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# Effects of external shear stress on anomalies of physical quantities at phase transitions in ferroelectrics of the $\text{K}_2\text{SeO}_4$ family with incommensurate phase

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**Abstract.** For crystals of the  $\text{K}_2\text{SeO}_4$  family phase diagram on the temperature  $T$ –shear stress  $\sigma_{xz}$  plane is constructed. Analytical expressions for anomalies of physical quantities are calculated and analysed for the phase transitions shown in the phase diagram.

## 1. Introduction

Mechanical shear stress  $\sigma_{xz}$  (with  $x$  and  $z$  the incommensurate and polar axes, respectively) has a substantial effect on the sequence of the initial–incommensurate–commensurate ( $C_0$ – $I$ – $C_1$ ) phase transitions in  $\text{K}_2\text{SeO}_4$  and related crystals [1, 2]. This effect is more fundamental and more interesting than the effect of the electric field  $E_z$ . While  $E_z$  only shifts the temperature of the  $I$ – $C_1$  phase transition,  $\sigma_{xz}$ , for values sufficiently large, leads to a more complex sequence of phase transitions with the participation of one more commensurate phase  $C_2$ . The  $\alpha$ – $\gamma'$  phase diagram was constructed for one value of  $\sigma_{xz}$  [1, 2], where  $\alpha$  and  $\gamma'$  are coefficients of thermodynamic potential (see equation (1)). From the experimental point of view the  $T$ – $\sigma_{xz}$  phase diagram is of interest since it can be obtained directly by taking measurements at different  $T$  and  $\sigma_{xz}$  values for a given crystal. It is also desirable to know how anomalies of physical quantities such as polarisation  $P_z$ , shear strain  $u_{xz}$ , dielectric susceptibility  $\chi = dP_z/dE_z$ , elastic stiffness  $S = du_{xz}/d\sigma_{xz}$  and the specific heat  $C = -Td^2\phi/dT^2$  vary at phase transitions for  $\sigma_{xz}$  acting on a crystal. These questions are addressed in this paper.

Experimental studies of the effect of  $\sigma_{xz}$  on the  $I$ – $C$  phase transition in the ferroelectrics  $\text{K}_2\text{SeO}_4$  and  $\text{Rb}_2\text{ZnCl}_4$  were initiated by Gladkii *et al* [3], although  $\sigma_{xz}$  was comparatively small (up to  $50 \text{ kg cm}^{-2}$ ; see below).

## 2. Thermodynamic potential

The thermodynamic potential  $\phi$  for  $\text{K}_2\text{SeO}_4$  can be represented in the form [4]:

$$\phi = \int \phi(x) dx / \int dx \quad (1)$$

where

$$\phi(x) = \alpha\rho^2 + \beta\rho^4 + \gamma'\rho^6 \cos 6\varphi - \nu/\rho^2 d\varphi/dx + \delta[(d\rho/dx)^2 + \rho^2(d\varphi/dx)^2] \\ + aE_z\rho^3 \sin 3\varphi + b\sigma_{xz}\rho^3 \cos 3\varphi - E_z^2/2\kappa - \sigma_{xz}^2/2c.$$

Here  $\rho$  and  $\varphi$  are amplitude and phase of the two-component order parameter  $\eta = \rho \cos \varphi$ ,  $\xi = \rho \sin \varphi$  describing the symmetry changes of the phase  $C_1(C_{2v}^9)$  and  $C_2(C_{2h}^5)$  with respect to the initial phase  $C_0(D_{2h}^{16})$ . A specific feature of potential (1) is its inclusion of the invariant  $\gamma'\rho^6 \cos 6\varphi$  of degree  $n = 6$ , which is anisotropic in the  $\eta$ ,  $\xi$  space, i.e., dependent on  $\varphi$ . According to this feature we relate crystals to the  $K_2SeO_4$  family.

$P_z$  and  $u_{xz}$  are defined from (1) using the relations  $P_z = -\partial\phi/\partial E_z$ ,  $u_{xz} = -\partial\phi/\partial\sigma_{xz}$  as follows

$$P_z = \int P_z(x) dx / \int dx \quad P_z(x) = E_z/\kappa - a\rho^3 \sin 3\varphi \\ u_{xz} = \int u_{xz}(x) dx / \int dx \quad u_{xz}(x) = \sigma_{xz}/c - b\rho^3 \cos 3\varphi. \quad (2)$$

Two commensurate phases  $C_1$  and  $C_2$ , apart from the initial phase  $C_0$ , correspond to potential (1). The  $C_1$  phase is stable for  $\gamma' > 0$  and has a spontaneous value of  $P_z$ , while the  $C_2$  phase is stable for  $\gamma' < 0$  and has a spontaneous value of  $u_{xz}$  (for  $E_z = 0$ ,  $\sigma_{xz} = 0$ ). In crystals of the  $K_2SeO_4$  family the sequence of phase transitions  $C_0$ -I- $C_1$  (improper ferroelectrics) or  $C_0$ -I- $C_2$  (improper ferroelastics) can be realised [5]. In what follows we consider the case  $\gamma' > 0$  and the effect of  $\sigma_{xz}$  on the sequence of transitions  $C_0$ -I- $C_1$  in ferroelectrics. All the results obtained can also be applied to the case  $\gamma' < 0$  of the effect of  $E_z$  on the sequence of transitions  $C_0$ -I- $C_2$  in ferroelastics. It is only necessary to replace  $E_z \leftrightarrow \sigma_{xz}$ ,  $P_z \leftrightarrow u_{xz}$ ,  $\chi \leftrightarrow S$  in all the formulae below. Indeed, substituting  $\varphi + \pi/6$  for  $\varphi$  in (1) (i.e., changing the origin of the phase  $\varphi$ ) we obtain the replacement  $\sin 3\varphi \leftrightarrow \cos 3\varphi$  and the changing of the sign of  $\gamma'$ , which is equivalent to the transition from one case to another.

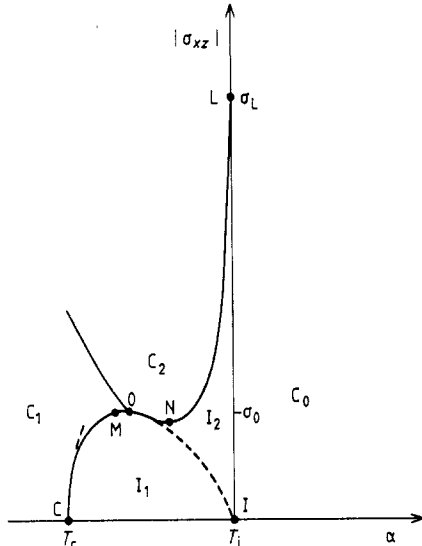
In (1) the inequalities  $\beta > 0$ ,  $\delta > 0$ ,  $\kappa > 0$ ,  $c > 0$  are assumed. Suppose as is usually done that only coefficient  $\alpha$  depends on  $T$ :  $\alpha = \alpha_T(T - \theta)$ . Within this approximation, inclusion of the invariant  $\gamma\rho^6$  in (1) would lead to excessive accuracy since it results in the same corrections as are obtained, for example, by taking into account the dependence of  $\beta$  on  $T - \theta$  or the next term in the expansion of  $\alpha$  in powers of  $T - \theta$ . Note that  $\gamma\rho^6$  should be taken into account for the stability of the crystal at  $\rho \rightarrow \infty$ ; moreover the inequality  $|\gamma'| < \gamma$  should hold, but this requirement is formal and is usually assumed.

### 3. The phase diagram

For convenience we now give the phase diagram corresponding to potential (1) (see figure 1). The following notation is useful

$$\alpha_0 = \frac{\nu^2}{4\delta} \quad q_0 = \frac{|\nu|}{2\delta} \quad \sigma_0 = \left( \frac{8\alpha_0\beta\varepsilon}{b^2} \right)^{1/2} \\ \varepsilon = \left( \frac{\gamma'\alpha_0}{2\beta^2} \right)^{1/2} \quad F = b\sigma_{xz}. \quad (3)$$

When  $\alpha = \alpha_0$  (since  $\alpha_0$  is independent of  $\sigma_{xz}$ ) the  $C_0$ -I second-order phase transition is



**Figure 1.** Phase diagram on the plane  $\alpha = T - \theta, \sigma_{xz}$ .  $C_0$  is the initial phase,  $C_1$  and  $C_2$  are commensurate phases,  $I_1$  and  $I_2$  are two states of the incommensurate phase. Dimensionless variables  $\alpha\varepsilon/\alpha_0$  and  $|\sigma_{xz}|/\sigma_0$  are used. The coordinates of the points in terms of these variables are:  $I(\varepsilon, 0)$ ,  $C(-\pi/2, 0)$ ,  $O(-1, 1)$ ,  $L(\varepsilon, 1/\sqrt{2}\varepsilon)$ . For  $K_2SeO_4$ :  $T_1 = 129$  K,  $T_1 - \theta = 0.6$  K,  $T_c = 93$  K,  $\sigma_0 = 300$  kg cm $^{-2}$ ,  $\sigma_L = 1200$  kg cm $^{-2}$ .

realised. The value of  $\sigma_0$  is chosen in such a way that at point  $O$  (see figure 1)  $|\sigma_{xz}| = \sigma_0$ . The dimensionless parameter  $\varepsilon$  characterises anisotropy in the  $\eta, \xi$  space for crystals with  $n = 6$ . Note that  $\alpha_0 = \delta q_0^2$ , where  $q_0$  is the wavevector of the  $I$  structure for  $T = T_1$ . Since  $q_0$  is always small, i.e.,  $q_0 \ll a^*$ , the reciprocal lattice vector  $[6]$ ,  $\alpha_0$  is also small. Hence the parameter  $\varepsilon \approx \alpha_0^{1/2}$  is small (for usual values of  $\gamma'$  and  $\beta$ ). Subsequently all small quantities will be expressed through  $\varepsilon$ .

The phase diagram in dimensionless variables  $\alpha\varepsilon/\alpha_0$  and  $|\sigma_{xz}|/\sigma_0$  is universal, i.e., it can be applied to any crystal with  $n = 6$ . Using numerical estimates of the thermodynamic potential coefficients [4, 2] the numerical values of  $T$  and  $\sigma_{xz}$  (see figure 1) for  $K_2SeO_4$  can be represented on the abscissa and ordinate, respectively. We give estimates of  $\sigma_0$  and  $\sigma_L$  for  $K_2SeO_4$ :

$$\sigma_0 = \frac{4}{\pi} (T_c - \theta) \left( \frac{\gamma'}{b^2} \frac{\alpha_T^2}{\beta} \varepsilon \right)^{1/2} \approx 300 \text{ kg cm}^{-2}$$

$$\sigma_L = \sigma_0 / (2\varepsilon)^{1/2} \approx 1200 \text{ kg cm}^{-2}.$$

Note that  $\varepsilon$  in (3) differs from  $\varepsilon$  in [4] by  $1/\sqrt{2}$ . We shall return to the phase diagram later.

#### 4. Commensurate phases

For the initial phase  $C_0$ :

$$\begin{aligned} \rho = 0 & & \phi = -\sigma_{xz}^2/2c & & P_z = 0 \\ u_{xz} = \sigma_{xz}/c & & \chi = 1/\kappa & & S = 1/c. \end{aligned} \tag{4}$$

In what follows all the values  $\phi, P_z, u_{xz}, \chi, S, C$  will be measured from their values in the

phase  $C_0$ . The results for the phases  $C_1$  and  $C_2$  will be given initially without neglecting any invariants in (1) since in various regions of the phase diagram these can play different roles.

For the commensurate phase  $C_1$

$$\begin{aligned} \cos 3\varphi &= -\frac{F}{4\gamma'\rho^3} & \alpha + 2\beta\rho^2 - 3\gamma'\rho^4 &= 0 \\ \phi &= \alpha\rho^2 + \beta\rho^4 - \gamma'\rho^6 \left[ 1 + 2\left(\frac{F}{4\gamma'\rho^3}\right)^2 \right] \\ P_z &= \mp a\rho^3 \left[ 1 - \left(\frac{F}{4\gamma'\rho^3}\right)^2 \right]^{1/2} & u_{xz} &= \frac{bF}{4\gamma'} \\ \chi &= \frac{a^2}{4\gamma'} \left(\frac{F}{4\gamma'\rho^3}\right)^2 \left[ 1 - \left(\frac{F}{4\gamma'\rho^3}\right)^2 \right]^{-1} \\ S &= \frac{b^2}{4\gamma'} & C &= \frac{T\alpha_T^2}{2\beta} \left(1 - \frac{3\gamma'\rho^2}{\beta}\right)^{-1}. \end{aligned} \quad (5)$$

There are six domains in this phase, three of which differ from the other three by the sign of the spontaneous value  $P_z$ . After averaging over the domains, we obtain  $P_z = 0$ . Note that  $\chi$  in (5) is calculated in the approximation  $\gamma'\rho^2 \ll \beta$ .

For the commensurate phase  $C_2$ :

$$\begin{aligned} \sin 3\varphi &= 0 & \cos 3\varphi &= -\frac{F}{|F|} & \alpha + 2\beta\rho^2 + 3\gamma'\rho^4 \left(1 - \frac{|F|}{2\gamma'\rho^3}\right) &= 0 \\ \phi &= \alpha\rho^2 + \beta\rho^4 + \gamma'\rho^6 \left(1 - \frac{|F|}{\gamma'\rho^3}\right) & P_z &= 0 & u_{xz} &= b\rho^3 \frac{F}{|F|} \\ \chi &= \frac{a^2}{4\gamma'} \left(\frac{|F|}{4\gamma'\rho^3} - 1\right)^{-1} & S &= \frac{9b^2}{8\beta} \rho^2 \left[ 1 + \frac{3\gamma'\rho^2}{\beta} \left(1 - \frac{|F|}{8\gamma'\rho^3}\right) \right]^{-1} \\ C &= \frac{T\alpha_T^2}{2\beta} \left[ 1 + \frac{3\gamma'\rho^2}{\beta} \left(1 - \frac{|F|}{8\gamma'\rho^3}\right) \right]^{-1}. \end{aligned} \quad (6)$$

There are three domains in this phase (for  $F \neq 0$ ).

## 5. Phase transitions between commensurate phases

The boundary between phases  $C_1$  and  $C_2$ , which starts at point 0 (see figure 1) is defined from the condition  $|\cos 3\varphi| = 1$  (see (5) and (6)), i.e., from the condition  $|F| = 4\gamma'\rho^3$  which gives for the value  $\alpha$  (defined as  $\alpha_{21}$  on this boundary) the expression

$$\alpha = \alpha_{21} = -\beta \left(\frac{F^2}{2\gamma'^2}\right)^{1/3} \left[ 1 - \frac{3\gamma'}{4\beta} \left(\frac{F^2}{2\gamma'^2}\right)^{1/3} \right]. \quad (7)$$

The  $C_2$ - $C_1$  phase transition is of the second order: all the values  $\rho$ ,  $\varphi$ ,  $P_z$ ,  $u_{xz}$  are continuous at the transition point. If the natural approximation  $\gamma'\rho^2 \ll \beta$  is assumed which, for example, at 0 point is reduced to the inequality  $\varepsilon \ll 1$  then the second term in brackets in (7) can be neglected.

In the vicinity of the  $C_2$ – $C_1$  phase transition when  $|\alpha - \alpha_{21}|/|\alpha_{21}| \ll 1$  we obtain

$$\chi = \frac{a^2}{6\gamma'} \frac{-\alpha_{21}}{\alpha - \alpha_{21}} \quad \chi = \frac{a^2}{12\gamma'} \frac{-\alpha_{21}}{\alpha_{21} - \alpha} \quad (8)$$

in the phases  $C_2$  and  $C_1$ , respectively. As can be seen from (8),  $\chi$  varies in both phases according to the Curie–Weiss law  $\chi = C_\chi/|T - T_{21}|$ , where the Curie constant is dependent on the external force  $C_\chi \approx F^{2/3}$ ; see (7).  $C_\chi$  is small, for example, at point 0:  $C_\chi \approx \varepsilon$ . However,  $\alpha_{21} = \alpha_0\pi/2$  at point 0 and therefore  $C_\chi$  differs only by a multiplier close to unity from  $C_\chi$  at the I– $C_1$  transition ( $F = 0$ ); see (37) below. At the I– $C_1$  transition the Curie–Weiss law is distinctly observed. Therefore the  $C_2$ – $C_1$  phase transition can be reliably revealed in experiment by measuring  $\chi$ . Moreover, at the  $C_2$ – $C_1$  transition,  $S$  undergoes an upward jump by a value  $\approx b^2/4\gamma'$ , while  $C$  undergoes a small jump upwards (for example,  $\sim \varepsilon$  at point 0).

The boundary between the phases  $C_0$  and  $C_2$  that starts at point L is defined from (6):

$$\alpha = \alpha_{02} = F^2/4\beta. \quad (9)$$

This expression is obtained in the approximation  $\gamma'\rho^2 \ll \beta$  which reduces to the inequality  $\varepsilon^2 \ll 1$ . The  $C_0$ – $C_2$  phase transition is realised as a weak first-order transition because of the presence in (1) of the invariant  $F\rho^3 \cos 3\varphi$  of the third power in  $\rho$ . At the  $C_0$ – $C_2$  transition  $\chi$  and  $S$  undergo very small upward jumps, for example, at point 0,  $\chi = a^2\varepsilon^2/\gamma'$ ,  $S = 9b^2\varepsilon^2/\gamma'$ , while  $C$  undergoes the usual jump upwards  $C \approx \alpha_0^2 T_{02}/2\beta$ ; see (6). Note that the presence of the I phase (for example, its closeness on the phase diagram) in no way affects the anomalies of the physical quantities in the commensurate phases  $C_1$  and  $C_2$ .

## 6. Solution for $\varphi$ in the I phase

In considering the I phase we use the constant amplitude approximation  $\partial\rho/\partial x = 0$  [7]. Such an approximation can be applied when anisotropy in the  $\eta$ ,  $\xi$  space is small. In this case both the intrinsic anisotropy defined by the invariant  $\gamma'\rho^6 \cos 6\varphi$  and the anisotropy induced by the external force, which is defined by the invariant  $F\rho^3 \cos 3\varphi$ , should be small; see (1). When these conditions are satisfied independently, they are reduced to the following inequalities (see [6] for  $n = 6$  and  $n = 3$ )

$$\varepsilon \ll 1 \quad \varepsilon\sigma_{xz}^2/\sigma_0^2 \ll 1. \quad (10)$$

It should be emphasised that the coefficient  $\gamma'$  by itself need not necessarily be small: the condition  $\varepsilon \ll 1$  holds for the usual values of  $\gamma'$  and  $\beta$  due to a small value of  $\alpha_0$ . In  $K_2\text{SeO}_4$  according to estimations of [4, 2],  $\varepsilon = 0.03$ . At the point 0  $\sigma_{xz} = \sigma_0$ , and hence the second inequality in (10) will also be satisfied up to the values of  $\sigma_{xz}$  not exceeding  $\sigma_0$  by too much.

Minimising  $\phi$  in (1) with respect to  $\varphi(x)$ , assuming the constant amplitude approximation, we obtain

$$2\delta\rho^2 d^2\varphi/dx^2 + 6\gamma'\rho^6 \sin 6\varphi + 3F\rho^3 \sin 3\varphi = 0. \quad (11)$$

Multiplying this equation by  $d\varphi/dx$  and integrating, we obtain

$$\delta\rho^2(d\varphi/dx)^2 - \gamma'\rho^6 \cos 6\varphi - F\rho^3 \cos 3\varphi = C \quad (12)$$

where  $C$  is an integration constant. This equation can be solved by separation of variables

resulting in an expression for  $x$  in the form of an elliptic integral. By the standard transformation this integral is reduced to the normal form, i.e., the solution can be expressed, for example, as the Jacobian elliptic function. It is easier, however, first to transform equation (12) in such a way as to obtain the solution in the normal elliptic integral form.

Changing the variable  $u = \cos 3\varphi$  in (12) we get

$$\delta\rho^2 (du/dx)^2 = 9(1 - u^2)(2\gamma'\rho^6 u^2 + F\rho^3 u - \gamma'\rho^6 + C). \quad (13)$$

Now we apply the transformation of the form

$$u = (v - l)/(1 - lv) \quad (14)$$

where  $v$  is a new variable while the constant  $l$  is chosen in such a way that excludes in the equation for  $v$  a term linear in  $v$ . For this the following relation should be satisfied:

$$F\rho^3 l^2 - 2(\gamma'\rho^6 + C)l + F\rho^3 = 0 \quad (15)$$

which can be considered as a replacement of  $C$  by the new integration constant  $l$ . The equation for  $v$  can now be represented as

$$(dv/dx)^2 = 9F\rho(1 - l^2)(1 - v^2)(1 - k^2 - k^2 v^2)/2\delta l, \quad (16)$$

where  $C$  is excluded by using (15) and the constant  $k^2$  is introduced:

$$k^2 = l(4\gamma'\rho^3/F - l)/(1 - l^2). \quad (17)$$

The solution of equation (16) is the Jacobian elliptic function  $v = \text{cn}(3px, k)$  with modulus  $k$  (which can be verified by substitution), where

$$p^2 = F\rho(1 - l^2)/2\delta l. \quad (18)$$

The second integration constant  $x_0$  specifying the origin of  $x$  can be assumed to be zero. The solution of equation (11) takes the form

$$\cos 3\varphi = \frac{\text{cn}(3px, k) - l}{1 - l \text{cn}(3px, k)}. \quad (19)$$

Note that the solution (19) valid only if  $k^2 \leq 1$ ,  $|l| \leq 1$ . It follows from (18) that the sign of  $l$  coincides with the sign of  $F$ .

To analyse the results obtained it is convenient to use, instead of parameters  $k$  and  $l$ , other parameters  $m$  and  $n$ :

$$k^2 = m \quad l = \frac{F}{|F|} \sqrt{\frac{n}{n+1}} \quad (20)$$

with  $-\infty < m \leq 1$ ,  $0 \leq n < \infty$ . Relation (17) expresses  $n$  in terms of  $m$ :

$$\sqrt{n(n+1)}/(m+n) = |F|/4\gamma'\rho^3 \quad (21)$$

whereas  $m$  should be defined from the condition of minimum of the thermodynamic potential.

The values  $m > 0$  correspond to one state of the I phase:  $I_1$  which has solitons of two types, the values  $m < 0$  correspond to the other state  $I_2$ , which has solitons of one type. The  $I_1$ - $I_2$  boundary (not the phase transition line), is defined from the condition  $m = 0$  [1]. Note that the use of two signs for  $m$  makes it possible to represent the solution for various states  $I_1$  and  $I_2$  of the I phase in one and the same form (19).

**7. Expression for  $\phi$  in the I phase**

Substituting (19) into (1) and integrating  $\phi$  with respect to  $x$  (averaging  $\phi$  over the period of  $\phi(x)$  equal to  $4K/3p$ ) we get

$$\phi = \alpha\rho^2 + \beta\rho^4 + \gamma'\rho^6 - \frac{F\rho^3[(2n + 3)K - 2E - 2(n + 1)\Pi]}{2\sqrt{n(n + 1)K}} - \frac{\pi}{K} \left( \frac{\alpha_0\rho^2|F|\rho^3}{2\sqrt{n(n + 1)}} \right)^{1/2} \tag{22}$$

Here and in what follows  $K = K(m)$ ,  $E = E(m)$ ,  $\Pi = \Pi(n, m)$  are complete elliptic integrals of the first, second and third kinds, respectively, with modulus  $m$  and parameter  $n$ . To avoid confusion we give an expression for  $\Pi$ :

$$\Pi(n, m) = \int_0^{\pi/2} d\theta [(1 + n \sin^2 \theta)(1 - m \sin^2 \theta)^{1/2}]^{-1}.$$

From the condition  $\partial\phi/\partial m = 0$  using (22) for  $\phi$ , we have

$$[-K + E + (n + 1)\Pi]^2 = \pi^2 \alpha_0 \sqrt{n(n + 1)}/2|F|\rho. \tag{23}$$

Substituting (23) into (22), we simplify the expression for  $\phi$ :

$$\phi = \alpha\rho^2 + \beta\rho^4 + \gamma'\rho^6 - |F|(2n + 1)\rho^3/2\sqrt{n(n + 1)}. \tag{24}$$

**8. Expressions for  $q$ ,  $P_z$ ,  $u_{xz}$  and  $\chi$  in the I phase**

Since the period of the functions  $\eta(x)$ ,  $\xi(x)$  equals  $4K/p$ , we have for the wavenumber  $q$  characterising the I structure:

$$q = \frac{\pi p}{2K} = \frac{\pi}{2} \frac{1}{K} \left( \frac{|F|\rho}{2\delta\sqrt{n(n + 1)}} \right)^{1/2} = \left( \frac{\pi}{2} \right)^2 q_0 \{K[-K + E + (n + 1)\Pi]\}^{-1} \tag{25}$$

where (18), (20) and (23) are used.

Substituting (19) into (2) and integrating with respect to  $x$  (averaging over the period of  $P_z(x)$  and  $u_{xz}(x)$  equal to  $4K/3p$ ) we obtain

$$P_z = 0 \quad u_{xz} = \frac{b\rho^3}{l} \left( 1 - \frac{\Pi}{K} \right) = \frac{bF(m + n)}{4\gamma'n} \left( 1 - \frac{\Pi}{K} \right) \tag{26}$$

where (20) and (21) are used.

To obtain the expression for  $\chi$  in the I phase it is necessary to find the dependence  $P_z(E_z)$  in the linear approximation in  $E_z$ . One has to add to equation (11) the term  $3aE_z\rho^3 \cos 3\varphi$  and to the left-hand side of (12) the term  $aE_z\rho^3 \sin 3\varphi$ . A solution of this equation will be sought in the form  $\varphi = \varphi_0 + \varphi_1$ , where  $\varphi_1 \approx E_z$ . Using (11) for  $\varphi_0$  we obtain the solution of (12) for  $\varphi_1$ :

$$\varphi_1 = \frac{d\varphi_0}{dx} \int_0^x \frac{aE_z\rho \sin 3\varphi_0 + C}{2\delta(d\varphi_0/dx)^2} dx. \tag{27}$$

The integration constant  $C \approx E_z^2$  (since it specifies the period variation that can not be



linear in  $E_z$ ) and hence  $C$  can be neglected. Substituting the solution (19) into (24) and calculating the integral we get

$$\varphi_1 = \frac{aE_z l [k^2 \operatorname{cn}(3px) + l(1 - k^2) - (k^2 + l - lk^2) \operatorname{dn}(3px)]}{3F(1 - k^2)(1 - l^2)[1 - l \operatorname{cn}(3px)]}. \quad (28)$$

It follows from (2) that

$$P_z(x) = -a\rho^3 \sin 3\varphi = -a\rho^3 \sin 3\varphi_0 - 3a\rho^3 \varphi_1 \cos 3\varphi_0. \quad (29)$$

Substituting (28) into (29) and integrating (29) with respect to  $x$  (averaging  $P_z(x)$  over the period equal to  $4K/3p$ ) we get

$$P_z = \frac{a^2 E_z \rho^3 l [E - (1 - k^2)K]}{K^2(1 - k^2)F(1 - l^2)K}. \quad (30)$$

Taking into account (20) and (21) it follows that

$$\chi = \frac{a^2}{4\gamma'} \frac{m + n}{m} \left[ \frac{E}{(1 - m)K} - 1 \right]. \quad (31)$$

## 9. Expression for $\rho$ in the I phase

Until now it has been possible to do without an expression for  $\rho$  assuming only  $\rho = \text{const}$ . There are two main methods of defining this constant. The first consists in taking for  $\rho$  the same expression as in the C phase [7]. In this case the I–C transition happens to be continuous [6]; exact solutions (without assuming  $\rho = \text{const}$ ) obtained under specific conditions support this result [8]. The expression for  $\rho$  chosen in such a way is valid only in the vicinity of the I–C transition.

The second method consists in defining  $\rho$  from the condition  $\partial\phi/\partial\rho = 0$  [9] which allows one to obtain for  $\rho$  an expression well applicable to the wide interval of the existence of the I phase excluding the immediate vicinity of the I–C transition. Indeed, the transition turns out to be of first order.

In this paper  $\rho$  is defined according to the first method since it allows us to find anomalies of physical quantities in the vicinity of the I–C transition where they are particularly pronounced. Let us consider the  $I_1$ – $C_1$  phase transition and take expression (5) for  $\rho$  in the I phase. Then, according to (24),  $\phi$  in the  $I_1$  phase can be represented in the form

$$\phi = \phi_1 + 2\gamma'\rho^6 + \frac{F^2}{8\gamma'} - \frac{|F|(2n + 1)\rho^3}{2\sqrt{n(n + 1)}} = \phi_1 - \frac{F^2 m(1 - m)}{8\gamma' n(n + 1)} \quad (32)$$

where (21) is used and  $\phi_1$  is the value of  $\phi$  (see (5)) in the  $C_1$  phase.

Since  $\gamma' > 0$  and  $m > 0$  (in the  $I_1$  phase), then, as follows from (32),  $\phi < \phi_1$  and hence for  $m = 1$  a continuous  $I_1$ – $C_1$  phase transition is realised. Thus the phase transition also retains features of a continuous lock-in transition for  $\sigma_{xz} \neq 0$ . Similarly, assuming that  $\rho$  in the  $I_2$  phase in the vicinity of the transition is the same as in the  $C_2$  phase, it can be shown that the  $I_2$ – $C_2$  transition is a continuous lock-in transition.

**10. The  $I_1-C_1$  phase transition line**

The boundary between the  $I_1$  phase and the  $C_1$  phase is defined from the condition  $m = 1$ . Since the asymptotic expression for  $\Pi(m, n)$  as  $m \rightarrow 1$  is

$$\Pi = (K + \sqrt{n} \tan^{-1} \sqrt{n}) / (n + 1)$$

it will be convenient to introduce the parameter  $\psi$  instead of  $n$ :  $n = \tan^2 \psi$ . If we exclude  $F$  and then  $\rho$  from (21) and (23) we obtain the  $I_1-C_1$  transition line in a parametric form

$$-\alpha_s \varepsilon / \alpha_0 = f_1 [1 - (\frac{3}{2}) \varepsilon f_1] \quad |\sigma_{xz}| / \sigma_0 = f_1^{3/2} \sin \psi \tag{33}$$

$$f_1 = f_1(\psi) = (\pi/2) (\cos \psi + \psi \sin \psi)^{-1}$$

where  $\alpha_s$  denotes the value of  $\alpha$  at the line. The value  $\psi = 0$  corresponds to point C (with  $\alpha_s = \alpha_c$ ) and the value  $\psi = \pi/2$  corresponds to point 0. The value defined from the condition  $\psi \tan \psi = 2$  corresponds, as is easily verified, to point M (see figure 1).

In the vicinity of point C when  $\alpha_s - \alpha_c \ll |\alpha_c|$ , dependence (33) can be represented in explicit form;

$$(\alpha_s - \alpha_c) / (-\alpha_c) = (T_s - T_c) / (\theta - T_c) = (4/\pi^3) (\sigma_{xz} / \sigma_0)^2 \tag{34}$$

i.e., the shift of the transition temperature is  $T_s - T_c \approx \sigma_{xz}^2$ . Relation (34) is represented in figure 1 by the broken curve. Note that experimentally  $\sigma_{xz}$  is usually created by pressure on the crystal of an  $xz$  cut. Moreover, along with  $\sigma_{xz}$  the stresses  $\sigma_{xx}$  and  $\sigma_{zz}$  also arise. They enter the thermodynamic potential as  $\sigma_{xx,zz} \rho^2$ , and hence they lead to a linear shift in  $T_c$ :  $\Delta T_c \approx \sigma_{xx,zz}$  that is stronger than that obtained from (34):  $\Delta T_c \approx \sigma_{xz}^2$ .

**11. The  $I_2-C_2$  phase transition line**

On the  $I_2-C_2$  boundary we have  $m \rightarrow -\infty, n \rightarrow \infty$  and the asymptotic expression for  $\Pi$  is  $\Pi = \cos^{-1}(\sqrt{-m/n} / \sqrt{m+n})$ . Thus it is convenient to introduce the parameter  $\theta$ :  $m/n = -\cos^2 \theta$ . From (21) and (23) the  $I_2-C_2$  transition line is derived in a parametric form

$$-\alpha_s \varepsilon / \alpha_0 = f_2 [1 - (\frac{3}{2}) \varepsilon f_2 (1 - 2/\sin^2 \theta)] \quad |\sigma_{xz}| / \sigma_0 = f_2^{3/2} / \sin^2 \theta \tag{35}$$

$$f_2 = f_2(\theta) = (\pi/2) \tan \theta / (1 + 2\theta / \sin 2\theta).$$

The value  $\theta = \pi/2$  corresponds to point 0 and the value defined from  $\sin^2 \theta = \theta$  corresponds to point N, as is easily verified.

The location of point L on the phase diagram is independent of the approximation  $\rho = \text{const}$ . It is determined by the condition of the intersection of the transition lines  $C_0-C_2$  and  $C_0-I_2$ :  $\alpha = \alpha_0, \sigma_{xz} = \sigma_0 / \sqrt{2\varepsilon}$ . Here, as when obtaining equation (9) for the  $C_0-C_2$  transition line, the condition  $\gamma' \rho^2 \ll \beta$  is assumed, which reduces to  $\varepsilon^2 \ll 1$ . Notice that the triple point L is not the Lifshitz point in the usual sense [10], since the  $C_0-C_2$  phase transition is of the first order.

The lines of  $C_1-C_2, I_1-C_1$  and  $I_2-C_2$  (low part) phase transitions in figure 1 are drawn according to (7), (33) and (35) without taking into account the second terms in brackets. These terms in (33) and (35) within the approximation  $\rho = \text{const}$  are unreliable and small, since they are  $\sim \varepsilon$ . Note that curve (35) does not pass through the point L even though it represents a continuous transition; it results from the fact that the

approximation  $\rho = \text{const.}$  is inapplicable for not small anisotropy induced by the external force  $\sigma_{xz} = \sigma_L$ .

## 12. Anomalies of physical quantities in the I phase near $I_1-C_1$ and $I_2-C_2$ phase transitions

To find expressions for  $S$  and  $C$  in the I phase it is necessary to differentiate expressions for  $u_{xz}$  in (26) with respect to  $\sigma_{xz}$  and  $\phi$  in (24) with respect to  $T$ . It also should be taken into account that the parameters  $m$  and  $n$  depend on  $\sigma_{xz}$  and  $T$  as well. Therefore, final expressions turn out to be extremely clumsy. Of major interest, however, is the region close to the  $I_1-C_1$  and  $I_2-C_2$  phase transitions where anomalies are most pronounced. In this region one can expand expressions into a series in terms of a small value  $m' = 1 - m$  and one can retain, when differentiating, only the leading term in the expansion, i.e., a maximum one for  $m' \ll 1$ . As a result we obtain for the  $I_1-C_1$  phase transition

$$\begin{aligned}\chi &= \frac{a^2}{8\gamma'} \frac{-\alpha_s}{\alpha - \alpha_s} \frac{1}{1 - \psi \tan \psi/2} \\ S &= \frac{b^2}{4\gamma'} \frac{-\alpha_s}{(\alpha - \alpha_s) \ln^2 |\alpha - \alpha_s|} \frac{2\psi^2}{1 - \psi \tan \psi/2} \\ C &= \frac{T\alpha_T^2}{2\beta} \frac{2\pi\epsilon(-\alpha_s)}{(\alpha - \alpha_s) \ln^2 |\alpha - \alpha_s|} \frac{\cos \psi(1 - \psi \tan \psi/2)}{1 + \psi \tan \psi} \\ q &= \frac{\pi^2}{2} q_0 \frac{1}{\ln |\alpha - \alpha_s|} \frac{1}{1 + \psi \tan \psi} \quad u_{xz} = \frac{b^2}{4\gamma'} \sigma_{xz}.\end{aligned}\tag{36}$$

Here the expressions (25) for  $q$ , (26) for  $u_{xz}$  and (31) for  $\chi$  are expanded in terms of  $m'$ . Inequalities (10) are used for the derivation (36) and subsequently (37) and (38).

If we pass in (36) to the limit  $\sigma_{xz} \rightarrow 0$ , i.e., assume that  $\psi \rightarrow \sqrt{n} \rightarrow F/4\gamma'\rho_c^2 \rightarrow 0$  see (21), then we get

$$\begin{aligned}\chi &= \frac{a^2}{8\gamma'} \frac{-\alpha_c}{\alpha - \alpha_c} \quad S = 0 \quad C = \frac{T\alpha_T^2}{2\beta} \frac{2\pi\epsilon(-\alpha_c)}{(\alpha - \alpha_c) \ln^2(\alpha - \alpha_c)} \\ q &= \frac{\pi^2}{2} q_0 \frac{1}{\ln(\alpha - \alpha_c)} \quad u_{xz} = \frac{b^2}{4\gamma'} \sigma_{xz}.\end{aligned}\tag{37}$$

The expressions for  $\chi$  and  $C$  in (37) coincide with the leading terms of the expansions in terms of  $m'$  or in terms of  $\alpha - \alpha_c$  for the case  $\sigma_{xz} = 0$  [6]. For  $S$  in (37) we obtain 0 instead of  $b^2/4\gamma'$ , since only the leading term of the expansion is taken into account in (36).

Proceeding in the same way as we did when deriving (36) we obtain for the vicinity of the  $I_2-C_2$  phase transition in the  $I_2$  phase the following results

$$\begin{aligned}\chi &= \frac{a^2}{8\gamma'} 2 \tan^2 \theta \\ S &= \frac{b^2}{4\gamma'} \frac{-\alpha_s}{(\alpha - \alpha_s) \ln^2 |\alpha - \alpha_s|} \frac{4\theta^2}{1 - \theta/\sin 2\theta} \\ C &= \frac{T\alpha_T^2}{2\beta} \frac{2\pi\epsilon(-\alpha_s)}{(\alpha - \alpha_s) \ln^2 |\alpha - \alpha_s|} \frac{2}{\tan \theta} \frac{1 - \theta/\sin 2\theta}{1 + 2\theta/\sin 2\theta}\end{aligned}\tag{38}$$

$$q = \frac{\pi^2}{2} q_0 \frac{1}{\ln^2 |\alpha - \alpha_s|} \frac{1}{1 + 2\theta/\sin 2\theta}$$

$$u_{xz} = \frac{b^2}{4\gamma'} \sigma_{xz} \sin^2 \theta.$$

Let us consider the four temperature dependences (36)–(38), all of which occur in the case  $\sigma_{xz} = 0$  (37). It follows from (36) that in the vicinity of the  $I_1$ – $C_1$  transition,  $\chi$  varies according to the Curie–Weiss law just as in the case when  $\sigma_{xz} = 0$  (see (37)). The Curie constant in (36) has an additional factor compared to (37) that depends on  $\psi$ . This factor increases with  $\psi$  from 1 at the point C ( $\psi = 0$ ) to  $\infty$  at the point M and then decreases to zero at point 0 ( $\psi = \pi/2$ ). According to (38), in the vicinity of the  $I_2$ – $C_2$  transition,  $\chi$  is a constant independent of  $T$  that decreases with  $\theta$  from  $\infty$  at point 0 ( $\theta = \pi/2$ ) and tends asymptotically to become 0 as  $\theta \rightarrow 0$ . It is easily seen that  $\chi$  is continuous at the  $I_2$ – $C_2$  transition.

In the vicinity of both the  $I_1$ – $C_1$  (36) and  $I_2$ – $C_2$  transitions (38)  $S$  and  $C$  have temperature dependences of the same kind as  $C$  in (37) for  $\sigma_{xz} = 0$ . These dependences can be conventionally called the Curie–Weiss law. The corresponding Curie ‘constants’ strongly depend on  $T$  because of  $\ln^2 |\alpha - \alpha_s|$  in the denominator and for the same reason are very small. The additional terms depending on  $\psi$  and  $\theta$  vary in such a way that at points C, M, 0, N shown in figure 1 take the following values for S: 0,  $\infty$ , 0,  $\infty$  and the term tends to 0 as  $\theta \rightarrow 0$ . For C: 1, 0, 0, 0 and it tends to  $\infty$  as  $\theta \rightarrow 0$ . It follows from the comparison of dependences  $S(T)$  for  $\sigma_{xz} \neq 0$  (36) and (38), and for  $\sigma_{xz} = 0$  (37) that  $\sigma_{xz}$  induces a narrow peak of  $S$  in the vicinity of  $T = T_s$ . For  $\sigma_{xz} = 0$ ,  $S$  does not depend on  $T$  in the vicinity of  $T = T_c$  and is continuous at  $T = T_c$ .

The wavenumber  $q$  depends on  $T$  in the vicinity of the transitions  $I_1$ – $C_1$  (36) and  $I_2$ – $C_2$  (38) in the same way as for  $\sigma_{xz} = 0$  (37). The additional factor varies in such a way as to assume at points C, M, 0, N the values 1,  $\frac{1}{2}$ , 0,  $\frac{1}{3}$  and it tends to 0 as  $\theta \rightarrow 0$ .  $u_{xz}$  is independent of  $T$  and continuous at the transitions  $I_1$ – $C_1$  and  $I_2$ – $C_2$ .

The above treatment of anomalies of physical quantities at phase transitions  $I_1$ – $C_1$  and  $I_2$ – $C_2$  and also  $C_2$ – $C_1$  will hopefully help to identify these transitions in experiments.

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