# Impossibility of observing a continuous commensurate-incommensurate transition

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It has been shown previously [J. Lajzerowicz and A. P. Levanyuk, Phys. Rev. B **49**, 15 475 (1994)] that in a *perfect* three-dimensional crystal the commensurate-incommensurate transition is always discontinuous due to a fluctuation-induced long-range *attraction* between domain walls. At the same time it has been concluded long ago that in *real* crystals a strong *repulsion* between the domain walls exists due to impurity-induced roughening of the domain walls. This poses the question whether the commensurate-incommensurate transition becomes continuous in real crystals. We argue that the most important point to answer this question is that a very slow activation motion of domain walls over disorder-induced potential barriers is necessary for making the repulsion operative, so that over a reasonable time of experiment this interaction ''propagates'' to distances that are no more than one order of magnitude bigger than the domain-wall width. Meanwhile the attractive interactions between the domain walls ''propagate'' almost instantaneously, thus leading to the conclusion that experimentally observed commensurate-incommensurate transition will always be discontinuous. Our estimates show that for structural incommensurate systems the ''equilibrium'' distance between the domain walls near transition point has the same order of magnitude as the domain-wall width. [S0163-1829(96)01841-3]

In physical systems exhibiting a commensurate (C) -incommensurate (IC) phase transition the domain-wall free energy becomes negative somewhere inside the IC phase thus making possible spontaneous creation of domain walls.[1–4] The character of this phase transition depends crucially on the domain-wall interaction: if it is repulsive at all the distances the phase transition is continuous. If, on the other hand, the interaction is attractive at large or intermediate distances (and the minimum of the interaction energy is negative in the latter case) the phase transition is discontinuous. In (academic) three-dimensional impurity-free systems without long-range fields and zero domain-wall width the domain walls repel each other exponentially, and the C-IC transition is continuous.

However, recently two of us have demonstrated[5] that thermal fluctuations of domain walls produce long-range fields in crystals and this, in turn, induces a long-range *attractive* interaction between the domain walls, thus making the phase transition discontinuous. The conclusion about the existence of a power-law attraction between the domain walls made in Ref. 5 is rather general and is valid even for nonferroelectric, nonferroelastic, and nonferromagnetic crystals. Moreover the estimates[5] show that the typical spacing between the domain walls has the same order of magnitude as the domain-wall width. This leads to the conclusion that the well defined domainlike regime (when the distance between the domain walls is much larger than the domain-wall width) is hardly realizable in impurity-free crystals.

Is this conclusion going to change if one takes into account the presence of defects in any real crystal? We remind the reader that, as it was established a while ago, the presence of quenched disorder drastically changes the domain-wall interaction (for reviews see, e.g., Refs. 6 and 7). For the simplest case of no underlying long-range forces involved, the exponential repulsion between the domain walls typical for impurity-free systems gets converted into a long-range power-law repulsion in the presence of defects. For example, in the presence of so-called random local field disorder this repulsion is proportional to $h^{-1}$ where $h$ is the distance between the domain walls. At the same time the fluctuation-induced attraction[5] decays as $h^{-2}$ or faster (not mentioning that the domain-wall fluctuations are hampered by defects) and the van der Waals attraction falls off as $h^{-4}$. Can one therefore expect that discontinuous C-IC phase transition occurring in ideal crystals becomes continuous in real crystals with defects? Addressing this issue constitutes the subject of this paper.

Before we start let us emphasize that we *do not know* what the nature of the C-IC transition in a crystalline system with defects would be if the fluctuation-induced attraction between the domain walls could be ''switched off.'' The matter is that in all the papers treating this question it was assumed that the interaction between the domain walls is due to their contacts, the defect-induced ''collisions.'' This is quite natural in the case of Refs. 6 and 7 because systems without long-range forces are considered there but, unfortunately, any crystalline system is not among them. From another side in systems with long-range fields[8,9] the defect-induced twisting of the domain walls leads to their interaction irrespective to the ''collisions,'' i.e., the treatment in Refs. 8 and 9 where, once again, the collisions were considered as the only origin of the interaction, is inconsistent.

 

One can expect that the ''collisionless'' interaction between the domain walls is attractive just as the fluctuation interaction and, therefore, the net interwall interaction induced by disorder is not known.

Below we favor a continuous C-IC transition neglecting the defect-induced attraction and take into account only the defect-induced repulsion as it has been calculated in Refs. 6–9. One can easily show that this repulsion becomes stronger than the fluctuation-induced attraction for quite a moderate impurity concentration. Then one would conclude (assuming that the neglection is reasonable) that in the truly equilibrium situation the C-IC transition in crystals with disorder is continuous.

On the other hand the very nature of the defect-induced interaction is such as it becomes operative only after the system ''visits'' spacial configurations when neighboring domain walls ''collide'' with each other, i.e., when they approach the distance of the order of the domain-wall width. Exploring those configurations requires activation motion over disorder-induced potential barriers, and one can expect (as shown below) that the time necessary for neighboring domain walls to collide increases exponentially with the distance between domain walls. In other words the disorder-induced interaction propagates very slowly and for a reasonable time of experiment the true equilibrium may not be reached. At the same time the fluctuation and van der Waals attractions become operative almost instantaneously, and therefore they dominate the large-distance behavior of the domain-wall interactions. We conclude that experimentally seen C-IC transitions in real three-dimensional crystals will be discontinuous similar to the ideal impurity-free case.

The real significance of this conclusion depends on what is really meant while referring to ''large distances,'' i.e., what is the typical falloff of the propagation velocity of the disorder-induced interaction. Therefore the necessary step in the theory of a C-IC transition pretending to have relevance to experiments on real three-dimensional systems should consist of estimates. The estimates cannot be completely general and should refer to a particular class of the materials. In this paper we make such estimates for structural IC systems.

It will be shown that the characteristic falloff of the propagation velocity of the disorder-induced repulsion can only be one order of magnitude bigger than the domain-wall width *practically independently of the defect concentration and their type*. Therefore ''the large distances'' referred to above are not really large at all.

We start from the situation when no underlying long-range interaction is associated with the domain-wall bending, and the effective power-law repulsion between the walls is purely due to defects. This interaction depends on wandering properties of a domain wall placed in a random medium. These properties are accumulated in the displacement-displacement correlation function, or equivalently in the dependence of typical transverse displacement of the domain wall $W$ on its linear size $L$. Similar to the case of the Brownian motion one can write[6,7].

$$W \approx \lambda^{1-\zeta} L^{\zeta}, \tag{1}$$

where $\lambda$ is a length scale dependent both on the type and strength of disorder and $\zeta$ is the wandering exponent dependent only on the disorder type. Their calculation is generally a difficult task but happily we will not need to know their precise values for the three-dimensional case under consideration. The effective ''collision''-induced repulsive interaction between the domain walls can be estimated as[6,7]

$$\Gamma\left(\frac{h}{L_{\max}}\right)^2, \tag{2}$$

where $\Gamma$ is the domain-wall stiffness and $L_{\max}$ is calculated from Eq. (1) setting $W=h$.

Let us now estimate the height of the barrier the domain wall has to overcome to assume the collision configuration, i.e., $W=h$, $L=L_{\max}$. This can be approximated as the ''elastic energy'' corresponding to a given $L$:

$$E(L) \approx \Gamma \frac{W^2(L)}{L^2} L^2 = \Gamma W^2, \tag{3}$$

i.e., the barrier height for the ''collision'' configuration is $\Gamma h^2$. This barrier is jumped over in time:[7]

$$t(h) \approx \tau_0 \exp[\Gamma h^2/T], \tag{4}$$

where $\tau_0$ has the of order of magnitude of atomic time, and $T$ is the temperature. It is remarkable that the time Eq. (4) does not depend on the defect concentration or type.

Within the mean-field region the domain-wall stiffness $\Gamma$ and the domain-wall width (an order-parameter correlation length) $r_c$ can be estimated as[10]

$$\Gamma \approx \Gamma_{\text{at}}\left(\frac{T_c - T}{T_0}\right)^{3/2}, \quad r_c \approx d\left(\frac{T_0}{T_c - T}\right)^{1/2}, \tag{5}$$

where $\Gamma_{\text{at}}$ is the ''atomic'' domain-wall stiffness coefficient that can be estimated as $T_{\text{at}} d^{-2}$ with $T_{\text{at}}$ the being ''atomic'' temperature ($T_{\text{at}} \approx 10^4$–$10^5$ K) and $d$ is of the order of lattice spacing. The parameter $T_c$ entering Eq. (5) is the temperature of the normal-C phase transition that is not realizable due to the IC phase formation, and $T_0 \approx T_c$ for the order-disorder and $T_0 \approx T_{\text{at}}$ for the displacive systems. Introducing $x = h/r_c$ and setting $T \approx T_c$, $T_c - T_l \approx T_c \approx T_l$ ($T_l$ is the C-IC transition temperature), one finds that the argument of the exponential in Eq. (4) can be estimated as $(T_0/T_c)^{1/2} x^2$. In other words, the characteristic length of the propagation velocity of the defect-induced repulsion between the domain walls is given by $r_c (T_c/T_0)^{1/4}$, i.e., both for the displacive and the order-disorder systems it is not longer than the domain-wall width. Even for order-disorder systems and, let's say $x=10$, the time in question is too large and the defect-induced repulsion does not propagate to distances larger than $10 r_c$. At these distances the domain walls attract each other due to Van der Waals and the fluctuation-induced forces.[5] Thus the C-IC transition should be discontinuous.

In the case of a ferroelectic domain wall[8,9] one has to remember that due to the Coulomb forces the typical domain-wall configurations caused by the defects are elongated along the direction of the spontaneous polarization. Assuming the latter to be directed along $x$ axis, one expects that for the bump of the domain wall of linear dimensions $L_x$ and $L_y$ one has $L_x \gg L_y$. Using the notations of Ref. 5 the energy per unit area of a distorted piece of the domain wall of height $W$ and linear sizes $L_x$ and $L_y$ can be estimated as

$$(\Gamma L_y^{-2} + aL_x^{-2}L_y)W^2, \tag{6a}$$

where

$$a = 2\pi P_0^2/\epsilon, \tag{6b}$$

$P_0$ is the spontaneous polarization, $\epsilon$ is the dielectric constant, and dielectric anisotropy is neglected, i.e., it is assumed that all the components of the dielectric tensor are either large or small (proper cubic ferroelectics or improper ones). The domain-wall energy is minimized for

$$L_x = \frac{L_y^{3/2}}{h_D^{1/2}}, \tag{7}$$

where $h_D = \Gamma/a$. It has been shown in Ref. 5 that $h_D \approx r_c$ for both cubic and improper ferroelectrics with quadratic dependence of polarization on the order-parameter components. One concludes that indeed $L_x \gg L_y$ in these cases for all the distances in consideration. For improper ferroelectics with higher-order dependence of the spontaneous polarization on the order parameter $\eta_0$ of the form $P_0 \propto \eta_0^s$ $(s \geqslant 3)$, one finds[5] $h_D > r_c$. In this case $L_x > L_y$ for $L_y > h_D$ only, for $L_y < h_D$ one has to set $L_x \approx L_y$, i.e., the long-range fields are unimportant for smallest distances. We have established previously that even in the absence of underlying long-range forces it is the distances between domain walls of the order $10r_c$ that are of importance. At the same time for an improper ferroelectric with $s=3$ one has[5] $h_D = r_c[T_0/(T_c - T)] \gg r_c$ at least for displacive systems. Thus the improper ferroelectrics with $s \geqslant 3$ are covered in our previous analysis of nonferroelectric systems. The case of uniaxial ferroelectrics will be discussed separately.

For $L_y > h_D$ one has

$$W = \lambda_1^{1-\zeta_1} L_y^{\zeta_1}, \tag{8}$$

the values of $\lambda_1$ and $\zeta_1$ are discussed in Refs. 8 and 9; in the range of the applicability of the theory is $\lambda_1 \ll r_c$.

Let us use the same simplified approach as above to estimate the time which one has to wait for the collisions to happen. In this case the energy of the deformed domain wall can be estimated as $E(L_x, L_y) \approx \Gamma W^2 L_x/L_y$. Setting $W = h$ and using Eqs. (7) and (8) one finds for proper ferroelectrics and the improper ones with $s=2$ (i.e., $h_D = r_c$)

$$\frac{E(h)}{T} = \frac{\Gamma h^2 h^{1/2\zeta_1}}{T\lambda_1^{(1-\zeta_1)/2\zeta_1} h_D^{1/2}} \approx \frac{\Gamma h^2}{T}\left(\frac{h}{r_c}\right)^{1/2\zeta_1} \approx \frac{T_{at}}{T_0^{1/2} T_c^{1/2}}\left(\frac{h}{r_c}\right)^{2+1/2\zeta_1}, \tag{9}$$

where we have set $\lambda_1 \approx r_c$ (underestimating the barrier) and used Eq. (5) with the same assumption as previously: $T \approx T_c$, $T_c - T_l \approx T_c \approx T_l$. Since for the random-field disorder one has[9] $\zeta_1 = 1/2$ and for the random temperature one[9] $\zeta_1 \approx 0.227$, we conclude that the propagation velocity of the disorder-induced repulsion falls off with $h$ even more rapidly compared with the case of short-range underlying interactions—the characteristic length scale is even shorter than $r_c$ for both order-disorder and displacive systems.

For displacive systems with random-field-type disorder it is already at $h = 3r_c$ when the time needed to realize the ''collisions'' is too large compared with the time of experiment as indicated by Eq. (9). The same conclusion is valid for order-disorder systems and random-temperature-type defects.

We emphasize once more that we have overestimated the disorder-repulsion and even under such circumstances have found almost no room for it. A more realistic theory would take into account the fact that the disorder-induced fluctuations of the domain walls are correlated due to the long-range fields induced by domain-wall wandering. Obviously such theory would leave even less room for disorder-induced repulsion of domain walls.

Equations (6) remain valid for uniaxial ferroelectrics as well if $\epsilon$ is the dielectric constant along a nonferroelectric axis.[9] As a result one finds[5] $h_D \approx r_c$ and Eq. (9) still applies.

The qualitative discussion of the influence of disorder on the interaction between ferroelastic domain walls is straightforward. Assuming independence of domain-wall wandering it has been shown[10] that underlying exponential repulsion between the domain walls stays intact in the presence of quenched disorder. At the same time the interaction between the domain walls arising due to elastic fields induced by domain-wall twisting is attractive and expected to be power-like: even weaker thermal fluctuations provoke a power-law attraction of the ferroelastic domain walls.[5] Thus we conclude that the interaction of ferroelastic domain walls is always attractive and at the C-IC phase transition with formation of such walls, the equilibrium distance between the walls is of the same order of magnitude as their width. A reservation is needed, however. For improper ferroelastics with $s \geqslant 3$, similar to improper ferroelectrics, the influence of the long-range fields may be unimportant at small distances between the walls and the results of the first part of this work seem to be relevant for these systems.

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