Phenomenological description of a Devil's staircase

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A phenomenological approach is used to discuss the successive phases of a crystal corresponding to various values of the wave vector for normal coordinates belonging to one optical branch of the crystal's phonon spectrum. A phase diagram is constructed in terms of the variables which determine the minimum of the branch. The effect of an external excitation on the diagram is clarified. A comparison is made with experiment for a specific crystal.

INTRODUCTION

In 1964, Dzyaloshinskii[1] noted that a system with a structure characterized by a wave vector q has a thermodynamic potential Φ which is not a smooth function of q: in fact, $\Phi(q)$ is discontinuous for any value of q (more precisely), the value of Φ at any point in q-space with rational coordinates differs by a finite but usually very small amount from its value at a point arbitrarily close to it which also has rational coordinates). Therefore, when such a crystal has an incommensurate phase, the variation with temperature T of the structural period of this phase is discontinuous. Although the discontinuities are negligibly small near the point T_0 of transition from the original phase to the incommensurate phase, they can attain considerable values at temperatures far from T_0.

A structure which behaves in this way is said to exhibit a "Devil's staircase." Structures of this type have been investigated repeatedly in the context of microscopic models (see the review Ref. 2 and the literature cited therein); however, the goal of this work is to carry out such an investigation by means of a phenomenological approach. In particular, this approach, which is in the spirit of Landau's theory, allows us to interpret a variety of experiments on structural phase transitions in certain crystals which exhibit a complicated succession of phases with the participation of an incommensurate phase.

ENERGY OF THE NORMAL OSCILLATIONS OF A CRYSTAL

For definiteness, we will discuss structural phase transitions of displacement type. We will consider one optical branch of the normal oscillations of the crystal, and for simplicity we restrict ourselves to one direction of the wave vector $q_z \equiv q$, assuming that this branch is doubly degenerate, i.e., the normal oscillations with q and $-q$ have the same frequency. Let us compare the energy of the normal oscillations belonging to this branch at various points of the Brillouin zone. The elastic energy has the form $a\rho^2$, where ρ is the amplitude of the normal oscillations: $\eta = \rho\cos\varphi$, $\xi = \rho\sin\varphi$. The (doubled) elastic coefficient α is a continuous function of q. Usually this function $\alpha(q)$ is represented in terms of a branch of the normal oscillations of the crystal: $\alpha \propto \omega^2$; here ω is the eigenfrequency, i.e., the frequency of oscillation when attenuation is neglected. The crystal is understood to be infinite, i.e., q takes on a continuous sequence of values from $-1/2$ to $1/2$ (q is conveniently measured in units of $c^* = 2\pi/c$, where c is the period of the crystal along the z axis). Furthermore, the coefficients of the anharmonic terms in the energy, which are proportional to higher powers of ρ^2, e.g., the term $\beta\rho^4$, are also continuous functions of q. However, along with these terms there also exist anharmonic terms of the form $\alpha_l'\rho^{2l}\cos 2l\varphi$ (or $\alpha_l'\rho^l\cos l\varphi$; here we will discuss only the first case) which differ from zero only at certain points of the Brillouin zone: those with rational values of $q = q_l \equiv m/l$, where m and l are integers. In other words, the coefficient α_l', as well as the coefficients of higher-order terms in ρ of the form $\beta_l'\rho^{2l+2}\cos 2l\varphi, \beta_l''\rho^{4l}\cos^2 2l\varphi$, etc., are nonzero only at discrete values $q = q_l$.

Let us discuss a specific portion of the Brillouin zone, e.g., from $q_3 = 1/3$ to $q_2 = 1/2$ (see Fig. 1), and expand the coefficient α in a power series in $(q-b)$, where b is the coordinate of the soft mode responsible for the minimum of the branch $\alpha(q)$:

$$\alpha = a + \delta(q-b)^2. \tag{1}$$

In fact, this implies that the soft optical branch is approximated in the neighborhood of its minimum by a parabola; obviously, this approximation becomes more precise as the portion of the Brillouin zone we choose to study becomes narrower. In principle, the expansion (1) can also be used for the entire branch as long as the branch has no fixed maximum (extremum) at any point of the Brillouin zone, i.e., there exists a Lifshits invariant for η, ξ at any point. This condition is fulfilled for those branches whose coordinates η, ξ at the center of the Brillouin zone (i.e., for $q = 0$) transform as two-dimensional representations of the point groups D_6, D_4, D_2, when q is directed along the z axis (x, y transform as two-dimensional representations of these groups) The presence of a fixed maximum at one of the limits of the chosen interval of values of q requires a somewhat altered approach, which will not be discussed here. We will assume that the remaining coefficients β, α_l' and others do not de-

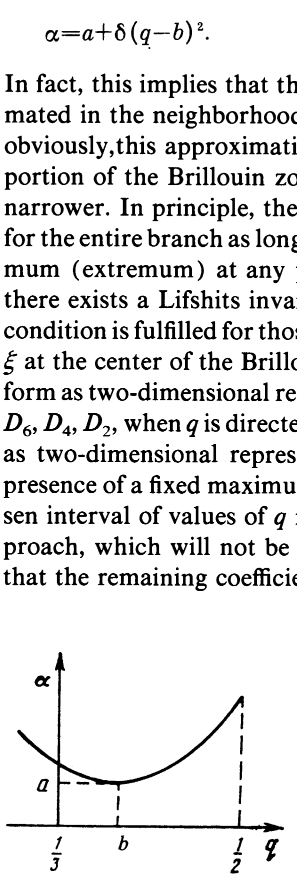

FIG. 1. A segment of an optical branch of the normal-mode spectrum of the crystal. Along the axes; q is the wave vector along the z-axis in units of $c^* = 2\pi/c$, α is the elasticity coefficient (4); a,b are the coordinates of the soft mode corresponding to the minimum of the branch.

pend on q. This implies, in particular, that α_l' is the same for $q_l = m/l$ with the same l and different m within the interval of q values under discussion.

THERMODYNAMIC POTENTIAL

As we are interested in the possible transitions from the original phase of the crystal, we will write down the thermodynamic potentials for various values of q and compare them. If q has the rational value $q_l = m/l$, then according to (1) the coefficient α acquires the value

$$\alpha_l = a + \delta(q_l - b)^2, \tag{2}$$

and the thermodynamic potential can be written in the form

$$\Phi_l = \alpha_l\rho^2 + \beta\rho^4 - \alpha_l'\rho^{2l}\cos 2l\varphi. \tag{3}$$

Here we have included the two isotropic invariants and the single anisotropic, i.e., φ-dependent, invariant which are lowest order in ρ. We may limit ourselves to these invariants if the coefficient satisfies $\beta > 0$ and is not too small, and if we neglect the possibility that along with the commensurate phases C_{l1}, C_{l2} for which $\sin 2l\varphi = 0$ there also can occur a phase C_{l3} for which $\sin 2l\varphi \neq 0$ (see Ref. 3). It is obvious that the potential (3) describes a transition to a commensurate phase (C_l) which is characterized by wave vectors q_l.

If l is large, or $l \to \infty$ (irrational values of q), then

$$\Phi = \alpha\rho^2 + \beta\rho^4, \tag{4}$$

where α is taken from (1). This potential describes the transition to an incommensurate (I) phase; on the basis of what we said earlier, we will understand this term to include not only phases with irrational values of q but also phases with values of $q_l = m/l$ for which l is sufficiently large.

EQUILIBRIUM VALUES OF THE THERMODYNAMIC POTENTIAL

It is obvious from (1) that the minimum of $\Phi(4)$ is realized for $q = b$; consequently, by varying Φ with respect to ρ, we obtain

$$\rho^2 = -a/2\beta, \quad \Phi = -a^2/4\beta. \tag{5}$$

The phase transition from the original (C_0) phase to the I phase comes about for $a = 0$.

We will seek a minimum of Φ_l given by (3), (2) in the weak-anisotropy approximation (see Ref. 4), i.e., when the anisotropic invariant in (3) is small compared to the isotropic one $\beta\rho^4$. This reduces to the condition

$$\varepsilon_l = \frac{|\alpha_l'|\rho_c^{2l}}{2\beta\rho_c^4} = \frac{|\alpha_l'|}{2\beta}\left(-\frac{\alpha_c}{2\beta}\right)^{l-2}$$
$$= -\frac{\alpha_0}{\alpha_c} = \frac{\alpha_0}{2\beta}\left(\frac{|\alpha_l'|}{\alpha_0}\right)^{1/(l-1)} \ll 1, \tag{6}$$
$$\alpha_0 = \delta(q_l - b)^2, \quad \alpha_c = -2\beta\left(\frac{\alpha_0}{|\alpha_l'|}\right)^{1/(l-1)},$$
$$\rho_c^2 = -\frac{\alpha_c}{2\beta}.$$

Here α_0 is the value of α_l at the C_0–I phase transition point, determined from (2) by setting $a = 0$; α_c is the value of α_l at the I–C_l phase transition point determined from (9); and ρ_c is the value of ρ when $\alpha = \alpha_c$.

Varying Φ_l with respect to φ as in (3), we obtain

$$C_{l1},\ C_{l2}\text{:}\quad \sin 2l\varphi = 0, \quad \cos 2l\varphi = \pm 1, \tag{7}$$

which corresponds to two C_l-phases: C_{l1}, which is stable for $\alpha_l' > 0$, and C_{l2}, which is stable for $\alpha_l' < 0$. Varying Φ_l in (3) with respect to ρ in the weak-anisotropy approximation, i.e., when condition (6) holds, we obtain

$$\rho^2 = -\frac{\alpha_l}{2\beta}, \quad \Phi_l = -\frac{\alpha_l^2}{4\beta}\left[1 - 2\frac{|\alpha_l'|}{\alpha_l}\left(-\frac{\alpha_l}{2\beta}\right)^{l-1}\right]. \tag{8}$$

BOUNDARY BETWEEN DIFFERENT PHASES

Setting the potentials (5) and (8) equal to each other, we find the following equation for the boundary between the I and C_l phases:

$$-\delta(q_l - b)^2 + |\alpha_l'|(-\alpha_l/2\beta)^{l-1} = 0. \tag{9}$$

Setting the potentials (8) equal for the two different commensurate phases C_l and C_L, corresponding to q_l and q_L, we find the following equation for the boundary between these two phases:

$$-\delta(q_l - b)^2 + |\alpha_l'|(-\alpha_l/2\beta)^{l-1}$$
$$= -\delta(q_L - b)^2 + |\alpha_L'|(-\alpha_L/2\beta)^{L-1}. \tag{10}$$

In deriving (9) and (10), we have used condition (6), i.e., the condition of weak anisotropy. In this approximation we must replace α_l and α_L in (9) and (10) with a, i.e., we will neglect $\delta(q_l - b)$ compared to a. Actually, it is clear from (9) and (6) that $\delta(q_l - b)^2/a \sim \varepsilon_l$, and consequently the ratio is small; this estimate is especially good in the case of (10).

PHASE DIAGRAM

In Fig. 2 we show the phase diagram in the ab-plane (see Fig. 1). The remaining quantities δ, β, α_l' are assumed fixed. We choose the dimensionless variables X, Y_l:

$$X = \frac{b - q_3}{Q}, \quad Y_l = -\frac{a}{\delta Q^2}\varepsilon_l,$$

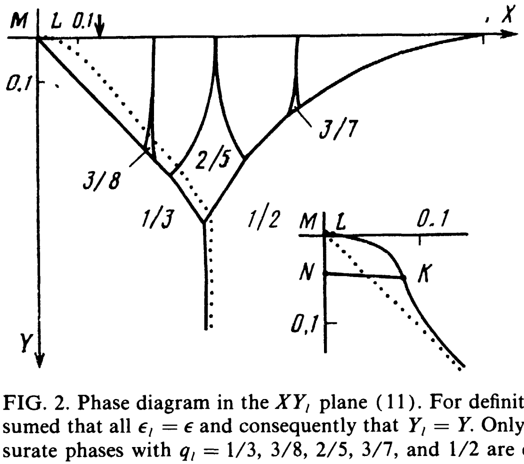

FIG. 2. Phase diagram in the XY_l plane (11). For definiteness, it is assumed that all $\epsilon_l = \epsilon$ and consequently that $Y_l = Y$. Only the commensurate phases with $q_l = 1/3$, 3/8, 2/5, 3/7, and 1/2 are discussed. We show the boundary for the phases $l = 3$ for $E_1 \neq 0$ with a dotted line. The inset shows a segment of the diagram with $E_2 \neq 0$ (for details see text).

$$\epsilon_l = \frac{\delta Q^2}{2\beta}\left(\frac{|\alpha_l'|}{\delta Q^2}\right)^{1/(l-1)} = \varepsilon_l\left(\frac{Q}{q_l-b}\right)^{2(l-2)/(l-1)},$$

$$\Delta_l = \frac{q_l-q_3}{Q}. \qquad (11)$$

In place of ε_l defined in (6) it is convenient to use ϵ_l defined in (11), which in contrast to ε_l does not depend on q. As a characteristic value of Q we can take the width of the interval of values of q under investigation (see Fig. 1): $Q = 1/2 - 1/3 = 1/6$. If Q is not too large, then $\epsilon_l \ll 1$ while ε_l still remains $\ll 1$. Let us note that, generally speaking, the larger l is, the more nearly valid are the conditions $\varepsilon_l \ll 1$ in (6) and $\epsilon_l \ll 1$, since $\alpha_0 = \delta(q_l - b)^2$ is an anomalously small quantity. Actually, for any value of b there is a nearby rational value $q_l = m/l$ with sufficiently small l. For the special value $l = 2$, the parameter α_0 does not enter into the definition of ε_l:$\varepsilon_2 = \alpha_2'/2\beta$; therefore, it is necessary to include the special requirement that the ratio α_2'/β be small in order to fulfil the weak-anisotropy condition used here.

In Fig. 2, we have chosen only the values $q_3 = 1/3$, $q_8 = 3/8$, $q_5 = 2/5$, $q_7 = 4/7$, $q_2 = 1/2$ from the set of all commensurate values of q. All the boundaries between the I phase with the C_l phases were constructed by using Eqs. (9), (10). In the dimensionless variables X, Y_l of (11), which were used in Fig. 2, these equations have the corresponding form

$$-(\Delta_l-X)^2+Y_l^{l-1}=0, \qquad (9')$$

$$-(\Delta_l-X)^2+Y_l^{l-1}=-(\Delta_L-X)^2+Y_L^{L-1}. \qquad (10')$$

For definiteness we have assumed that the ϵ_l are the same for different l and, consequently, $Y_l = Y$. It is clear from Fig. 2 that the regions in which the C_l-phases with $l = 8$ and $l = 7$ exist are very narrow. The regions of existence of C_l-phases with still larger l (even if we assume that all the ϵ_l are the same) are so narrow that they would appear on Fig. 2 as simple vertical lines. These lines would have to be drawn for any rational q_l, which obviously is impracticable on the scales of Fig. 2. We should also recall that fluctuations can wash out the small discontinuities.

Let us emphasize that the phase diagram shown in Fig. 2 is very sensitive to the choice of values of the ϵ_l. This is connected with the fact that higher powers of ϵ_l enter into Eqs. (9), (10) for the boundaries between the phases ($\epsilon_l^{l-1} \propto \alpha_l'$). Thus, e.g., if ϵ_7 increases by only a factor of two, the region in which the C_l-phase with $l = 7$ exists in Fig. 2 is broadened so much that for $Y > 1/2$ it will occupy all the interval of X values from 0 to 1, i.e., b from 1/3 to 1/2. This happens because the boundary between the C_l-phases with $l = 3$ and $l = 7$ moves sharply to the left as Y increases, while the boundary between the C_l-phases with $l = 7$ and $l = 2$ moves sharply to the right.

We note that since a and b are functions of temperature T, pressure p, and composition x of the crystal, a phase diagram similar to the one shown in Fig. 2 can be constructed using these other variables, e.g., T and p.

SINGLE-HARMONIC APPROXIMATION

In writing down the thermodynamic potentials (3), (4), we tacitly assumed that only one harmonic of q (or q_l) is present, thereby neglecting the higher harmonics nq (or nq_l). From this it is clear that we have in fact used a single-harmonic approximation.For the case of weak anisotropy, we also can obtain an analytic solution which includes higher harmonics of the order parameter in the I-phase by expressing it in terms of elliptic functions (see Ref. 4).This solution will differ significantly from the single-harmonic case in the immediate vicinity of the I–C_l phase diagram.^{1} This difference is most apparent in the character of the transition itself: it will be a continuous (i.e., lock-in) transition, in contrast to the usual first-order transition in the single-harmonic approximation. The difference also manifests itself in the anomalous thermodynamic quantities, e.g., certain susceptibilities will diverge at the lock-in transition point, in contrast to the absence of significant anomalies in the single-harmonic approximation (see Ref. 4). However, this difference is not apparent in the phase diagram shown in Fig. 2. Thus, the value $-\alpha_c$ will be larger by a factor of $(\pi^2/8)^{1/(l-1)}$ than that predicted in Eq. (6); however, this factor differs little from 1. The difference is the phase diagrams remains insignificant even when external forces act on the crystal.

THE INFLUENCE OF EXTERNAL FORCES

Let us discuss the influence of external forces on the crystal. These forces could be the components of the electric field intensity vector E_α or the mechanical stress tensor $\sigma_{\alpha\beta}$ (and also the magnetic field intensity vector H_α if we are interested in the magnetic structure and corresponding phase transitions). The forces of fundamental interest are those which enter linearly into the potential. Let us now write the thermodynamic potential (3) in the form

$$\Phi_l=\alpha\rho^2+\beta\rho^4-\alpha_l'\rho^{2l}\cos 2l\varphi+a_1E_1\rho^l\cos l\varphi$$
$$+a_2E_2\rho^l\sin l\varphi-E_1^2/2\varkappa_1-E_2^2/2\varkappa_2, \qquad (12)$$

where E_1 and E_2 are external forces which transform according to the point symmetry group of the original phase of the crystal. E_3 also enters into (12) linearly, in the form $a_3E_3\rho^{2l}\sin 2l\varphi$; however, the effect of E_3 is of little interest and therefore will not be discussed here. The generalized coordinates P_1 and P_2 corresponding to the generalized forces E_1 and E_2 are determined from (12) by using the relations ($P_{1,2} = -\partial\Phi/\partial E_{1,2}$). If $E_{1,2}$ are the components of E_α and $\sigma_{\alpha\beta}$, then $P_{1,2}$ are the corresponding components of the polarization vector P_α or the strain tensor $U_{\alpha\beta}$.

The coefficients $\varkappa_1$, $\varkappa_2$ are continuous functions of q, just as α, β are. The coefficients a_1, a_2, like α_l', have nonzero values only for the discrete values $q = q_l = m/l$. For the potential under discussion here, there will be three different values of $E_{1,2}$, $P_{1,2}$; for l odd and m odd, for l odd and m even, and for l even and m odd. In other words, for these three cases E_1, P_1 and E_2, P_2 transform according to different irreducible representations of the symmetry groups of the original crystal phase. Strictly speaking, E_1, E_2, a_1, a_2 ought to be furnished with indices l and m; this is not done in order to avoid overly-awkward expressions. Only those terms in (12) which are quadratic in $E_{1,2}$ should be included in the thermodynamic potential (4).

We will be interested in the effect of external forces E_1 and E_2 on the phase diagram shown in Fig. 2. For a given l, depending on the sign of the coefficient α_l' the commensurate C_{l1} or C_{l2} phase is realized in Fig. 2, if $\alpha_l' > 0$, then we can refer to the external force E_1 as the "native field", since the quantity P_1 conjugate to E_1 has spontaneous values when the phase C_{l1} is realized. The external force E_2 we may refer to as the "foreign field", since it is conjugate to the quantity P_2 which has spontaneous values in the phase C_{2l}, and which is not realized for $\alpha_l' > 0$. If $\alpha_l' < 0$, then all these statements should be reversed.

EFFECT OF E_1 ON THE PHASE DIAGRAM

For definiteness, we will assume that $\alpha_l' > 0$ and discuss the influence of its field E_1, setting $E_2 = 0$. Varying Φ given by (12) with respect to φ, we obtain

$$\begin{gathered} C_{l1}:\ \sin l\varphi=0,\quad \cos l\varphi=-a_1E_1/|a_1E_1|,\\ \Phi_l=\alpha_l\rho^2+\beta\rho^4-\alpha_l'\rho^{2l}-|a_1E_1|\rho^l-E_1^2/2\varkappa_1,\\ C_{l2}:\ \cos l\varphi=a_1E_1/4\alpha_l'\rho^l,\\ \Phi_l=\alpha_l\rho^2+\beta\rho^4+\alpha_l'\rho^{2l}+(a_1E_1)^2/8\alpha_l'-E_1^2/2\varkappa_1, \end{gathered} \tag{13}$$

which corresponds to the same equation (7) for the C_l phases with $E_1 = 0$.

We will seek the equilibrium values of Φ_l in (13) assuming that the anisotropy induced by the external force is weak, i.e., where the anisotropic term, which is $\sim a_1E_1\rho^l$ in (12), is small compared to the isotropic term $\beta\rho^4$ [compare (6)]:

$$\begin{gathered} \varepsilon_{El}=\frac{|a_1E_1|\rho_{c1}{}^l}{2\beta\rho_{c1}{}^4}=\frac{|a_1E_1|}{2\beta}\left(-\frac{\alpha_{c1}}{2\beta}\right)^{(l-4)/2}\\ =-\frac{\alpha_0}{\alpha_{c1}}=\frac{\alpha_0}{2\beta}\left(\frac{a_1E_1}{\alpha_0}\right)^{2/(l-2)}\ll 1,\\ \alpha_0=\delta(q_l-b)^2,\\ \alpha_{c1}=-2\beta(\alpha_0/a_1E_1)^{2/(l-2)},\\ \rho_{c1}{}^2=-\alpha_{c1}/2\beta. \end{gathered} \tag{14}$$

Here $\alpha_0, \alpha_{c1}, \rho_{c1}$ are values determined in the same way as in (6), but under the condition $\alpha_l' \equiv 0$. The case $l = 2$ is omitted from this discussion.

Varying Φ_l (13) with respect to ρ, in the weak-anisotropy approximation, i.e., under the conditions (6) and (14), we obtain

$$\begin{aligned} C_{l1}:\ \rho^2=-\frac{\alpha_l}{2\beta},\quad \Phi_l=-\frac{\alpha_l^2}{4\beta}\biggl[1-2\frac{\alpha_l'}{\alpha_l}\left(-\frac{\alpha_l}{2\beta}\right)^{l-1}\\ -2\frac{|a_1E_1|}{\alpha_l}\left(-\frac{\alpha_l}{2\beta}\right)^{(l-2)/2}\biggr]-\frac{E_1^2}{2\varkappa_1}. \end{aligned} \tag{15}$$

The phase C_{l2} is stable only for values of $\alpha_l' < 0$.

Setting the potential (15) equal to the potential of the I phase, where now we should add the term $-E_1^2/2\varkappa$, we obtain for the boundary between the C_{l1} and I phases

$$-\delta(q_l-b)^2+\alpha_l'(-\alpha_l/2\beta)^{l-1}+|a_1E_1|(-\alpha_l/2\beta)^{(l-2)/2}=0. \tag{16}$$

For those $q_l = m/l$ for which the field E_1 does not enter into the potential, Eq. (9) remains applicable.

For the boundary between the C_l phase ($a_1 \neq 0$) and the C_L phase ($a_1 = 0$) we obtain correspondingly the equation [compare (10)]

$$\begin{aligned} -\delta(q_l-b)^2+\alpha_l'(-\alpha_l/2\beta)^{l-1}+|a_1E_1|(-\alpha_l/2\beta)^{(l-2)/2}\\ =-\delta(q_L-b)^2+|\alpha_L'|(-\alpha_L/2\beta)^{L-1}. \end{aligned} \tag{17}$$

In (16), (17), just as in (9) and (10), we can replace α_l and α_L by a, neglecting $\delta(q_l - b)^2$ compared to a.

In the dimensional variables (11), equations (16), (17) takes the following form

$$\begin{gathered} -(\Delta_l-X)^2+Y_l^{l-1}+\varkappa_lY_l^{(l-2)/2}=0,\\ -(\Delta_l-X)^2+Y_l^{l-1}+\varkappa_lY_l^{(l-2)/2}=-(\Delta_L-X)^2+Y_L^{L-1},\\ \epsilon_{El}=\frac{\delta Q^2}{2\beta}\left(\frac{a_1E_1}{\delta Q^2}\right)^{2/(l-2)},\\ \varkappa_l=\left(\frac{\epsilon_{El}}{\epsilon_l}\right)^{(l-2)/2}=\frac{|a_1E_1|}{\delta Q^2}\left(\frac{\delta Q^2}{|\alpha_l'|}\right)^{(l-2)/2(l-1)}. \end{gathered} \tag{18}$$

Here we have introduced ϵ_{El}, which in contrast to ε_{El} (14) does not depend on q_l [compare ε_l (6) and ϵ_l (11)], and also $\varkappa_l$, which is convenient for abbreviating the written expressions.

In Fig. 2 a dotted curve is used to represent the boundaries (18) for $q_l = 1/3$, and $q_L = 3/8$, $2/5$, $1/2$, i.e., under the condition that E_1 corresponds to off l and odd m. The effect of E_1 on the boundary of the C_{l1} phase for $q_l = 3/7$ is extremely weak, and the corrections are so small that on the scale of Fig. 2 it is difficult to show them. The value $\varkappa_3 = 0.04$ was taken in Fig. 2 (for the reason this value was chosen; see below for the field E_2).

The distinctive feature of the diagram in Fig. 2 is the appearance of a boundary of first-order phase transitions in the presence of the field E_1 (due to the term $\sim E_1\rho^3$ in the potential) between the phases C_0 and C_{l1} (the curve ML in Fig. 2). At the point L three phase transition lines meet: C_0–I ($a = 0$), I–C_3, and C_0–C_3. This last boundary is given by the equation ($l = 3$)

$$\alpha_3=(a_1E_1)^2/4\beta,\quad Y_3=-{}^1/_2\epsilon_3{}^2\varkappa_3{}^2+\epsilon_3X^2, \tag{19}$$

which is reduced to dimensionless variables (11) as were the equations for the other boundaries. In deriving (19), the field E_1 is not assumed to be small. The condition for (19) to be applicable is the inequality $\epsilon_3^2\epsilon_{E3} = \epsilon_3^2\varkappa_3^2 \ll 1$, which is well fulfilled under the condition (6). The coordinates of the points M and L are determined from the conditions $X = 0$ for M and $Y = 0$ for L, and consequently [see (19)],

$$\begin{gathered} M:\ X=0,\quad Y_3=-{}^1/_2\epsilon_3\epsilon_{E3}=-{}^1/_2\epsilon_3{}^2\varkappa_3{}^2,\\ L:\ X=({}^1/_2\epsilon_{E3})^{1/2}=({}^1/_2\epsilon_3)^{1/2}\varkappa_3,\quad Y_3=0. \end{gathered} \tag{20}$$

We note that Eq. (16) is inapplicable in the vicinity of the L point, since the anisotropy induced by the field E_1 here is not small, so only the condition (6) can be used; however, the corresponding equation is so involved that there is no advantage to presenting it here.

EFFECT OF E_2 ON THE PHASE DIAGRAM

Let us assume, as before, that $\alpha_l' > 0$, and discuss the effect of the "foreign" field E_2 setting $E_1 = 0$. The effect of this field will be qualitatively different from the effect of the "native" field E_1, and a new phase C_{l2} appears on the phase diagram of Fig. 2 (see the inset).

Varying Φ_l, (12) with respect to φ, we obtain

$$C_{l1}:\ \sin l\varphi=-a_2E_2/4\alpha_l'\rho^l,$$

$$\Phi_l=\alpha_l\rho^2+\beta\rho^4-\alpha_l'\rho^{2l}-(a_2E_2)^2/8\alpha_l'-E_2^2/2\varkappa_2, \tag{21}$$

$$C_{l2}:\ \cos l\varphi=0,$$

$$\sin l\varphi=-a_2E_2/|a_2E_2|,$$

$$\Phi_l=\alpha_l\rho^2+\beta\rho^4+\alpha_l'\rho^{2l}-|a_2E_2|\rho^l-E_2^2/2\varkappa_2.$$

Note that (21) is obtained from (13) if we interchange $\alpha_l'\leftrightarrow-\alpha_l'$,$\sin l\varphi\leftrightarrow\cos l\varphi$, $1\leftrightarrow2$, as we should expect from the form of the potential (12).

Varying Φ_l, given by (21), with respect to ρ in the weak-anisotropy approximation with $\epsilon_l\ll1$ [Eq. (11)] and $\epsilon_{El}\ll1$ [Eq. (18)], where it is necessary to exchange a_1E_1 and a_2E_2 just as in (14) for ε_{El}, we obtain

$$\begin{aligned}
C_{l1}:\ \rho^2&=-\frac{\alpha_l}{2\beta},\quad \Phi_l=-\frac{\alpha_l^2}{4\beta}\left[1-2\frac{\alpha_l'}{\alpha_l}\left(-\frac{\alpha_l}{2\beta}\right)^{l-1}\right.\\
&\left.-2\frac{(a_2E_2)^2}{\alpha_l8\alpha_l'}\left(-\frac{\alpha_l}{2\beta}\right)^{-1}\right]-\frac{E_2^2}{2\varkappa_2},\\
C_{l2}:\ \rho^2&=-\frac{\alpha_l}{2\beta},\quad \Phi_l=-\frac{\alpha_l^2}{4\beta}\left[1+2\frac{\alpha_l'}{\alpha_l}\left(-\frac{\alpha_l}{2\beta}\right)^{l-1}\right.\\
&\left.-2\frac{|a_2E_2|}{\alpha_l}\left(-\frac{\alpha_l}{2\beta}\right)^{(l-2)/2}\right]-\frac{E_2^2}{2\varkappa_2}\ .
\end{aligned} \tag{22}$$

It is obvious that with the same replacement $\alpha_l'\leftrightarrow-\alpha_l'$,$1\leftrightarrow2$, the second expression (22) is transformed into (15).

Setting the potential (22) for the C_{l1} phase equal to the potential I-phase, we obtain the equation

$$\begin{gathered}
-\delta(q_l-b)^2+\alpha_l'(-a/2\beta)^{l-1}+{}^1/_8(a_2E_2)^2(-a/2\beta)^{-1}=0,\\
-(\Delta_l-X)^2+Y_l^{l-1}+{}^1/_8\varkappa_l^2Y_l^{-1}=0.
\end{gathered} \tag{23}$$

Setting the potentials (22) for the C_{l1} phase the C_L phase ($a_2=0$) equal, we obtain the equation

$$\begin{gathered}
-\delta(q_l-b)^2+\alpha_l'(-a/2\beta)^{l-1}+{}^1/_8(a_2E_2)^2(-a/2\beta)^{-1}\\
=-\delta(q_L-b)^2+|\alpha_L'|(-a/2\beta)^{L-1},\\
-(\Delta_l-X)^2+Y_l^{l-1}+{}^1/_8\varkappa_l^2Y_l^{-1}=-(\Delta_L-X)^2+Y_L^{L-1}.
\end{gathered} \tag{24}$$

Setting the potentials (21) for the C_{l2} phase equal to the potential of the C_{l1} phase, we obtain the equation (the line NK in Fig. 2)

$$\begin{gathered}
-\alpha_l=2\beta(a_2E_2/4\alpha_l')^{2/l},\\
Y_l=(\varkappa_l/4)^{2/l}+\epsilon_l(\Delta_l-X)^2.
\end{gathered} \tag{25}$$

Setting the potential (22) for the C_{l2} phase equal to the potential for the I phase, we obtain the equation (the line LK in Fig. 2)

$$\begin{gathered}
-\delta(q_l-b)^2+\alpha_l'(-a/2\beta)^{l-1}-|a_2E_2|(-a/2\beta)^{(l-2)/2}=0.\\
-(\Delta_l-X)^2+Y_l^{l-1}-\varkappa_lY_l^{(l-2)/2}=0.
\end{gathered} \tag{26}$$

This equation is inapplicable in the vicinity of the point L, where the field E_2 cannot be assumed to be small. The corresponding expressions for the line LK are complicated and therefore will not be presented here.

The line ML in Fig. 2 is determined by Eq. (19), in which we must replace a_1E_1 by a_2E_2. Analogously, the coordinates of the points M and L are also determined by using Eq. (20). The coordinates of the points N and K are

$$\begin{gathered}
N:\quad X=0,\quad Y=(\varkappa_3/4)^{2/3},\\
K:\quad X=3^{1/2}(\varkappa_3/4)^{2/3},\\
Y=(\varkappa_3/4)^{2/3}+3\epsilon_3(\varkappa_3/4)^{4/3}.
\end{gathered} \tag{27}$$

The point K lies at the intersection of three lines, and its coordinates (27) satisfy all three equations (23), (25), and (26) for $l=3$ to within the neglected terms in ϵ_3.

In the inset the value $\varkappa_3=0.04$ is assumed, just as in Fig. 2 itself. For this value of $\varkappa_3$ the field E_2 is more than twice as small as the critical field at which the point K is reached for the crystal K_2SeO_4. For K_2SeO_4 we have $b=1/3-\Delta$, where $\Delta=0.07/3$ (Ref. 5); the corresponding point is marked in Fig. 2 with an arrow (obviously we must locate this point to the left of the coordinate origin $b=1/3$; however, Fig. 2 is almost mirror-symmetric with respect to this origin in its vicinity). We further note that for K_2SeO_4 we have $\varepsilon_3=0.02$, $\epsilon_3=1/7$.

COMPARISON WITH EXPERIMENT

As we have already noted, there exist many crystals in which a succession of several phase transitions is observed with the participation of an incommensurate phase. We will discuss only one example—that of crystals denoted by the chemical formula $[N(CH_3)_4]MCl_4$, i.e., metallic tetramethylammonium tetrachlorides, where the metal M can be Zn, Co, Fe, Mn, etc., and H can be replaced by D (see, e.g., the review Ref. 6). For such compounds the T,p phase diagrams have been obtained experimentally, and a universal, i.e., reduced diagram has been constructed.[6,7] This diagram is in qualitative agreement with the diagram show in Fig. 2, with commensurate phase corresponding to $q_l=1/3$, 2/5, 3/7, 1/2 chosen from the interval of values of q_l discussed above. By choosing specific values of ϵ_l and the simplest, linear, dependence of a and b on T and p, qualitative agreement between the experimental and theoretical diagrams can be achieved; however, this requires a special discussion which is unnecessary here. Instead, we present only the results of a group-theoretic discussion.

According to the experimental data, the symmetric space groups which are observed on the universal phase diagram[6] are the following. The original phase is D_{2h}^{16}. If we pick the x,y,z coordinate system used in the majority of experimental papers, the symmetry group in international notation is $Pmcn$. The incommensurability axis is the z-axis. The commensurate phases are: $P112_1/n$ (C_{2h}^5) with $q_l=1/3$; $P2_12_12_1$ (D_2^4) with $q_l=3/7$; $P2_1cn$ (C_{2v}^9) with $q_l=2/5$; and $P2_1/c11$ (C_{2h}^5) with $q_l=1/2$. The commensurate phase with $q_l=0$ has the symmetry group $P12_1/c1$(C_{2h}^5). A transition occurs to a phase with this symmetry from the original phase $Pmcn$ according to the representation B_{2g} of the point group D_{2h}. Therefore, we will discuss that branch of the normal modes of the crystal which includes a mode which transforms according to the representation B_{2g} at the center of the Brillouin zone. Let us construct the irreducible representations with the star $\pm q_z$ for the normal coordinates of this branch in the original phase *Pmcn* of the crystal. The two-dimensional representation and the thermodynamic potential corresponding to it have the form (12). For $q_l = m/l$ with odd l and m (the values taken from the interval between 1/3 and 1/2 under discussion are $q_l = 1/3$, 3/7, and also 5/11, 5/13, 7/15, etc.), E_1 and E_2 transform according to the representations $A_u\,(xyz)$ and $B_{1g}\,(xy)$ of the point group D_{2h} respectively, where we indicate in brackets the components of the tensors of lowest rank which transform according to these representations. For q_l with odd l and even m ($q_l = 2/5$, and also 4/9, 4/11, 6/13, etc.), E_1 and E_2 transform according to the representations $B_{2g}\,(xy)$ and $B_{3u}\,(x)$, respectively. For q_l with even l and odd m ($q_l = 3/8$, 1/2), and also 5/12, 5/14, 7/16, etc., E_1 and E_2 transform according to the representations $B_{2u}\,(y)$ and $B_{3g}\,(yz)$ respectively. Note that in all cases E_3 transforms according to the representation $B_{1u}\,(z)$.

The symmetry groups of the commensurate phases are given as follows: C_1: $P2_12_12_1$ (D_2^4), C_2: $P112_1/n$ (C_{2h}^5) for l and m odd; C_1: $P12_1/c1$ (C_{2h}^5), C_2: $P2_1cn$ (C_{2v}^9) for l odd, m even; C_1: $Pc2_1n$ (C_{2v}^9), C_2: $P2_1/c11$ (C_{2h}^5) for l even, m odd. From a comparison with the experimental symmetry groups of the commensurate phases it follows that the coefficients α_l^1 must be <0 for $l = 3,5,2$ and >0 for $l = 7$. Let us note the symmetry groups of the C_3 phase in the three cases under discussion are respectively $P112_1/n$ ($C_2{}^2$), $P1c1$ ($C_5{}^2$), and $Pc11$ ($C_5{}^2$); not one of these has been seen in experiment.

There is still another phase on the experimental phase diagram with $q_l = 1/3$, whose symmetry group $P2_12_12_1$ (D_2^4) corresponds to values of the coefficient $\alpha_3' > 0$, and also the previously mentioned phase with $q_l = 0$. In order to fully describe this diagram it is necessary to include the dependence of the coefficient α_3' on temperature, and also to add to Fig. 2 a discussion of all the values of q_l in the Brillouin zone, which requires, as we noted above, certain modifications of the approach. Let us emphasize one more time the agreement between the theoretical and experimental phase diagram and symmetry groups of the commensurate phases which correspond to one optical branch of the normal mode spectra of crystals of the compounds discussed above.

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