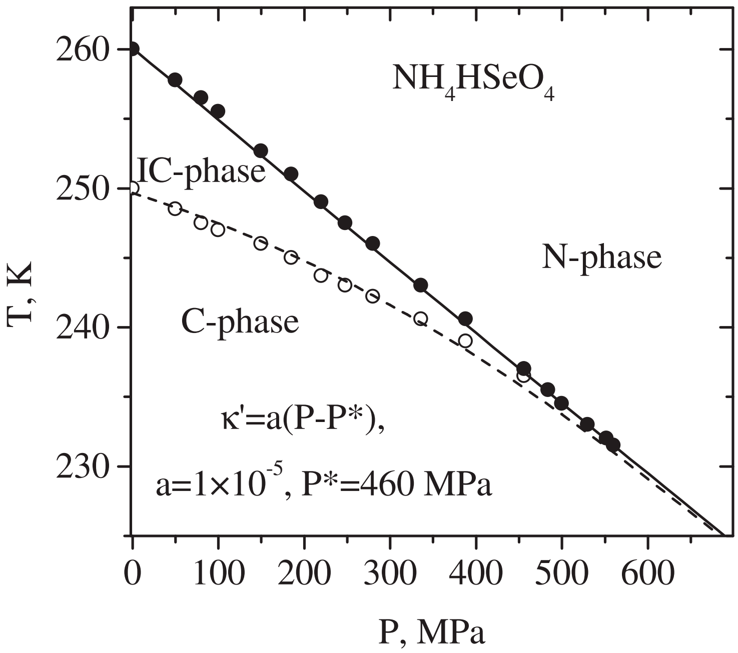

Figure 3. The phase diagrams (figure 2) presented in the $P-T$ coordinate plane for NH_4HSeO_4 crystals. At sufficiently high pressures the lines of N-IC and IC-C phase transitions cannot be experimentally resolved.

such an assumption follows from the fact, that the pressure behaviour of these coefficients is at least not critical in the experimental range of pressures. Otherwise, the appearance of the polycritical points of other types would be inevitable. One must remember that $P-T$ phase diagram of NH_4HSeO_4 crystals has been determined from the ultrasonic measurements [1]. Taking into account a slightly smeared character of the elastic anomalies in the vicinity of both N-IC and IC-C transitions one can estimate the limit of experimental resolution for T_i and T_c as about 0.5 K. Since above 455 MPa the lines of N-IC and IC-C phase transitions are separated by a temperature interval smaller than 0.5 K, they cannot be experimentally resolved. Thus, the triple point in the phase diagram (figure 1) can be considered as an artificial point.

In conclusion, we have presented here the phenomenological analysis of the pressure-temperature phase diagram of NH_4HSeO_4 crystals. A serious disagreement between the experimental results and the theory can be removed assuming that this compound shows the $P-T$ phase diagram with an infinite Lifshitz point. An alternative explanation for this phase diagram can be obtained assuming the existence of the tetracritical point at about 455 MPa. Precise X-ray experiments in this temperature-pressure range would be quite desirable.

References

1. Kityk A.V., Vlokh O.G., Zadorozhna A.V., Czapla Z. On the pressure-temperature phase diagram of NH_4HSeO_4 crystals: acoustical treatment. // Ferroelectrics Lett., 1994, vol. 17, No. 1–2, p. 1–4.
2. Bruce A.D., Cowley R.A., Murray A.F. The theory of structurally incommensurate systems. II. Commensurate-incommensurate phase transitions. // J. Phys. C.: Solid State Phys., 1978, vol. 11, No. 17, p. 3591–3608.
3. Sannikov D.G. Lifshitz points for bidimensional representations. // Pisma JETP, 1979, vol. 30, No. 3, p. 173–175.
4. Kityk A.V., Zadorozhna A.V., Mokry O.M., Sahraoui B. Infinite Lifshitz point in incommensurate type-I dielectrics. // Phys. Rev. B., 1999, vol. 60, No. 1, p. 10–13.
5. Shimomura S., Terauchi H., Hamaya N., Fujii Y. Multicritical point in structurally incommensurate $[N(CH_3)_4]_2CuCl_4$. // Phys. Rev. B., 1996, vol. 54, No. 10, p. 6915–6920.
6. Ishibashi Y. Phenomenology of incommensurate phases in the A_2BX_4 family. – In: Incommensurate Phases in Dielectrics 2 (ed.by R. Blinc and A. P. Levanyuk), Elsevier Science Publishers B.V., 1986, p. 49–69.
7. Denoyer F., Rozycki A., Parlinski K., More M. Neutron investigation of incommensurability and metastability in NH_4HSeO_4 and ND_4DSeO_4. // Phys. Rev., 1989, vol. 39, No. 1, p. 405–415.
8. Kind R., Muralt P. Unique Incommensurate-commensurate phase transitions in layer-structure perovskite. – In: Incommensurate Phases in Dielectrics 2 (ed.by R. Blinc and A. P. Levanyuk), Elsevier Science Publishers B.V., 1986, p. 301–318.
9. Cummins H.Z. Experimental studies of structurally incommensurate crystal phases. // Phys. Rep., 1990, vol. 185, No. 5–6, p. 211–409.

Фазові діаграми неспівмірного сегнетоелектрика NH_4HSeO_4

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Представлений феноменологічний аналіз фазової діаграми тиск-температура ($P - T$) кристалів NH_4HSeO_4. Показано, що неузгодження між експериментальними результатами і теорією може бути зняте, припускаючи, що коефіцієнт κ при градієнтному члені $(\mathrm{d}q/\mathrm{d}z)(\mathrm{d}q^*/\mathrm{d}z)$ в розкладі вільної енергії Ландау змінює знак в області прикладеного тиску. Відповідно до представленої моделі, потрійна точка, спостережена в NH_4HSeO_4 при $P_\mathrm{K} \approx$ 455 MPa, $T_\mathrm{K} \approx$ 236 K, може розглядатись як штучна точка, яка є результатом експериментального обмеження. Отже, навіть вище P_K ще існують дві дуже близькі лінії неспівмірних фазових переходів.

Ключові слова: *фазова діаграма, потрійна точка, неспівмірна фаза*

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