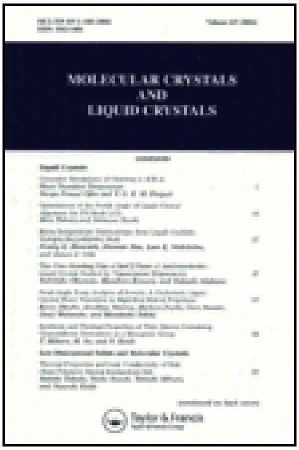

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Bifurcational Analysis of the Prost Model

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Bifurcational Analysis of the Prost Model

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On the basis of the bifurcational analysis it is shown that the Prost model of a frustrated smectic liquid crystal with interacting antiferroelectric and translational order parameters permits three modes of behaviour of molecular systems which correspond to three qualitatively different types of separatrices—manifolds dividing the control parameters space into open areas with topologically different structures of a thermodynamic potential. Phase diagrams of the model for each of the separatrices are built. It is established that phase diagrams with two tri-critical points on equilibrium lines similar to those described by the original Prost theory and found experimentally in mixtures of cyanobiphenyls correspond to two types of separatrices. Phase diagrams with three tri-critical points (two of which are located on the curve of coexistence of mono- and bilayer smectics and the third one occurs on the curve of co-existence of bilayer smectic and nematic mesophases) are inherent to the third type of separatrices.

Keywords: frustrated smectic liquid crystals, interacting order parameters, separatrices, phase diagrams

1. INTRODUCTION

In recent years, a variety of liquid crystal substances has been discovered which exhibit complicated phase diagrams with multicritical points whose behavior can be explained in terms of coupled order parameters only. Among such systems, frustrated smectrics, layered compounds with competing translational and antiferroelectric order parameters (see References 1 and 2), are one of the most interesting objects for study. The Prost model is an important phenomenological model allowing to describe a wide range of problems relevant to frustrated smectic liquid crystals: critical points in phase diagrams,[2,3] reentrant mesomorphism,[4] correlations and x-ray scattering in polar phases,[5] in-commensurate effects,[6,7] polymorphism of polar mesogenes.[2] A doubtless achievement of the Prost model is that it reproduces the phase diagram topology of a mixture of cyanobiphenyls in the "concentration—temperature" coordinates plane.[1,2,4] In microscopic approaches the thermodynamic potential of the Prost model arises in Landau expansions upon corresponding order parameters (see, for example, Reference 8). All mentioned above allows to consider the Prost model as a basic one for the range of data concerning frustrated mesomorphism. However, analysis of the multiparametric thermodynamic potential of the Prost model has been originally fulfilled in the exceptional case only (see below) at concrete numerical values of control parameters. The purpose of the present paper is to perform its complete investigation from the unified viewpoint at arbitrary parameters on the basis of bifurcational analysis techniques and, thus, to describe all the mean-field peculiarities of corresponding phase diagrams.

2. FORMALISM

It is shown in References 1–4 that two one-dimensionally modulated order parameters

$$\Psi_1(z) = |\psi_1|\cdot\exp(iq_p z), \qquad \Psi_2(z) = |\psi_2|\cdot\exp(iq_\rho z) \tag{1}$$

are required for description of frustrated smectics in the approximation of ideal orientational ordering. In (1), the function $\Psi_1(z)$ characterizes "head-to-tail" correlations of polar molecules paired owing to constant dipoles of cyanogroups; the function $\Psi_2(z)$ characterizes a distribution of molecular mass centers in the smectic phase; q_ρ and q_p are wave vectors corresponding to density and polarization waves. The Z axis is chosen parallel to the liquid crystal director and perpendicular to smectic layers. The thermodynamic Landau-Ginzburg potential of the Prost model is expressed through the fields (1), according to the relation

$$\Delta F[\Psi_1, \Psi_2] = \int dz[y_1|\Psi_1|^2 + D_1|(\Delta + k_1^2)\Psi_1|^2 + \alpha_1|\Psi_1|^4 + y_2|\Psi_2|^2 + D_2|(\Delta + k_2^2)\Psi_2|^2 + \alpha_2|\Psi_2|^4 + 2\varkappa|\Psi_1|^2|\Psi_2|^2 - 2wRe(\Psi_1^2\Psi_2^*)], \tag{2}$$

where positive values $D_1, D_2, \alpha_1, \alpha_2, \varkappa$ and w are material constants and parameters $y_1 = a_1(t - t_{c1}), y_2 = a_2(t - t_{c2})$ $(a_i > 0, i = 1,2)$ characterize a deviation of the system temperature t from temperatures t_{c1}, t_{c2} of corresponding mean-field phase transitions bound up with the order parameters (1) in the case when the latters are non-interacting.

In the investigation of phase diagrams of linearly modulated mesophases we assume that $q_\rho = 2q_p = 2k_1 = k_2$. Then, proceeding from (1), (2) we get a thermodynamic potential density in the Prost's form

$$f[|\psi_1|, |\psi_2|] = y_1|\psi_1|^2 + y_2|\psi_2|^2 + \alpha_1|\psi_1|^4 + \alpha_2|\psi_2|^4 + 2\varkappa|\psi_1|^2|\psi_2|^2 - 2w|\psi_1|^2|\psi_2|. \tag{3}$$

The expression (3) corresponds, from a mathematical point of view, to the particular case of the type $X_{1,0}$ catastrophe[9] and from a physical one- to the Landau-de Gennes theory with two coupled translational and antiferroelectric order parameters and six coefficients $y_1, y_2, \alpha_1, \alpha_2, \varkappa, w$. Analysis performed for such a multiparametric potential at not fixed parameters values (as in the original Prost model[1,2] where it is considered that $\alpha_1 = \alpha_2 = \varkappa = w = 1$) but in the general form (i.e. in the six-dimensional control space $\{(y_1, y_2, \alpha_1, \alpha_2, \varkappa, w)\}$) encounters sufficient calculational difficulties. Overcoming the latters, one may suppose, can lead to description of new effects. The expression (3) allows to determine the equations of state

$$2y_1|\psi_1| + 4\alpha_1|\psi_1|^3 + 4\varkappa|\psi_1||\psi_2|^2 - 4w|\psi_1||\psi_2| = 0, \quad 2y_2|\psi_2| + 4\varkappa|\psi_1|^2|\psi_2| + 4\alpha_2|\psi_2|^3 - 2w|\psi_1|^2 = 0 \tag{4}$$

and the stability matrix

$$\left[\frac{\partial^2 f}{\partial|\psi_i|\partial|\psi_j|}\right] = 2\begin{bmatrix} y_1 + 6\alpha_1|\psi_1|^2 + 2\varkappa|\psi_2|^2 - 2w|\psi_2| & 4\varkappa|\psi_1||\psi_2| - 2w|\psi_1| \\ 4\varkappa|\psi_1||\psi_2| - 2w|\psi_1| & y_2 + 2\varkappa|\psi_1|^2 + 6\alpha_2|\psi_2|^2 \end{bmatrix} \tag{5}$$

of the molecular system. It can be found from Equations (4) that their possible solutions fall into three groups

$$|\psi_1| = 0, \qquad |\psi_2| = 0, \tag{6}$$

$$|\psi_1| = 0, \qquad y_2 + 2\alpha_2|\psi_2|^2 = 0, \tag{7}$$

$$\begin{cases} y_1 + 2\alpha_1|\psi_1|^2 + 2\varkappa|\psi_2|^2 - 2w|\psi_2| = 0, \\ y_2|\psi_2| + 2\varkappa|\psi_1|^2|\psi_2| + 2\alpha_2|\psi_2|^3 - w|\psi_1|^2 = 0, \end{cases} \tag{8}$$

the first (6) of which corresponds to the nematic (N), the second (7) one – to the monolayer smectic (SmA_1) and the third (8) one – to the bilayer smectic (SmA_2) states.

As it is known from catastrophe theory,[10] the zero value of the stability matrix (5) determinant defines, at the account of the solutions (6), (7), (8), bifurcational sets (separatrices) dividing the control space $\{(y_1, y_2, \alpha_1, \alpha_2, \varkappa, w)\}$ into open areas with topologically different structures of the thermodynamic potential (3). It follows from Equations (5)–(8) that separatrices of the N, SmA_1 and SmA_2 phases can be written as

$$y_1 \cdot y_2 = 0, \tag{9}$$

$$\alpha_2^2 y_1^2 - 2\alpha_2\varkappa y_1 y_2 + \varkappa^2 y_2^2 + 2\alpha_2 w^2 \cdot y_2 = 0, \tag{10}$$

$$\begin{cases} y_1 = \dfrac{8(\alpha_1\alpha_2 - \varkappa^2)}{w} \cdot S^3 + 6\varkappa S^2, \\ y_2 = \dfrac{8\varkappa(\alpha_1\alpha_2 - \varkappa^2)}{\alpha_1 \cdot w} \cdot S^3 - \dfrac{6(\alpha_1\alpha_2 - 2\varkappa^2)}{\alpha_1} S^2 - \dfrac{6\varkappa w}{\alpha_1} S + \dfrac{w^2}{\alpha_1}, \end{cases} \tag{11}$$

respectively.

3. RESULTS AND DISCUSSION

We now seek to determine bifurcatioin sets and corresponding phase diagrams in the (y_2, y_1) plane, considering the rest of the parameters to be arbitrary but fixed ones (in every concrete calculation). Then, Equation (9) determines curves coinciding with coordinates axes and Equation (10) determines a parabola whose vertex is located at the point with the coordinates

$$y_2 = -(w^2\varkappa^2\alpha_2)/[2(\varkappa^2 + \alpha_2^2)^2],$$

$$y_1 = w^2\varkappa(2\alpha_2^2 + 2\varkappa^2)/[2(\alpha_2^2 + \varkappa^2)^2]$$

and which is symmetrical relatively the curve

$$y_1 = \varkappa y_2/\alpha_2 + w^2\varkappa/(\alpha_2^2 + \varkappa^2).$$

Equations (11) define the SmA_2 phase separatrix in parametric representation (with the parameter "S" as a parameter of the curve). The latter is a parabola at the condition $\alpha_1\alpha_2 - \varkappa^2 = 0$ and a curve of the more general type (with a turning point) at the condition $\alpha_1\alpha_2 - \varkappa^2 \neq 0$.

It is evident from the point of view of the control phase parameterization that the first case

$$\alpha_1\alpha_2 - \varkappa^2 = 0 \tag{12}$$

corresponding to the original Prost theory is less general than the two remainders

$$\alpha_1\alpha_2 - \varkappa^2 > 0, \tag{13}$$

$$\alpha_1\alpha_2 - \varkappa^2 < 0. \tag{14}$$

Analysis shows that the separatrices (9), (10) have a similar structure in the (y_2, y_1) plane at different α_1, α_2, $\varkappa$ parameters and the separatrix (11) has unique features in each of the cases (12)–(14). Figures 1–3 shows examples of calculation of the separatrices (9)–(11) and phase diagrams corresponding to them at choice of the following parameters: 1) $\alpha_1 = \alpha_2 = \varkappa = w = 1$ (case 12)), 2) $\alpha_1 = 2$, $\alpha_2 = \varkappa = w = 1$ (case (13)), 3) $\alpha_1 = \alpha_2 = w = 1$, $\varkappa = 2$ (case (14)). The SmA_2 phase separatrix (11) has a point of tangency with the straight line $y_1 = 0$ (N phase separatrix) in all the three cases (12)–(14) and this point of tangency is a tri-critical one for the SmA_2 – N transition. And besides, if the condition (12) is fulfilled the two parabolae being the SmA_1 and SmA_2 phase separatrices have one common point of tangency which is a tri-critical one for the SmA_2 – SmA_1 transition. Hence, if the case (12) is valid two tri-critical points being points of tangency of the separatrices (9) and (11), (10) and (11) take place in the SmA_2-SmA_1 – N phase diagram (see Figure 1) what corresponds to the original Prost model and is experimentally observed in mixtures of cyanobiphenyls.

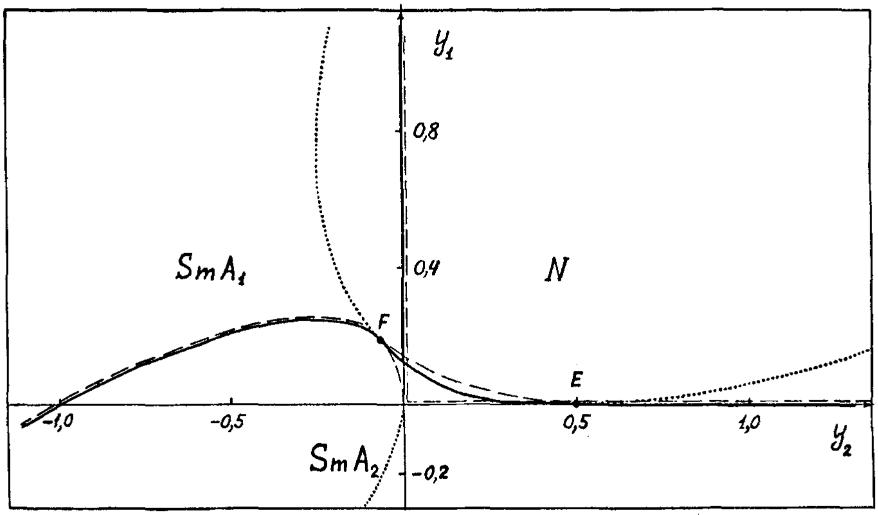

FIGURE 1 Separatrices and phase diagrams of a frustrated liquid crystal in the Prost model at the condition $\alpha_1\alpha_1 - \varkappa^2 = 0$ ($\alpha_1 = \alpha_2 = \varkappa = w = 1$). Solid lines (——) are lines of phase transitions; dotted lines (·····) are bifurcation lines corresponding to non-physical (negative) solutions; dashed lines (- - - - -) are bifurcation lines corresponding to physical (positive) solutions. Parts of solid lines on which dashed ones are superimposed correspond to lines of second order phase transitions. Symbols SmA$_2$, SmA$_1$, N indicate stability ranges of bilayer and monolayer smectic and nematic phases. Point E is a tri-critical one on the line of SmA$_2$-N phase transitions. Point F is a tri-critical one on the line of SmA$_2$-SmA$_1$ phase transitions.

As it is seen from Figure 2, the separatrices (10) and (11) have, at the fulfilment of the condition (13), two points of tangency one of which correspond to non-physical solutions range (where the order parameters $|\psi_1|$ or $|\psi_2|$ are negative) and the other one—to a tri-critical point on the SmA$_2$-SmA$_1$ curve. Hence, the phase diagram structure of a frustrated smectic is, at the condition (13), similar to the one at the condition (12) (compare Figures 1 and 2). Note that equations of spinodales and phase boundaries at first order SmA$_2$-N and SmA$_2$-SmA$_1$ transformations and also the thermodynamic potential (3) topology at the conditions (12) and (13) are, of course, essentially different.

As it is seen from Figure 3, the separatrices (10) and (11) have, at the fulfilment of the inequality (14), two points of tangency located on their physical branches (where the order parameters $|\psi_1|$ and $|\psi_2|$ are positive). This indicates that the both points of tangency of the curves (10) and (11) are tri-critical ones on the SmA$_2$-SmA$_1$ equilibrium boundary and this result is a fundamentally new one for the class of multiparametric models with the type (3) potential under consideration. We especially note that, in terms of the bifurcational analysis performed, the latter conclusion about a possibility of the existence of three tri-critical points on the SmA$_2$-SmA$_1$-N phase diagram two of which are located on the SmA$_2$-SmA$_1$ phase boundary is more general than the one about a possibility of the existence of two tri-critical points in the SmA$_2$-SmA$_1$-N equilibrium curve (obtained in the original Prost model) in that sense in which the condition (14) is more general than the condition (12).

Temperature dependences of order parameters characterizing the SmA$_2$-SmA$_1$

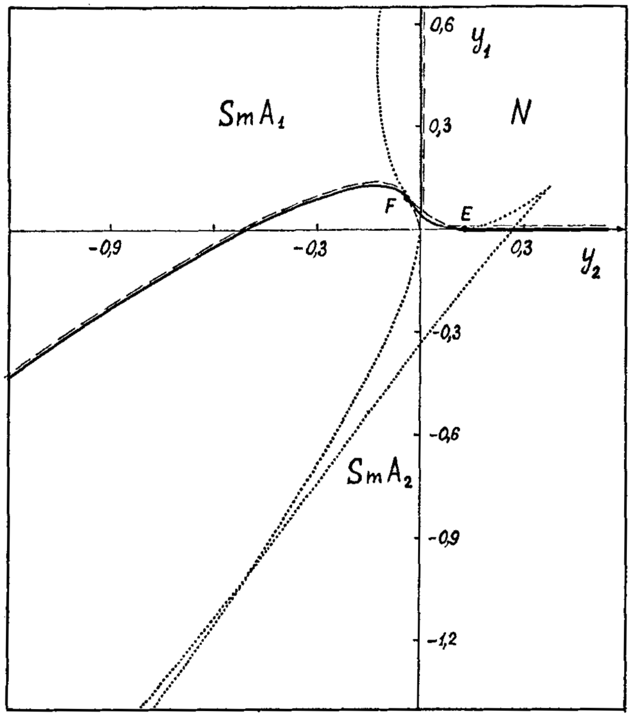

FIGURE 2 Separatrices and phase diagram of the Prost model at the condition $\alpha_1\alpha_2 - \varkappa^2 > 0$ ($\alpha_1 = 2$, $\alpha_2 = \varkappa = w = 1$). Designations are the same as in Figure 1.

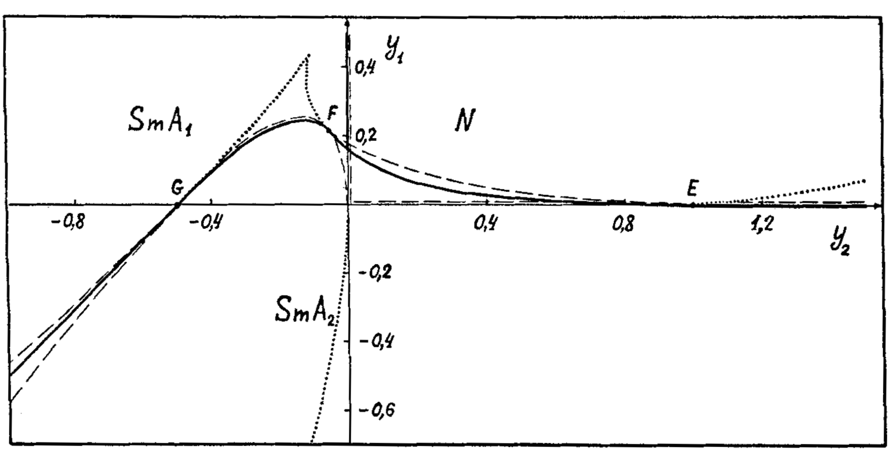

FIGURE 3 Separatrices and phase diagrams of a frustrated liquid crystal in the Prost model at the condition $\alpha_1\alpha_2 - \varkappa^2 < 0$ ($\alpha_1 = \alpha_2 = w = 1$, $\varkappa = 2$). Point E is a tri-critical one on the SmA$_2$-N phase transition line. Points F and G are tri-critical ones on the SmA$_2$-SmA$_1$ phase transition line.

phase transition in the sequence SmA_2-SmA_1-N as a transformation of the first (Figure 4a) or the second order (Figure 4b) are shown in Figure 4. Note that, depending on choice of the thermodynamic evolution way, both the standard (corresponding to the monotonous decrease, Figure 4b) and non-standard (corresponding to the monotonous increase, Figure 4a) behavior of translational order parameters can be found. These dependences are always convex relative to phase diagrams

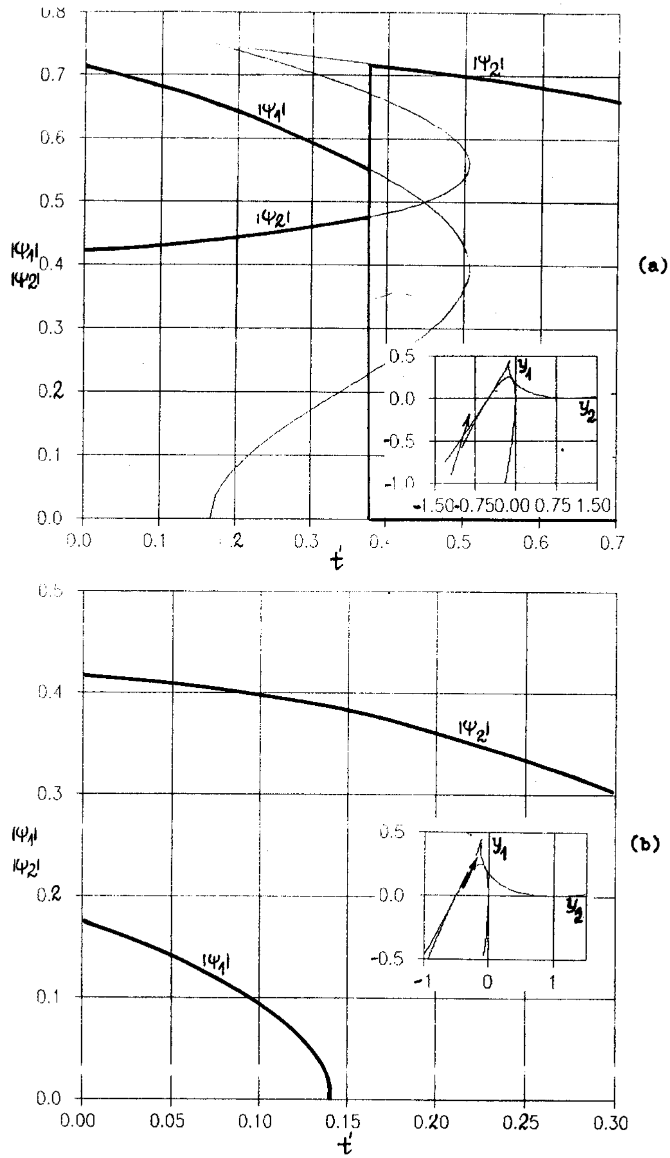

FIGURE 4 Possible types of temperature behavior of translational $|\psi_2|$ and ferroelectric $|\psi_1|$ order parameters of a frustrated liquid crystal in the Prost model at the condition $\alpha_1\alpha_2 - \varkappa^2 < 0$ ($\alpha_1 = \alpha_2 = w = 1, \varkappa = 2$) for evolution trajectories (see arrows in the inserts) whose parametric representations are $y_2 = -1.2 + 0.45t'$, $y_1 = -0.9 + 0.89t'$ (a), $y_2 = -0.4 + 0.71t'$, $y_1 = 0.075 + 0.91t'$ (b).

with two tri-critical points (Figures 1, 2) and they can also be concave as regards phase diagrams with three tri-critical points (Figure 3). And besides, temperature dependences of the antiferroelectric order parameters are monotonously decreasing in all the cases (12)–(14) considered above.

Thus, analysis fulfilled shows that the existence of three tri-critical points on the phase boundary of a frustrated smectic is possible at the condition $\alpha_1\alpha_2 - \varkappa^2 < 0$ only, i.e., at the condition that the interaction of translational and antiferroelectric order parameters are not small. It should be especially emphasized that this possibility exists only when the both terms $2\varkappa|\psi_1|^2|\psi_2|^2$ and $2w|\psi_1|^2|\psi_2|$ describing the coupling between these order parameters in the thermodynamic potential (3) are are essentially non-zero (see formulae (9) in which the coefficient w is at the denominator). Hence, the strengthening of the coupling between order parameters drives to increase of the tendency for frustrated smectic to have not one but two tri-critical points on the phase SmA_2-SmA_1 boundary. One may suppose that such a structure of the phase diagram could be experimentally found in the "concentration—temperatures" plane in mixtures of cyanocompounds whose molecules have large dipole moments responsible for molecular pairing. In particular, such molecules could be the cyanocontaining tri-benzenes carring out extra dipoles collinear to the cyanodipole. This appears to lead to formation of a pronounced polarization wave against the background of center-of-mass smectic density wave and their mutual intensification, i.e. such factors which are especially important from the viewpoint of the theory under consideration.

4. CONCLUSION

The main result of the present paper is prediction of the existence of the three tri-critical points in the frustrated smectic phase diagram including nematic, smectic A_1 and A_2 states. Note that this is possibly only when both of the non-linear terms $2w|\psi_1|^2|\psi_2|$ and $2\varkappa|\psi_1|^2|\psi_2|^2$ present in the potential (3) and the condition (14) is valid. Besides, two tri-critical points may be realized when even $w = 0$, $\varkappa \neq 0$.

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