Theoretical Temperature-Pressure Phase Diagram for $\{N(CH_3)_4\}_2ZnI_4$

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Theoretical phase diagrams for $\{N(CH_3)_4\}_4ZnI_4$ crystal are constructed using the phenomenological approach, which was developed earlier for $\{N(CH_3)_4\}_4MCl_4$ family crystals. On these diagrams there are three commensurate phases and there is no incommensurate phase. To explain this the phase transition from the initial phase to the phase with $q = 1/2$ is assumed to be first order. The theoretical temperature-pressure phase diagram is plotted and is found to be in agreement with the experimental diagram. The approximations and assumptions made in the construction of theoretical diagrams are discussed.

KEYWORDS: phenomenological theory, thermodynamic potential, T-P phase diagram, commensurate phase, TMAI-Zn compound

1. Introduction

The crystal TMAI-Zn ($\{N(CH_3)_4\}_2ZnI_4$), as many other crystals out of the large family TMAX-M, where X and M are halogen and divalent metal, respectively, was measured and the experimental $T-P$ phase diagram was obtained (Fig. 1).[1)] The peculiarities of this diagram are the existence of three commensurate phases, including the initial, C, phase in the absence of the incommensurate, IC, phase. Becides, the phase diagram has the triple point between the C, $C_{0/1}$ and $C_{1/2}$ phases (the suffixes indicate the values of $q = q_{m/l} = m/l$ in the commensurate phases). The point of this type is met, apparently, for the first time. Such peculiarities of the phase diagram can be explained by assumption that the C-$C_{1/2}$ phase transition is first order. Then we can construct the theoretical $T-P$ phase diagram. For this purpose we use the phenomenological approach developed previously.[2)]

2. Thermodynamic Potentials

The symmetry groups of the commensurate phases are $Pmcn = D_{2h}^{16}$ for the C phase, $P121/c1 = C_{2h}^5$ for the $C_{0/1}$ phase and $Pbc21 = C_{2v}^5$ for the $C_{1/2}$ phase (with the doubling of the lattice spacing b)[1)] (see also Table I in ref. 3). We assume that all phases, observed in experiment, are produced by a single optical branch which has, in some range of parameters, two minima. The soft optical branch or, more precisely, the dependence of elastic coefficient α on the

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wave number q can be presented by the expressions

$$\alpha(q) = \alpha - \delta q^2 - \kappa q^4 + \tau q^6 = a + \Delta(q), \tag{1}$$

where

$$\Delta(q) = \tau(b^2 - q^2)^2[2(b^2 - q_L^2) + q^2],\ a = \alpha - \Delta_0,$$
$$\Delta_0 = \Delta(0) = 2\tau b^4(b^2 - q_L^2),\ \delta = \tau b^2(3b^2 - 4q_L^2),\ q_L = \kappa/2\tau. \tag{2}$$

The first expression for $\alpha(q)$ is more familiar, it is an approximation of the function $\alpha(q)$ by four-term polynomial. The fourth term, τq^6, supplies possibility of existence of two minima of the branch ($\kappa > 0$, $\delta > 0$). The second expression for $\alpha(q)$ is more convenient introducing two new quantities a and b which are the coordinates of the soft branch minimum at an arbitrary point of the Brillouin zone: $q = b$, $\alpha(b) = a$. The minimum at the center of the Brillouin zone is determined by the coordinates $q = 0$, $\alpha(0) = \alpha$.

It is necessary, besides the thermodynamic potential of the initial C phase, which is trivial, $\phi = 0$, to write down the potentials of the $C_{0/1}$ and $C_{1/2}$ phases. We take the expressions for them in the form:[4)]

$$\phi_{1/2} = \alpha_{1/2}\rho^2 + \beta\rho^4 - |\alpha_2'|\rho^4 + \gamma\rho^6,$$
$$\phi_{0/1} = \alpha\zeta^2 + \frac{2}{3}\beta\zeta^4 + \frac{2}{5}\gamma\zeta^6, \tag{3}$$

where

$$\alpha_{1/2} = \alpha(1/2) = a + \Delta_{1/2},\ \Delta_{1/2} = \Delta(1/2),\ \alpha = \alpha(0) = a + \Delta_0,\ \Delta_0 = \Delta(0). \tag{4}$$

(For details, see ref. 4.) We suppose that $\beta > 0$, $\bar{\beta} = \beta - |\alpha_2'| < 0$, $\gamma > 0$. Minimizing potentials (3), with respect to ρ and ζ, we obtain the expressions

$$\phi_{1/2} = -\frac{2|\bar{\beta}|^3}{27\gamma^2}\{[1 - \frac{3\gamma\alpha_{1/2}}{\bar{\beta}^2}]^{3/2} + (1 - \frac{9\gamma\alpha_{1/2}}{2\bar{\beta}^2})\},$$
$$\phi_{0/1} = -\frac{50}{27}\frac{2\beta^3}{27\gamma^2}\{[1 - \frac{9}{10}\frac{3\gamma\alpha}{\beta^2}]^{3/2} - (1 - \frac{9}{10}\frac{9\gamma\alpha}{2\beta^2})\}. \tag{5}$$

Note that the expression for $\phi_{1/2}$ given in ref. 4 is valid only at $\bar{\beta} > 0$.

Although all coefficients α, δ, κ, τ, a and b are dimensionless, it is convenient to introduce new variables, which are also dimensionless:

$$A = -a/\tau Q^6,\ D = \delta/\tau Q^4,\ B = b/Q,\ Q_L = q_L/Q,\ Q_{1/2} = q_{1/2}/Q,$$
$$D_0 = \Delta_0/\tau Q^6 = 2B^4(B^2 - Q_L^2),\ D_{1/2} = \Delta_{1/2}/\tau Q^6 = (B^2 - Q_{1/2}^2)[2(B^2 - Q_L^2) + Q_{1/2}^2]. \tag{6}$$

Here Q is mere a number and we take it as $Q = 1/2$.

3. Phase boundaries

By equating potentials (5) to each other we obtain the following expressions for the boundaries between different phases (the expressions are given in different variables). The C-$C_{0/1}$ boundary is given by

$$\alpha = 0,\ a + \Delta_0 = 0,\ A = D_0. \tag{7}$$

The C-$C_{1/2}$ boundary is given by

$$\frac{3\gamma\alpha_{1/2}}{\bar{\beta}^2} = \frac{3}{4},\ A = -\frac{1-2|A_2|}{16A_\gamma^2} + D_{1/2}. \tag{8}$$

The $C_{0/1}$-$C_{1/2}$ boundary is given by

$$[1+10.8A_\gamma^2(A-D_0)]^{3/2} - [1+16.2A_\gamma^2(A-D_0)] = 0.54[1-2A_2]^3\{[1+12A_\gamma^2\frac{A-D_{1/2}}{(1-2A_\gamma)^2}]^{3/2} + [1+18A_\gamma^2\frac{A-D_{1/2}}{(1-2A_\gamma)^2}]\}. \tag{9}$$

We construct the phase diagram on the $D-A$ plane, because these two quantities are small and their dependences on T and P are essential. The variable D is expressed according to eqs. (1) (2) and (6) as

$$D = B^2(3B^2 - Q_L^2). \tag{10}$$

Setting values of B^2 we determine values of A from eqs. (7)-(9) and values of D from eq. (10).

In order to construct the D-A phase diagram it is necessary to set the values of Q_L, A_2 and A_γ. Their choice is determined by the condition of the best fitting of the theoretical $T-P$ phase diagram, which is obtained from the $D-A$ diagram, to the experimental $T-P$ diagram. We choose

$$Q_L^2 = 0.9,\ A_2 = 0.7,\ A_\gamma = 0.4. \tag{11}$$

4. Phase Diagrams

Figure 2 shows the $D-A$ phase diagram constructed in accordance with eqs. (7)-(11). Note that the C-IC boundary is determined by the expression $A = 0$. The extension of the C-$C_{0/1}$ boundary up to the transaction it with the line $A = 0$ (the extension is shown by the point curve) would determine a triple Lifshitz-type, LT, point (between the C, IC, and $C_{0/1}$ phases) which was introduced in ref. 5. On the other hand, the extension of the C-$C_{1/2}$ boundary up to the transaction it with the line $A = 0$ (the extension is also shown by the point curve) would determine another triple LT point (between the C, IC, and $C_{1/2}$ phases) which was introduced in ref. 6. The transaction of the C_0-$C_{0/1}$ and C-$C_{1/2}$ boundaries prevents the appearing of these two triple LT points on the phase diagram (See the attempt at explaining the $T-P$ diagram for TMAI-Zn in ref. 7 by the assuming occurrence of the LT point[6] on the diagram). Note that a classification of

the triple points with participance of the IC phase is given in ref. 8. The triple point on the $D-A$ phase diagram (Fig. 2) between the phases C, $C_{0/1}$ and $C_{1/2}$ is encountered, apparently, at the first time. The transaction of the C-$C_{0/1}$ and C-$C_{1/2}$ boundaries prevents also the appearing of the IC-phase on the phase diagram. Such transaction is a consequence of the C-$C_{1/2}$ phase transition being first order.

5. Remarks

In conclusion we enumerate the main positions of the approach. We assume that a single soft optical branch, which has two minima at some range of parameters, produces all phases observed in experiment. We also assume that the C-$C_{1/2}$ phase transition is first order. Due to this the IC phase is absent and a new triple point exists on the phase diagrams. Only two small quantities D and A are assumed to be dependent on T and P. The remaining quantities Q_L, A_γ, and A_2 (or κ, τ, β, γ and α_2') are considered to be constant, independent of T and P. Dispersions (dependencies on q) of the coefficients β, γ, and α_2' are neglected.

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Fig. 1. The experimental T-P phase diagram for TMAI-Zn from ref. 1.

Fig. 2. The D-A phase diagram plotted for TMAI-Zn.

Fig. 3. The theoretical T-P phase diagram plotted on the basis of Fig. 2 for TMAI-Zn.

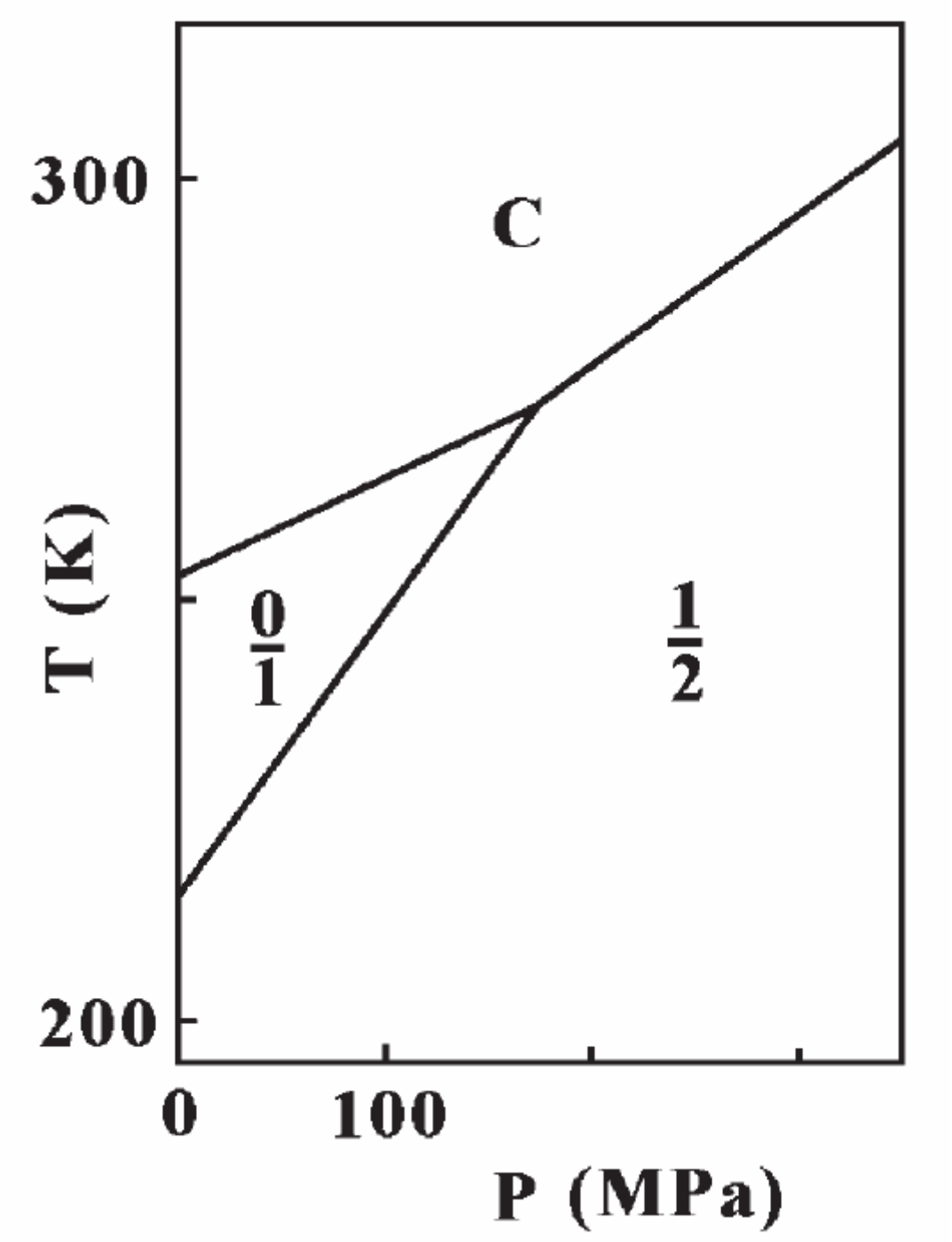

Fig. 1.

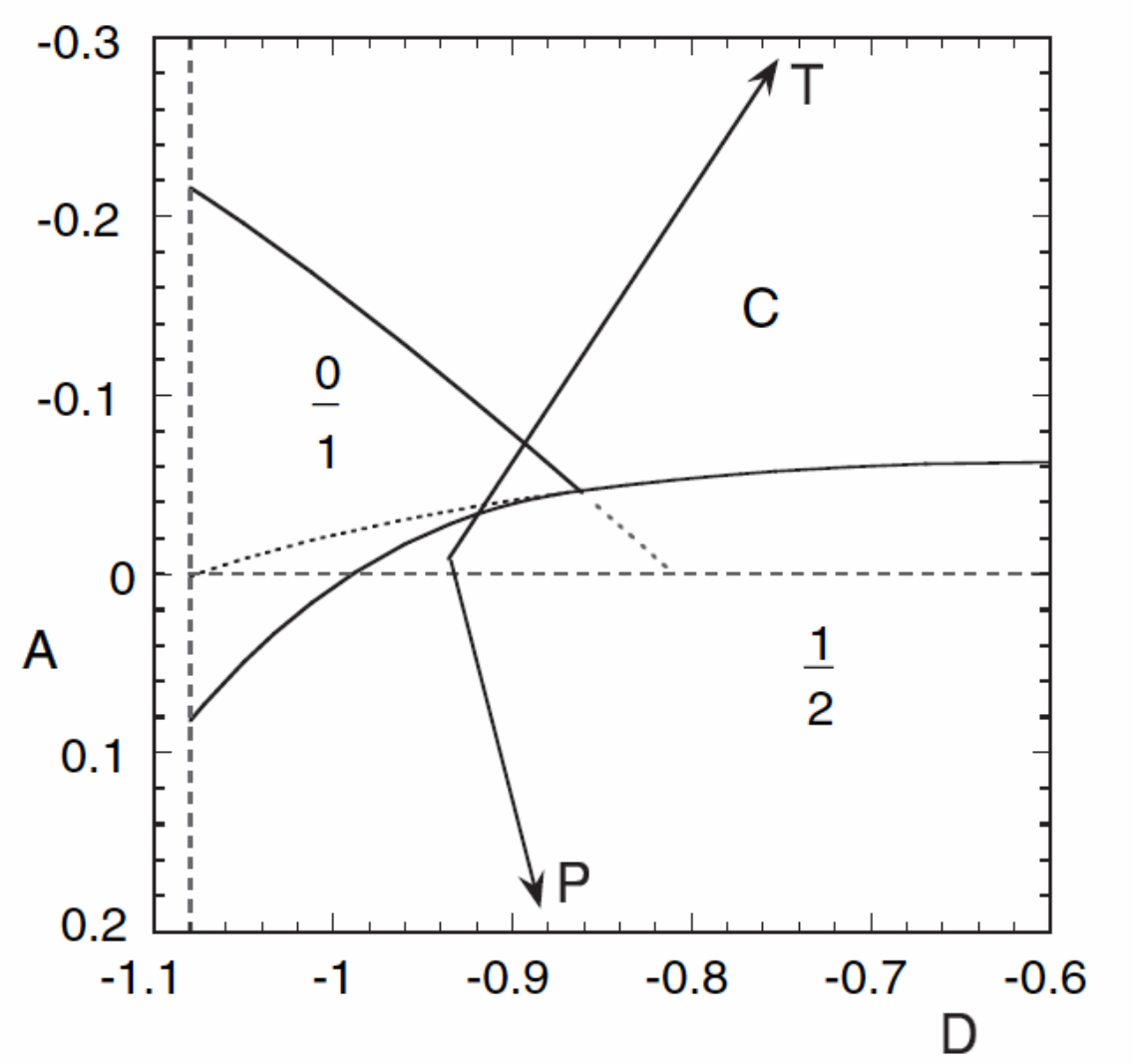

Fig. 2.

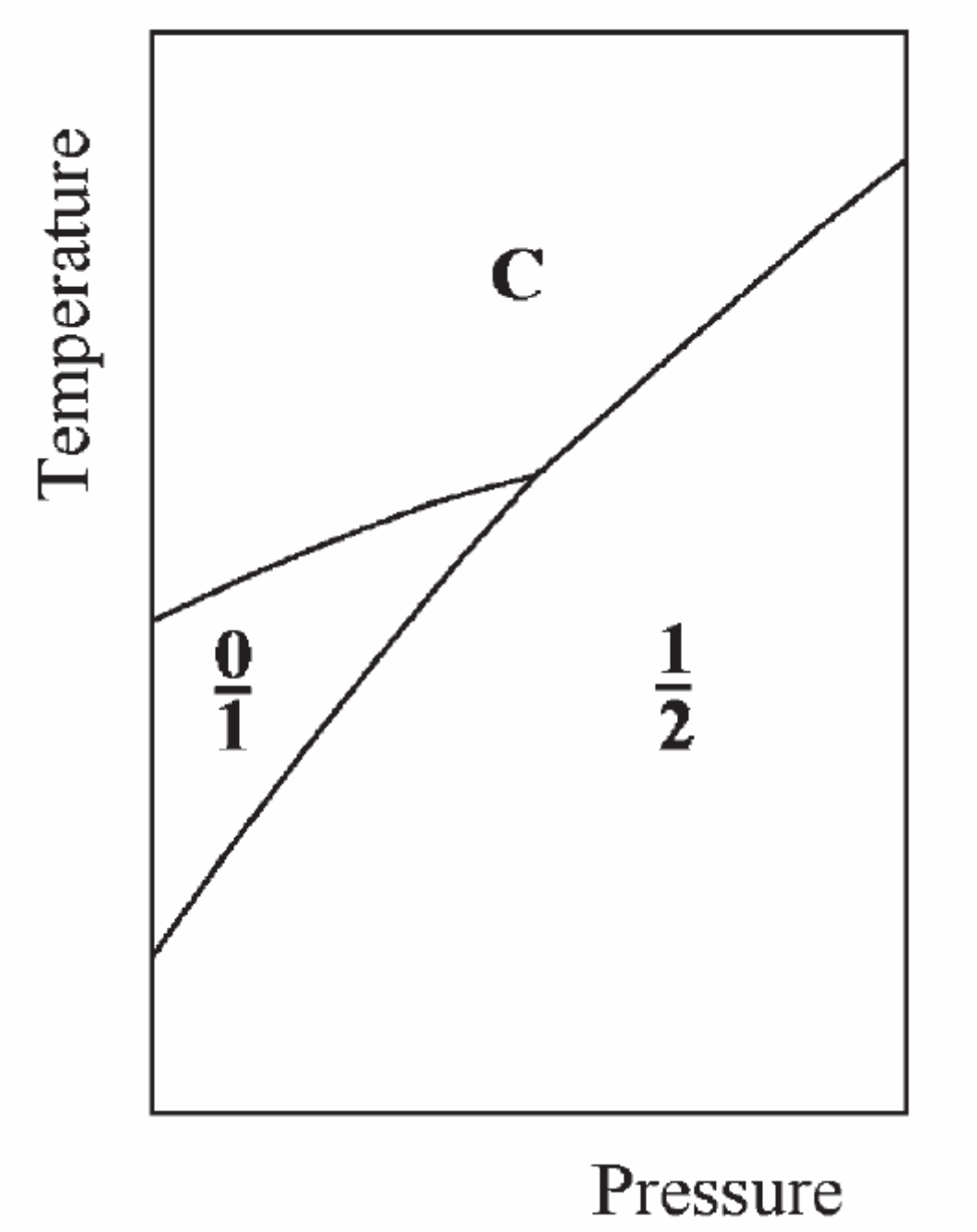

Fig. 3.