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A zig-zag domain-wall structure of the incommensurate phase in $A_2BX_4$-type crystals

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Résumé. — Dans le cadre d’une théorie de Landau des cristaux de type $A_2BX_4$, nous introduisons dans l’énergie libre un nouveau terme — de type Umklapp — du 3e ordre. Dans la phase incommensurable ce terme peut induire une nouvelle transition de phase avec rotation du vecteur de modulation en dehors de la direction $a^*$. Dans ces cristaux qui sont des ferroélectriques impropres l’énergie électrostatique peut induire de fait une structure des parois de domaines en zig-zag, c’est-à-dire modulé aussi selon $b^*$.

Abstract. — Within Landau theory of phase transitions in $A_2BX_4$ — type crystals we introduce in the free energy a new third-order Umklapp term. In the incommensurate phase this term can induce a new phase transition connected with a rotation of the wave vector of modulation away from the $a^*$ direction. The electrostatic energy in these improper ferroelectrics could induce in fact a zig-zag domain-wall structure, i.e. a structure also modulated along $b^*$.

1. Introduction.

Several $A_2BX_4$-type crystals exhibit an incommensurate (IC) phase in a temperature range between the high-symmetry phase Pnma ($D_{2h}^5$) above $T_I$ and a commensurate (C) phase below $T_C$ with tripped translational period along the crystallographic $x$-direction. The sequence of phase transitions occurring at $T_I$ and $T_C$ can be qualitatively well described by Landau theory (see for example [1]) with a two-component order parameter at the point $k_C = \frac{1}{3} a^*$ of the Brillouin zone. From this macroscopic point of view the IC phase can be looked upon as the C phase which is due to the Lifshitz invariant in the free-energy density $f$, space modulated along the $x$-direction. It is generally accepted that near $T_C$ the IC phase is actually a stripe phase, i.e. it has a form of a periodic domain structure in which large almost perfect C regions are separated by narrow planar parallel domain walls (discommensurations). Domain walls are considered to be exactly perpendicular to the crystallographic $x$-direction. Recently, however, it has been shown by general symmetry arguments [2] that the position of an isolated wall perpendicular to the $x$-axis is not stable and hence an isolated wall must rotate away from this crystallographic orientation. Although the orientation perpendicular to the $x$-axis is for a perfectly periodic stripe phase again a prominent orientation with extremal energy (minimal or maximal) [2], an interesting question arises what term in $f$ is responsible for rotation of an individual wall and whether even the stripe phase could under some circumstances rotate away from the crystallographic orientation. In other words, we shall investigate the problem whether the minimum of energy of the stripe phase perpendicular to the $x$-axis could change into a maximum at a temperature within the interval of the existence of the IC structure.

2. SPW approximation.

The stripe phase would be rotated away from the $x$-direction provided the wave vector $k$ of the structure modulation has also a component perpendicular to the $x$-axis below a temperature say $T_R$. $T_C < T_R < T_I$. In general, the temperature dependence of $k$ is due to frozen-in higher harmonics which are induced by U(Umklapp) — terms in the free energy $f$ [3]. In the case of $A_2BX_4$-type crystals, the U-terms usually considered are of sixth-order in the order parameter.

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at least. Since we are mainly interested in a component of $k$ perpendicular to the $x$-axis, we shall neglect these high-order $U$-terms and consider, in this single plane-wave (SPW) approximation, $k_x$ as temperature independent. Thus we take $f$ in the form [1]

$$f = \frac{1}{2} a(T - T_0) (p^2 + q^2) + \frac{1}{4} \beta (p^2 + q^2)^2 + \delta \left( \frac{\partial p}{\partial x} q - \frac{\partial q}{\partial x} \right) + \frac{\kappa_1}{2} \left( \frac{\partial p}{\partial y} \right)^2 + \left( \frac{\partial q}{\partial y} \right)^2 \right) \quad (1)$$

with $\alpha, \beta, \kappa_1 > 0$. Here $p, q$ are two components of the order parameter related to the phonon normal coordinate $Q$ with the wave vector $k_c = \frac{1}{3} a^*$ by the relation $Q = r e^{i \phi} = p + iq$. The $\delta$-term (for definiteness we choose $\delta < 0$) is the Lifshitz invariant which modulates the structure along the $x$-direction. Now we introduce the following important terms which so far have not been considered in the phenomenological theory of the IC structure in $A_2BX_4$-type crystals:

$$\lambda \left[ \frac{\partial p}{\partial x} \frac{\partial p}{\partial y} - \frac{\partial q}{\partial x} \frac{\partial q}{\partial y} \right] - \frac{\kappa_2}{2} \left( \frac{\partial p}{\partial y} \right)^2 + \left( \frac{\partial q}{\partial y} \right)^2 \right] \quad (2)$$

It should be emphasized that the $\lambda$-term is the lowest-energy $U$-term which induces a second harmonic of the soft mode provided the wave vector $k$ of the modulation has a $y$-component. Since a frozen-in harmonic reduces the free energy, it should be expected that the $\lambda$-term will pull $k$ out of the $x$-direction into the $(k_x, k_y)$ plane. To see this effect we first combine (1) and (2), take Fourier transform of $p, q$ and diagonalize the quadratic part of the free energy with Lifshitz invariant included by introducing new normal coordinates. Then the part of the total free-energy density $F$ associated with the soft-mode coordinate $Q_k$ reads

$$F = \frac{1}{V} \int f \, dV = \alpha_k Q_k Q^*_k + \beta(Q_k Q^*_k)^2 + \alpha_{-2k} Q_{-2k} Q^{*2}_{-2k} - 3 \sqrt{2} \lambda k_x k_y (Q_k Q_{-2k} + c.c.) \quad (3)$$

where

$$\alpha_k = a(T - T_0) + \kappa_1 k^2_x - 2 \delta k_x + \kappa_2 k^2_y = a(T - T_0) + \kappa_1 (k_x - k_0)^2 + \kappa_2 k^2_y$$

with $T_0 = T_0 + \delta^2/(a \kappa_1)$ and $k_0 = \delta/\kappa_1 < 0$.

We remind that $k_0, k_x, k_y$ denote deviations of the wave vector from the $C$ value $\frac{1}{3} a^*$ so that $Q_k$ and $Q_{-2k}$ represent in fact the phonon coordinates $Q_k$ and $Q_{-2k}$, respectively. The frequency squared of the second harmonic can be put into the form

$$\alpha_{-2k} = a(T - T_0) + 4 \kappa_1 k^2_x + 4 \delta k_x + 4 \kappa_2 k^2_y = a(T - T_0) + 9(T_1 - T_0) + 12 \frac{\delta^2}{\kappa_1} \left( k_x - k_0 \right)^2 + 3 \frac{\delta^2}{\kappa_1} \left( k_x - k_0 \right)^2 + 4 \kappa_2 k^2_y \ .$$

It should be pointed out that below $T_1$ $\alpha_k$ and $\alpha_{-2k}$ represent frequencies squared of bare soft modes and thus both may be negative. As we have already discussed we put in the following $k_x = k_0$ neglecting thus for simplicity a possible change of $k_x$ due to the $\lambda$-term. Eliminating now the second harmonic $Q_{-2k}$ from (3) and then minimizing $F$ with respect to the amplitude of $Q_k$ we get

$$F(k_\nu) = - \frac{\alpha^2}{4 \beta - 18 \lambda k^2_x k^2_y} = \frac{\left[ a(T_1 - T) + \kappa_2 k^2_y \right]^2}{4 \beta \left( 1 - \frac{2 s \kappa_2 k^2_y}{9 a(T_1 - T_0) - a(T_1 - T) + 4 \kappa_2 k^2_y} \right)} \quad (4)$$

where $s = 9 \lambda^2 k^2_0 / (a \kappa_2)$ is a positive dimensionless parameter. The stable equilibrium value of $k_\nu$ corresponding to (4) is

$$k^2_\nu = \frac{9(8 - s) \kappa^2_1}{16(2 - s) \kappa^2_2} \times \left\{ -1(t) + 1 - t \left[ 1 + \frac{32(2 - s)(1 + s)}{(s)^2} \right] \right\}^{1/2} \quad (5)$$

where $t = (T_1 - T)/(9(T_1 - T_0))$.

The temperature region of real $k_\nu$ depends on the magnitude of $s$. Assuming $s \leq 1$ it follows from (5) that $k^2_\nu$ is positive for $(1 + s)^{-1} < t < 1$, that is to say in the temperature interval

$$T_1 - 9(T_1 - T_0) \equiv T_2 < T < T_1 \equiv T_1 - \frac{9(T_1 - T_0)}{1 + s}$$

a rotated stripe phase may exist. We conventionally call the IC phase with $k_x \neq 0$ a rotated stripe phase although in the SPW approximation the domain walls are not yet well developed. The existence of two critical temperatures $T_1$ and $T_2$ can be understood from the formula (4) as it follows. The frozen-in harmonic $Q_{-2k}$ decreases the energy of the system provided $\alpha_{-2k} > 0$. However, $\alpha_{-2k}$ must be sufficiently small in order to compensate the decrease of $|\alpha_k|$.
when $k_y$ becomes nonzero; this compensation takes place at $T_1$. At $T_2$, however, $\alpha_{-2k}$ changes sign and thus the second harmonic would no longer decrease the energy. It is easy to show that in the interval $\langle T_1, T_2 \rangle$ the renormalized anharmonic coefficient $\beta' = \beta - 18 \lambda^2 k_y^2/k_{-2k}$ is always positive and thus the rotated phase is stable. Note that within our approximations (the free-energy expansion is restricted to fourth-order terms, $s \leq 1$) the phase transition into the rotated stripe phase would be continuous.

The temperature region of existence of the rotated stripe phase crucially depends on the magnitude of $s$ which is difficult to estimate since $\lambda$ is unknown. On the other hand $(T_1 - T_0)$ can be estimated from the dispersion curve of the soft mode. For $K_2\text{SeO}_4$ [4] ($T_1 = 128 \text{ K}, T_C = 93 \text{ K}, \omega_c/\omega_0 \approx 0.2$) we get $(T_1 - T_0) \approx 3 \text{ K}$. Taking $s \approx 1$ the rotated phase might exist in the temperature interval $\langle 101 \text{ K}, 114 \text{ K} \rangle$. The maximum angle of rotation $k_y/k_0 \approx (\omega_c/\omega_0)^{1/2}$ would be a degree or so in magnitude. These estimates cannot be taken too seriously and merely suggest that it might be of interest to search for rotated IC phase in some $A_2\text{BX}_4$-type crystals.

Although we propose that rotation of the stripe phase away from the crystallographic $x$-direction may occur spontaneously, the same effect can be induced by applying to the crystal the $\sigma_{xy}$ stress component. Indeed for $A_2\text{BX}_4$-type crystals there exists a stress-induced Lifshitz invariant of the form

$$\delta^1 \sigma_{xy} \left( \frac{\partial p}{\partial y} q - p \frac{\partial q}{\partial y} \right).$$

Obviously, due to this term the structure will be modulated also in the $y$-direction, i.e. under the stress $\sigma_{xy}$ the stripe phase will rotate away from the crystallographic orientation. No such experiment has been performed so far.

3. Domain-like approximation.

We cannot exclude that the rotated phase persists in the whole temperature range of the IC phase, i.e. that $T_2 < T_C$. Actually higher-order terms not included in $f(1)$ cause hardening of the soft branch below $T_1$ and consequently $\alpha_{-2k}$ changes sign, if at all, at lower temperature than $T_2$. It is well known that near $T_C$ the SPW approximation is not adequate for describing the IC structure. The U-terms as $\frac{1}{\delta}(Q^6 + Q^{*6})$ produce higher harmonics of $Q_k$ and the IC structure develops into a domain-like structure which in our case would be a rotated stripe phase. According to the sign of $k_y$ we must distinguish two equivalent stripe phases rotated by an angle $+\theta$ and $-\theta$, respectively, around the $z$-axis. These two equivalent stripe phases could coexist in the crystal as macroscopic textural blocks [2]. Each rotated stripe phase consists of a periodic sequence of six almost perfect C domains (1, 2, 3, 4, 5, 6) separated by domain walls at a distance $d = 2 \pi/|k|$.

It can be shown by symmetry arguments [2] that if a wall separating C domains say 1 and 2 (we shall denote such a wall $1/2$) is rotated by $-\theta$, the wall 2/3 is equivalent only if it is rotated by $+\theta$, the wall 3/4 by $-\theta$ etc. From this it follows that a rotated stripe phase cannot be built up from equivalent walls, i.e. the neighbouring walls have different negative energies $\sigma_-$ and $\sigma_+$, respectively. Since the position of an isolated wall perpendicular to the $x$-axis is not stable [2] its energy may be written in the form

$$\sigma_-(\theta) = \sigma - a\theta + b\theta^2 - c\theta^3 + d\theta^4, \quad d > 0$$

and hence

$$\sigma_+(\theta) = \sigma + a\theta + b\theta^2 + c\theta^3 + d\theta^4. \quad (6)$$

Now it is clear why the energy of a rotated stripe phase which is a periodic sequence of walls with energies $\sigma_-$ and $\sigma_+$, respectively, is a function of $\theta^2$ (4).

We recall our result that due to the $\lambda$-term in the free energy (3) the coefficient $b$ in (6) becomes negative in some temperature region and this is actually why we gain energy by rotating the stripe phase.

It is important to note that neighbouring rotated walls carry opposite electric charges due to the polarization $P_y$ which has an opposite sign in neighbouring C domains. Such a wall configuration is connected with the electrostatic energy

$$4 \pi(2N) \frac{dP_y^2}{\sin^2 \theta/e} \approx 4 \pi(2N) \frac{dP_y^2}{\theta^2/e} \quad (7)$$

where $2N$ is the number of walls and $e$ is the static permittivity (for simplicity we neglect the anisotropy of $\epsilon$ in the $(x, y)$ plane). The electrostatic energy can be reduced by forming a zig-zag structure as it is depicted in figure 1. Obviously, the energy of walls remain the same since the total area of $\sigma_-$ and $\sigma_+$ walls remains the same as with planar walls but now we have to take into account the energy $F_B$ due to the bending of walls. $F_B$ can be written in the form

$$F_B = \frac{2N}{a} K = \frac{2N}{a} D\theta^2 \quad (8)$$

where we have used the fact that the positive energy $K$

![Fig. 1. — The zig-zag structure of charged domain walls.](image-url)
of one bend should be proportional to $\theta^2$. The magnitude of $D$ can be estimated in the following way. The gain $\Delta F$ in the free-energy density due to the rotation of the stripe phase can be estimated from (4) (taking the first term in the $\lambda^2$-expansion of $F$) as

$$
\Delta F \simeq -\frac{9}{2} \frac{2}{\beta^2} \frac{2}{\pi^2} \frac{a^2}{k_0^2} \frac{\theta^2}{\alpha_{-2k}}
$$

(9)

where we put $k_1 \simeq k_0 \theta$. Let us admit that this energy gain is entirely localized in the wall. When we bend a wall a part of it of a characteristic length $\xi_{\gamma} \sim (\xi_{\gamma}/\alpha_{-2k})^{1/2}$ is not rotated and we thus loose the energy

$$
-\Delta F \xi_{\gamma}/k_0 = \frac{a^2}{2\beta} \xi_{\gamma}^3 \frac{\xi_{\gamma}}{\alpha_{-2k}}
$$

which is the energy of a bend. Comparing this estimate with (8) we have

$$
D = \frac{a^2}{\beta} \xi_{\gamma}^3.
$$

(10)

The electrostatic energy of the zig-zag structure is given by

$$
F_e = \frac{32}{\pi^2} \frac{(2N)}{a} \frac{P_0^2}{\varepsilon} \times
$$

$$
\times \theta^2 \sum_{n=0}^{\infty} \frac{(2n+1)}{(2n+1)^3} \tanh \left[ \frac{\pi d}{2a} (2n+1) \right].
$$

This formula has been calculated in the following approximation: the zig-zag structure has been replaced by parallel planes each consisting of bands of the width $a$ with alternating surface charge $\pm 4 \pi P_0 \theta$. Assuming $d \gg a$ ($d$ becomes infinite at $T_c$) $F_e$ can be approximated by

$$
F_e \approx \gamma(2N) \frac{P_0^2}{\varepsilon} \theta^2 (1 - 2 e^{-\frac{nd}{a}});
$$

$$
\gamma = \frac{32}{\pi^2} \sum_{n=0}^{\infty} (2n+1)^{-3} = 3.408.
$$

(11)

The optimal value of $a$ is determined by the competition of the electrostatic and the bending energies of walls. Keeping in $F_e$ just the electrostatic self-energies of walls and neglecting the exponential term which corresponds to the electrostatic wall interaction, we get using (8), (10), (11) for the optimal value $a_0$

$$
a_0^2 = \left( \frac{P_0^2}{\varepsilon} \right)^{-1} \frac{2}{\beta} \frac{a^2}{\xi_{\gamma}} \xi_{\gamma}^3.
$$

(12)

Now from (7), (8), (11) it follows that the zig-zag structure will have a lower energy than the planar structure provided

$$
\frac{\gamma a_0}{2\pi d} < 1.
$$

(13)

This inequality is compatible with our assumption $a \ll d$. Let us now check the validity of (13). Using (12) we shall estimate the quantity

$$
\left( \frac{\gamma}{2\pi d} \frac{a_0}{P_0^2/\varepsilon} \frac{a^2}{\xi_{\gamma}^3} \right) = \left( \frac{\gamma}{2\pi d} \frac{a_0}{P_0^2/\varepsilon} \frac{a^2}{\xi_{\gamma}^3} \right) \left( \frac{T_1 - T_c}{T_1} \right) \frac{n kT_c}{P_0^2/\varepsilon} \approx 10^{-2} \cdot 10^3
$$

which has to be smaller than 1. The ratio of the free-energy density to the density of electrostatic energy can be written as ($T_1 \approx T_c \sim 100 K$)

$$
\frac{a^2}{P_0^2/\varepsilon} \approx \frac{T_1 - T_c}{T_1} \frac{n kT_c}{P_0^2/\varepsilon} \approx 10^{-2} \cdot 10^3
$$

where $n$ is the number of interacting unit cells per unit volume. We took a typical ratio of the phase-transition energy to the dipolar energy in improper ferroelectrics from [5], $(k_0 \xi_{\gamma})$ is of the order of the ratio of the domain-wall width to the distance $d$ between walls and thus it is certainly smaller than $10^{-1}$. Then with $s \approx 1$ we get for (14) an estimate $10^{-3}$ or $\gamma a_0/d \sim 10^{-1}$. Thus we conclude that a zig-zag structure has indeed a lower energy than the rotated planar structure. Obviously, it should have also a lower energy than a stripe phase perpendicular to the $x$-direction. This would be the case when

$$
\frac{1}{2Nd} (F_e + F_w) < |\Delta F|.
$$

Using (8), (9), (11) this condition leads to the inequality

$$
\frac{\gamma a_0}{d} < \frac{a^2}{P_0^2/\varepsilon} s(k_0 \xi_{\gamma})^2 \sim 10^{-1}
$$

when we have used the same estimates as before. Since the value of $|\Delta F|$ is clearly underestimated (higher harmonics creating domain walls were not included) we could in fact expect near $T_c$ the occurrence of a zig-zag domain-wall structure.

It should be emphasized that in contrast to a rotated stripe phase, the proposed zig-zag structure can in fact be built from equivalent zig-zag walls (see Fig. 1).

It is interesting to note that the electric field associated with charged walls could affect the distribution of crystal defects which in turn could pin walls in their positions. It is generally accepted that the wall pinning is responsible for large hysteresis effects observed in IC phases.

Our discussion applies also to $A_2BX_4$-type crystals, such as $[N(CH_3)_4]_2CuCl_4$ [6], the C phase of which is not ferroelectric but ferroelastic (the shear deformation $u_{xy}$ sets in spontaneously). Besides the $\lambda$-term in the free energy there is now the term

$$
u_{xy} \left( \frac{\partial p}{\partial y} - p \frac{\partial^2 u_{ij}}{\partial y^2} \right)
$$

which is responsible for the rotation of domain walls.
The mis-orientation of rotated walls from the crystallographic direction produces a large elastic energy due to incompatible shear strains induced by the order parameters on different sides of a wall. It is well-known [7] that this elastic energy can be reduced again by forming a zig-zag structure.

4. Conclusion.

We have shown that there is a third-order U-term in the free energy of $\mathrm{A_2BX_4}$-type crystals which produces in some temperature range a $k_y$ wave-vector component of the IC structure modulation. If this effect persists in the domain-like region of the IC structure it would correspond to a rotated stripe phase. Unlike in the case of an isolated wall, rotation of the stripe phase is not dictated by symmetry and may exist only under favorable magnitudes of some free-energy coefficients. On the other hand rotation of the stripe phase will be always induced by an applied shear stress. We have shown that the electrostatic energy of a rotated stripe phase can be reduced by forming equivalent zig-zag walls. Consequently, rather than a planar domain-wall structure a zig-zag structure should be expected near $T_c$ to occur.

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References