Defects as a reason of continuity of normal-incommensurate phase transitions

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(August 12, 2021)

Abstract

Almost all normal-incommensurate phase transitions observed experimentally are continuous. We show that there is not any theoretical reason for this general behaviour in perfect crystals. A normal-incommensurate phase transition that is not too far from the mean-field tricritical point should be discontinuous and it is highly improbable that so far reported normal-incommensurate phase transitions lie very far from this point. To understand this behaviour we study influence of defects on a hypothetical first-order normal-incommensurate phase transition in a pure material. We have found that this influence is strikingly different from that on other kinds of first-order phase transitions. The change of the discontinuity of the order parameter at the transition is negative and formally diverges within our approximate theory. At the same time the diminishing of the phase transition temperature remains finite. We interpret these results as an indication that at least some of the observed seemingly second-order normal-incommensurate transitions would be first-order transitions in defectless crystals.

PACS numbers: 61.44.Fw, 64.60.-i
I. INTRODUCTION

Almost all observed structural normal-incommensurate (N-IC) phase transitions are continuous (see for instance Ref. [1] as example of continuous cases and Ref. [2] for rare examples of discontinuous ones). This is in contrast with other types of structural phase transitions that are generally discontinuous. Such a discontinuity is not surprising because, as was pointed out by many authors [3], the second-order (continuous) phase transitions convert into first-order (discontinuous) ones because of many factors like shear deformations, crystal anisotropy, etc..., except for phase transitions involving uniaxial ferroelectrics and ferroelastics. These factors are operative by virtue of order parameter fluctuations. We show that also a broad class of normal-incommensurate (N-IC) phase transitions should be discontinuous in pure materials due to the solid-state elasticity. We refer to transitions that are not too far from the mean-field tricritical point. Then a question arises: why all observed experimentally N-IC phase transition are continuous?

In perfect crystals the N-IC first-order phase transitions should exist but it is reasonable to assume that in real crystals the defects can smear them [4]. Indeed, it is well known [5] that some defects influence dramatically on the incommensurate phases, destroying the long-range order at any concentration. Therefore strictly speaking, there are no N-IC phase transitions in real crystals or in other words, these transitions are always smeared. However, this smearing is not observed in the experiments and N-IC phase transitions appears usually as ”ordinary” transitions, i.e. without apparent smearing in the measured anomalies. As we have mentioned, what is surprising is that almost all N-IC phase transitions are second-order ones. We try to understand this general behaviour showing that first-order N-IC transitions can assume a continuous appearance if the crystal contains defects.

The paper is organized as follows. In Sec.II we demonstrate that close to the mean-field tricritical point a second-order N-IC phase transition converts into a first-order one because of the combined effect of the solid-state elasticity and the order parameter fluctuations. It is important that the conversion takes place even in the framework of the first order
perturbation theory of effects of critical fluctuations. The vicinity of the tricritical point where this conversion takes place is shown to be broad. In Sec.III we present the method to consider influence of defects on first-order phase transitions within first order perturbation theory where only linear terms in defect concentration taken into account (see e.g. Ref. 8,9).

To simplify the treatment, the phase transition in the pure material is supposed to be describable within the classical Landau theory. In Sec.IV we apply the method to a first-order N-IC phase transition. Because of the specific features of an incommensurate phase, this theory is not rigorously applicable here but we use the fact that N-IC transitions can be considered as a limiting case of some normal-commensurate (N-C) transitions. So we consider influence of defects on a normal-commensurate (N-C) first-order phase transition where the perturbation theory is valid, and then trace the changes produced by defects when the phase transition approaches a N-IC one. As we will see, we cannot reach the N-IC phase transition because that means to go beyond the applicability of the perturbation theory, but we can reveal some qualitative trends which provide us a base for the speculations. In Sec.V we show that the same trends take place when the first-order phase transition in the pure material is due to the combined effect of order parameter fluctuations and the solid-state elasticity as in Sec.II. Finally, the Sec.VI is devoted to the conclusions.

II. FLUCTUATION-INDUCED FIRST-ORDER N-IC PHASE TRANSITIONS

Among several factors that are relevant in the conversion of a second-order phase transition into a first-order one the most important one seems to be the solid-state elasticity. Indeed, as it is shown in Ref. 10, close to the mean-field tricritical point the combined effect of the order parameter fluctuations and the solid-state elasticity is so strong that the second-order phase transition converts into a first-order one quite far away from the region where the critical fluctuations become too much important. In other words, this converted phase transition takes place in the region of applicability of the Landau theory where the effects of the critical fluctuations can be considered within the first order perturbation theory. This
question was reconsidered for structural displacive transitions in Ref. [11], and it was shown that the region where the above-mentioned mechanism of conversion of a second-order into first-order phase transition results operative is very broad. Only the case of one component order parameter was considered. We shall show now how the same conclusions are valid for a N-IC phase transition.

We restrict ourselves to the case of one- \( k \) incommensurate phase, i.e. the case of two component order parameter (designated as \( \eta(r) = (\eta_1(\mathbf{r}), \eta_2(\mathbf{r})) \))\(^{12} \). Then, the Landau continuous-media potential takes the form:

\[
\Phi(\eta, u_{ik}) = \int [\varphi_\eta(\eta) + \varphi_u(\eta, u_{ik})] \, dv \tag{1}
\]

with

\[
\varphi_\eta(\eta) = \frac{1}{2} A(\eta_1^2(\mathbf{r}) + \eta_2^2(\mathbf{r})) + \frac{1}{4} B(\eta_1^2(\mathbf{r}) + \eta_2^2(\mathbf{r}))^2 + \frac{1}{6} C(\eta_1^2(\mathbf{r}) + \eta_2^2(\mathbf{r}))^3 + \frac{1}{2} D((\nabla \eta_1(\mathbf{r}))^2 + (\nabla \eta_2(\mathbf{r}))^2) \tag{2}
\]

and

\[
\varphi_u(\eta, u) = r(\eta_1^2(\mathbf{r}) + \eta_2^2(\mathbf{r}))u_{\|}(\mathbf{r}) + \frac{1}{2} Ku_{\|}^2(\mathbf{r}) + \mu(u_{ik}(\mathbf{r}) - \frac{1}{3} u_{\|}(\mathbf{r})\delta_{ik})^2 \tag{3}
\]

where \( K \) is the bulk modulus and \( \mu \) is the shear modulus (to compare with Ref. [11]). We shall assume that the coefficient \( A \) in Eq. 2 is the only temperature dependent coefficient: \( A = \alpha(T - T_c) \) where \( \alpha \) is a positive constant and \( T_c \) would be the second-order transition temperature if coupling between elasticity and fluctuations is neglected. The other coefficients may depend on pressure but we consider them positive constants.

As usually, it is assumed that the Landau potential is obtained as result of a partial integration of the partition function over all degrees of freedom, except those that correspond to the long-wave Fourier components of \( \eta(\mathbf{r}) \) and \( u_{ik}(\mathbf{r}) \). To find thermodynamic quantities, one has to integrate besides all the degrees of freedom except those probed in experiment. For our purpose it is enough to leave unintegrated the zero Fourier component of the order parameter. As in Ref. [11] we minimize over the elastic degrees of freedom. At this point one
has to make out the spatially homogeneous \((u_{ij}^{(0)})\) and inhomogeneous \((u_{ij}^{(i)})\) parts of strain:

\[
 u_{ij}(r) = u_{ij}^{(0)} + u_{ij}^{(i)} = u_{ij}^{(0)} + \frac{1}{2} \sum_{k \neq 0} \left[ k_i u^j(k) + k_j u^i(k) \right] e^{ik \cdot r} \tag{4}
\]

where \(u(k)\) is \(k\)-Fourier component of the displacement vector. Minimizing over the homogeneous and the inhomogeneous strain separately one obtains:

\[
 \int \varphi_u(\eta, u) dv = -\frac{r^2}{2K} \left( \sum_{k} \left[ \eta_{1k} \eta_{2-k} + \eta_{2k} \eta_{1-k} \right] \right)^2 - \\
 -\frac{r^2}{2\gamma} \sum_{k \neq 0} \sum_{k_1, k_2} \left[ \eta_{1k_1} \eta_{1-k_1-k} + \eta_{2k_1} \eta_{2-k_1-k} \right] \left[ \eta_{1-k_2} \eta_{1+k_2+k} + \eta_{2-k_2} \eta_{2+k_2+k} \right] \tag{5}
\]

where \(\gamma = K + \frac{4}{\pi} \mu\) and we put the system volume equal to unity.

Taking these terms into account, the Landau potential can be rewritten (limiting us to harmonic terms) as:

\[
 \Phi(\eta_0, \ldots, \eta_k, \ldots) = \Phi_0(\eta_0) + \Phi_h(\eta_0, \eta_{k \neq 0}) \tag{6}
\]

where \(\Phi_0\) is the Landau potential that depends only on the zero Fourier components of \(\eta\) (designated for simplicity as \(\eta_0 = (\eta_1, \eta_2)\)):

\[
 \Phi_0(\eta_0) = \frac{1}{2} A (\eta_1^2 + \eta_2^2) + \frac{1}{4} B (\eta_1^2 + \eta_2^2)^2 + \frac{1}{6} C (\eta_1^2 + \eta_2^2)^3 \tag{7}
\]

and \(\Phi_h\) are the harmonic terms of the Landau potential that depend on \(\eta_0\) and \(\eta_{k \neq 0}\):

\[
 \Phi_h(\eta_0, \eta_{k \neq 0}) = \sum_{k \neq 0} \frac{1}{2} \eta_{ik} M_{ij} \eta_{j-k} \tag{8}
\]

where

\[
 M_{11} = A + 3B_1 \eta_1^2 + \bar{B} \eta_2^2 + C (5\eta_1^4 + \eta_2^4 + 6\eta_1^2 \eta_2^2) + Dk^2 \tag{9}
\]

\[
 M_{22} = A + 3B_1 \eta_2^2 + \bar{B} \eta_1^2 + C (5\eta_2^4 + \eta_1^4 + 6\eta_1^2 \eta_2^2) + Dk^2 \tag{10}
\]

\[
 M_{12} = (2\bar{B} + 3\Delta) \eta_1 \eta_2 + 4C(\eta_1 \eta_2^3 + \eta_1^3 \eta_2) \tag{11}
\]
In the preceding equations the constants $\tilde{B}, B_1$ are defined as:

\[ \tilde{B} \equiv B - \frac{2r^2}{K} \]  

(12)

\[ B_1 \equiv B - \frac{2r^2}{3K} - \frac{4r^2}{3\gamma} = \tilde{B} + \frac{16r^2\mu}{9K\gamma} \equiv \tilde{B} + \Delta \]  

(13)

As we have mentioned, we must integrate over the degrees of freedom corresponding to the non-zero Fourier components of the order parameter according to the Gibbs distribution. Thus, the incomplete thermodynamic potential is:

\[ \Phi = \Phi_0(\eta_0) - T \ln \left\{ \exp \left( \frac{\Phi_h(\eta_0, \eta_{k\neq0})}{T} \right) \prod_{k\neq0} d\eta_{1k} d\eta_{2k} \right\} \]  

(14)

As $\Phi_h$ is quadratic in $\eta_{1k}$ and $\eta_{2k}$, the integration can be easily performed, obtaining:

\[ \Phi(\eta_0) = \Phi_0(\eta_0) + \frac{T}{2} \left\{ \sum_k \ln \left( M_{11} M_{22} - M_{22}^2 \right) \right\} \]  

(15)

Using the fact that in the incommensurate phase, the system is invariant respect to the phase of the order parameter vector $\eta$, we can choose it freely. Taking $\eta_1 \neq 0, \eta_2 = 0$ we considerably simplify the expression of the thermodynamic potential because in this case $M_{22} = 0$. Then, carrying out the integration of the second term of Eq. 15, and bearing in mind that $Dk_{\text{max}}^2 \gg A + 3B_1\eta_1^2 + 5C\eta_1^4$, we obtain:

\[ \tilde{\Phi}(\eta_0) = \frac{1}{2} \left[ A + \frac{k_{\text{max}} T}{2\pi^2 D} (3B_1 + \tilde{B}) \right] \eta_1^2 + \frac{1}{4} \left[ \tilde{B} + \frac{k_{\text{max}} T}{\pi^2 D} 6C \right] \eta_1^4 + \frac{1}{6} C\eta_1^6 - \frac{T}{12\pi D^{3/2}} \left\{ (A + 3B_1\eta_1^2 + 5C\eta_1^4)^{3/2} + (A + \tilde{B}\eta_1^2 + C\eta_1^4)^{3/2} \right\} \]  

(16)

There is a trivial renormalization of the reference energy taken into account and denoted by the symbol $\tilde{\Phi}$ in the left side of the Eq. 16. From the first two terms, one can see that the fluctuations provoke a renormalization also in the coefficients $A$ and $\tilde{B}$. This renormalization also takes place in the rest of the terms because of higher order corrections. Since this renormalization is not of interest within our phenomenological theory, henceforth that all the coefficients correspond to their renormalized values. Then, the final form
of the thermodynamic potential including the effects of order parameter fluctuations and solid-state elasticity is:

$$\tilde{\Phi}(\eta_0) = \frac{1}{2} A\eta_2^2 + \frac{1}{4} B\eta_4^4 + \frac{1}{6} C\eta_6^6 - m \left\{ (A + 3B_1\eta_2^2 + 5C\eta_4^4)^{3/2} + (A + \tilde{B}\eta_2^2 + C\eta_4^4)^{3/2} \right\}$$  \hspace{1cm} (17)

where $m \equiv T/12\pi D^{3/2}$.

The same discussion as in Ref. [11] about the final character of the phase transition can be carried out now for a N-IC one. As in that work we can see that close to the mean-field tricritical point, the order parameter at the transition temperature is such that:

$$B_1\eta_2^2 \gg A, C\eta_4^4$$  \hspace{1cm} (18)

As in Ref. [11] we find the value of the coefficient $A$ at the transition temperature ($A'$) and the order parameter discontinuity at the transition ($\eta_2'^2$):

$$A' = \frac{(3m)^{4/3}}{2(2C)^{1/3}} (3B_1)^2$$  \hspace{1cm} (19)

$$\eta_2'^2 = \left( \frac{3m}{2C} \right)^{2/3} (3B_1)$$  \hspace{1cm} (20)

We must conclude that the combined effect of order parameter fluctuations and the solid-state elasticity over a N-IC phase transition forces it to be discontinuous. This assertion is correct in a region close to the mean-field tricritical point, i.e. as can be see in Ref. [11] in a region such that $\tilde{B} < \mu B/K$. It is highly unlikely that all the reported N-IC phase transitions lie out of this region because it is very broad for structural systems. Such a conclusion is only applicable when dealing with perfect crystals because in our treatment we have forgotten about the influence of defects.

### III. INFLUENCE OF DEFECTS: THE METHOD

In this section we expose briefly the simplest version of treatment of influence of defects on first-order phase transitions[3]. This allows us to present formulas that are easy to generalize.
in the cases of our interest. What is more important: in these formulas we keep a term that, although omitted in previous papers, it is essential in the context of this work.

Within this section we consider one component order parameter \( \eta \) and "random local field" (RLF) defects. The Landau continuous-media thermodynamic potential without defects has the form:

\[
\Phi = \int \varphi(\eta) dv \tag{21}
\]

with

\[
\varphi(\eta) = \frac{1}{2} A \eta^2(r) + \frac{1}{4} B \eta^4(r) + \frac{1}{6} C \eta^6(r) + \frac{D}{2} (\nabla \eta(r))^2 \tag{22}
\]

where \( A = \alpha(T - T_s) \), \( T_s \) is the temperature at the spinode of the symmetrical phase and all other coefficients are supposed to be temperature-independent. As we are considering a first-order transition we assume that \( B < 0 \) and all the other coefficients positive.

The first-order transition temperature and the value of the order parameter discontinuity at the transition is obtained with \( \nabla \eta(r) = 0 \) and using the equilibrium equations: \( \partial \Phi / \partial \eta = 0 \) (minimum of thermodynamic potential condition) and \( \Phi = 0 \) (equality of thermodynamic potentials of the two phases condition). One has:

\[
\tilde{A} + B \tilde{\eta}^2 + C \tilde{\eta}^4 = 0 \tag{23}
\]

\[
\tilde{A} \eta^2 + \frac{1}{2} B \eta^4 + \frac{1}{3} C \eta^6 = 0 \tag{24}
\]

where \( \tilde{A} \) and \( \tilde{\eta}^2 \) are the values corresponding to the first-order phase transition temperature. From these equations:

\[
\tilde{A} = \frac{3B^2}{16C} \tag{25}
\]

\[
\tilde{\eta}^2 = -\frac{3B}{4C} \tag{26}
\]

in a perfect crystal.
To take into account RLF defects one has to add to the thermodynamic potential density $\varphi(\eta)$ in Eq. 22 a term:

$$- h(r) \eta(r)$$

where $h(r)$ is a "random local field" in the form:

$$h(r) = \sum_j h_j \delta(r - r_j)$$

where $h_j = \pm H$, $H$ is a coefficient characterizing the "strength" of the defect localized at $r = r_j$, and the sign of $h_j$ is random.

The order parameter decomposition into Fourier ($\eta_k$) components is the basic tool to study the influence of defects, so expressing:

$$\eta(r) = \sum_k \eta_k e^{ik \cdot r}$$

we consider the thermodynamic potential $\Phi$ as a function of all Fourier components. The next step is to minimize this function over all Fourier components except for the zero component ($k = 0$, designated by $\eta_0$) that at this stage is consider as a fixed parameter. One obtains to the linear approximation:

$$\eta_k^{(eq)} = \frac{h_k}{A + 3B\eta_0^2 + 5C\eta_0^4 + Dk^2}$$

Then, we use these equilibrium values in the thermodynamic potential and average over the defect positions obtaining:

$$\Phi(\eta_0) = \frac{1}{2} A\eta_0^2 + \frac{1}{4} B\eta_0^4 + \frac{1}{6} C\eta_0^6 + \frac{NH^2}{8\pi D^{3/2}} (A + 3B\eta_0^2 + 5C\eta_0^4)^{1/2}$$

where $N$ is the defect concentration. Instead of Eqs. 23 and 24 that give to us the values of the order parameter discontinuity at the transition and the transition temperature, one has now:

$$\tilde{\Lambda} + B\tilde{\eta}_0^2 + C\tilde{\eta}_0^4 + n \frac{3B + 10C\tilde{\eta}_0^2}{(A + 3B\tilde{\eta}_0^2 + 5C\tilde{\eta}_0^4)^{1/2}} = 0$$
\[
\tilde{A}\tilde{\eta}_0^2 + \frac{1}{2}B\tilde{\eta}_0^4 + \frac{1}{3}C\tilde{\eta}_0^6 + 2n(\tilde{A} + 3B\tilde{\eta}_0^2 + 5C\tilde{\eta}_0^4)^{1/2} = 2n\tilde{A}^{1/2}
\]  
(33)

where \(n = NH^2/8\pi D^{3/2}\), \(\tilde{A}\) and \(\tilde{\eta}_0^2\) are the values at the first-order phase transition temperature. Let us mention that in previous papers\[4,6,7\] the right hand side of Eq. 33 corresponding to thermodynamic potential of the symmetrical phase was set equal to zero. This term would not really modify the previous papers results but plays a basic role for a N-IC phase transition.

The applicability conditions of these formulas at first-order phase transition temperature can be obtained in the same way as in Ref. \[8,9\] and implies for the symmetric and nonsymmetric phases:

\[
nC^{3/2}B^2 < 1
\]  
(34)

where the numerical factor (of magnitude order of unity) has been omitted.

Designating the changes produced by defects in \(\tilde{A}\) and \(\tilde{\eta}_0^2\) (Eqs. 25 and 26) as \(\delta\tilde{A}\) and \(\delta\tilde{\eta}_0^2\) one can linearize Eqs. 32 and 33 with respect to this values to obtain:

\[
\delta\tilde{A} = -2n\sqrt{\frac{C}{3}}
\]  
(35)

\[
\delta\tilde{\eta}_0^2 = -14n\sqrt{\frac{C}{3B^2}}
\]  
(36)

One sees that RLF defects provoke both lowering of the phase transition temperature and diminishing of the discontinuity of the order parameter at the transition\[14\]. According to Eq. 34 we cannot set \(B = 0\) in the last equation. Moreover this linear approximation to Eqs. 32 and 33 lose their applicability at the same time that the equations do. So nonlinear corrections to equations 33 and 36 would be inconsistent with the applicability criterion for equations 32 and 33.
IV. APPROACHING A NORMAL-INCOMMENSURATE TRANSITION:
DEFECTS AND LANDAU THEORY

In as follows we consider N-IC phase transition as a special case of phase transition with
two component order parameter \((\eta_1 \text{ and } \eta_2)\) corresponding to isotropy in order parameter
space. This means that all invariants that we must consider in Landau thermodynamics
potential are power of the second order invariant. In other words, taking the Landau
potential density in the form:

\[
\varphi(\eta) = \frac{1}{2}A(\eta_1^2 + \eta_2^2) + \frac{1}{4}B_1(\eta_1^2 + \eta_2^2)^2 + \frac{1}{2}B_2\eta_1^2\eta_2^2 + \frac{1}{6}C(\eta_1^2 + \eta_2^2)^3 + \frac{1}{2}D((\nabla \eta_1)^2 + (\nabla \eta_2)^2)
\]

(37)

we approach a N-IC first-order transition if \(B_2 \to 0\) and all other coefficients are considered,
positive except \(B_1\) and temperature independent except \(A = \alpha(T - T_s)\). Now to make
allowances for defects we add to the thermodynamic potential density a term:

\[-h_1(r)\eta_1(r) - h_2(r)\eta_2(r)\]

(38)

where \(h_1\) and \(h_2\) are the two components of a "random local field":

\[h_{1,2}(r) = \sum_j h_{1,2}^j(r - r_j)\]

(39)

We assume that \(\langle (h_1^2) \rangle = \langle (h_2^2) \rangle = H^2\) and that the "direction" of the "vector" \(h = (h_1, h_2)\)
is random, i.e. \(\langle h_1^j h_2^j \rangle = 0\), where \(\langle \rangle\) designates the average.

We apply the method of the preceding section to find out the thermodynamic potential as
a function of the zero Fourier components \((k = 0, \text{ designated for simplicity by } \eta_1 \text{ and } \eta_2)\). It
is convenient to suppose that \(B_2 > 0\). The same results can be obtained for the case \(B_2 < 0\)
but the expressions are considerably longer in the latter case. Thus in what follows we take
the case in what expressions are straightforward, i.e. \(B_2 > 0\). Then, non symmetrical phase
equilibrium state corresponds to \(\eta_1 \neq 0, \eta_2 = 0\) or vice versa. Taking \(\eta_2 = 0\) we obtain
instead of equation \(31\) for a one component order parameter, the thermodynamic potential
in the form:
\[ \Phi(\eta_1, \eta_2) = \frac{1}{2} A \eta_1^2 + \frac{1}{4} B_1 \eta_1^4 + \frac{1}{6} C \eta_1^6 + 
\]
\[ + n \left\{ (A + 3B_1 \eta_1^2 + 5C \eta_1^4)^{1/2} + (A + (B_1 + B_2) \eta_1^2 + C \eta_1^4)^{1/2} \right\} \]
\[ \text{(40)} \]

and instead of equilibrium equations 23 and 24:
\[ \tilde{A} + B_1 \tilde{\eta}_1^2 + C \tilde{\eta}_1^4 + n \left\{ \frac{3B_1 + 10C \tilde{\eta}_1^2}{(A + 3B_1 \tilde{\eta}_1^2 + 5C \tilde{\eta}_1^4)^{1/2}} + \frac{(B_1 + B_2) + 2C \tilde{\eta}_1^2}{(A + (B_1 + B_2) \tilde{\eta}_1^2 + C \tilde{\eta}_1^4)^{1/2}} \right\} = 0 \]
\[ \text{(41)} \]
\[ \tilde{A} \tilde{\eta}_1^2 + \frac{1}{2} B_1 \tilde{\eta}_1^4 + \frac{1}{3} C \tilde{\eta}_1^6 + 2n \left\{ (\tilde{A} + 3B_1 \tilde{\eta}_1^2 + 5C \tilde{\eta}_1^4)^{1/2} + 
\right. \]
\[ \left. + (\tilde{A} + (B_1 + B_2) \tilde{\eta}_1^2 + C \tilde{\eta}_1^4)^{1/2} \right\} = 4n \tilde{A}^{1/2} \]
\[ \text{(42)} \]

where as before \( n = NH^2/8\pi D^{3/2} \), \( \tilde{A} \) and \( \tilde{\eta}_1^2 \) are the values corresponding to the first-order phase transition temperature.

The applicability of these equations at the first-order phase transition for the non-symmetric phase in the limit \( B_2 \to 0 \) (to try to describe the N-IC phase transition), implies:
\[ n \frac{C^{3/2}}{B_1^{1/2} B_2^{3/2}} < 1 \]
\[ \text{(43)} \]

revealing only the dependence on thermodynamic potential coefficients. It is obvious that this condition is violated if \( B_2 \) is sufficiently small, and therefore we can approach but not reach the N-IC phase transition.

In the same way as before the changes produced by defects in \( \tilde{A} \) and \( \tilde{\eta}_1^2 \) (Eqs. 25 and 26), now for a two component order parameter potential, are given in the linear approximation by:
\[ \delta \tilde{A} = -4n \sqrt{\frac{B_2 C}{3 | B_1 |}} \]
\[ \text{(44)} \]
\[ \delta \tilde{\eta}_1^2 = -2n \sqrt{\frac{C}{3B_1^2}} \left\{ 9 - 2 \sqrt{\frac{B_2}{| B_1 |}} + \sqrt{\frac{B_1}{B_2}} \right\} \]
\[ \text{(45)} \]

The applicability criterion of this linear approximation to Eqs. 11 and 12 is found easily imposing the natural condition \( \delta \tilde{\eta}_1^2 < \tilde{\eta}_1^2 \). In the limit \( B_2 \to 0 \):
\[ \delta \tilde{A} = -4n \sqrt{\frac{B_2 C}{3 | B_1 |}} \]
\[ \text{(46)} \]
\[ \delta \eta_1^2 = -2n \sqrt{\frac{C}{3 \mid B_1 \mid B_2}} \] (47)

and without the numerical factor, his applicability criterion is:

\[ n \frac{C^{3/2}}{B_1^{3/2} B_2^{1/2}} < 1 \] (48)

In this case, this applicability criterion is less restrictive than Eq. 43. This means that one can, in principle, go beyond the linear approximation remaining within the region of applicability of Eqs. 41 and 42 but it is not necessary for our discussion.

As we can see from equations 46 and 47, for an approach a N-IC transition, the correction to the transition temperature goes to zero while the correction to the order parameter discontinuity is negative and diverges. This means, of course, that the perturbation theory is no more applicable here. But also indicate that while defects suppress very strongly the order parameter discontinuity they do not influence (or weakly influence) the phase transition temperature.

V. APPROACHING A NORMAL-INCOMMENSURATE TRANSITION: DEFECTS AND CRITICAL FLUCTUATIONS

In the preceding section we have considered phase transitions that are first-order irrespectively to the order parameter fluctuations. However there exist another type of first-order phase transitions: those that are discontinuous due to critical fluctuations. In Sec.II we shown that structural N-IC phase transitions belongs to this class if it takes place in a broad vicinity of the mean-field tricritical point. In this section we study influence of defects on this type of transitions.

We study a N-C phase transition of the same symmetry class that in Sec.IV and we follow the evolution of the results when a N-IC phase transition is approached. For the thermodynamic potential one has now:
\[ \Phi(\eta_0, \ldots, \eta_k, \ldots) = \frac{1}{2} A\eta_1^2 + \frac{1}{4} \tilde{B}_1 \eta_1^4 + \frac{1}{6} C\eta_1^6 - m \left\{ (A + 3\beta \eta_1^2 + 5C \eta_1^4)^{3/2} + (A + (\tilde{B}_1 + B_2) \eta_1^2 + C\eta_1^4)^{3/2} \right\} + \\
+ \sum_k \frac{1}{2} \chi^{-1}_1(\eta_1, k) \eta_{1k} \eta_{1-k} + \sum_k \frac{1}{2} \chi^{-1}_2(\eta_1, k) \eta_{2k} \eta_{2-k} \]  

(49)

where as before \( m = T/12\pi D^{3/2} \), but now making the definitions:

\[ \tilde{B}_1 \equiv B_1 - \frac{2r^2}{K} \]  

(50)

\[ \beta \equiv B_1 - \frac{2r^2}{3K} - \frac{4r^2}{3\gamma} \equiv \tilde{B}_1 + \Delta \]  

(51)

The coefficients

\[ \chi^{-1}_1(\eta_1, k) \equiv A + 3\beta \eta_1^2 + 5C \eta_1^4 + Dk^2 - 3m \left\{ (A + 3\beta \eta_1^2 + 5C \eta_1^4)^{1/2}(3\beta + 10C \eta_1^2) + \\
+ (A + (\tilde{B}_1 + B_2) \eta_1^2 + C\eta_1^4)^{1/2}(\tilde{B}_1 + B_2 + 2C\eta_1^2) \right\} \]  

(52)

\[ \chi^{-1}_2(\eta_1, k) \equiv A + (\tilde{B}_1 + B_2) \eta_1^2 + C\eta_1^4 + Dk^2 - 3m \left\{ (A + 3\beta \eta_1^2 + 5C \eta_1^4)^{1/2}(3\beta + 10C \eta_1^2) + \\
+ (A + (\tilde{B}_1 + B_2) \eta_1^2 + C\eta_1^4)^{1/2}(\tilde{B}_1 + B_2 + 2C\eta_1^2) \right\} \]  

(53)

are calculated as in Sec.II performing the integration in Eq. 14, but now keeping out of this integration \( \eta_0 \) and \( \eta_k \) where \( k' \) is a fixed wave vector.

Defects are considered adding to this potential the term:

\[ - \sum_k (h_{1k} \eta_{1-k} + h_{2k} \eta_{2-k}) \]  

(54)

Proceeding as before with this thermodynamic potential we obtain in the limit \( B_2 \to 0 \):

\[ \delta A' = -2n \left( \frac{2C}{3m} \right)^{1/3} \]  

(55)

\[ \delta \eta_1^2 = -n \left( \frac{2C}{3m} \right)^{1/3} \left( \frac{1}{3\beta B_2} \right)^{1/2} \]  

(56)

close to the mean-field tricritical point. We see that for an approach a N-IC transition, the correction to the order parameter discontinuity is negative and diverges in the same way that
it do for the Landau theory (Sec. IV). Here the correction to the transition temperature also remains finite but do not tends to zero. As well as in the preceding section this indicates that while the defects suppress very strongly the order parameter discontinuity even for small defect concentrations but they weakly influence the phase transition temperature.

VI. CONCLUSIONS

Hypothetical N-IC first-order phase transitions are strikingly different from other "ordinary" first-order phase transitions where phase temperature always diminishes because of influence of defects, see Fig.1. Lowering of transition temperature in Fig.1 (a), (b) is consistent with the expectation that at some high enough defects concentration the phase transition temperature becomes equal to zero and the phase transition no more exists. The practical absence of this shift for a N-IC first-order phase transition (Fig.1 (c)) seems to indicate that the crystal with defects ”remembers” the first-order transition temperature in the pure material. This temperature might correspond to fairly rapid but still continuous changes in the satellite intensities with the temperature that might be interpreted as second-order transition. The results of this paper emphasize once more the strong influence of defects in the properties of incommensurate phases.

We would like to thank S.A. Minyukov, J.J. Sáenz and the members of his group specially to A. García-Martin and L.S. Froufe for useful discussions. Special thanks to D. Sanchez-Soria for her help and support.
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14 Numerical coefficients of this results are different respect to their values in Ref. 4.
FIGURES

FIG. 1. (a) Influence of "random temperature" defects on the phase diagram of a first-order phase transition with elasticity taken account. (b) Influence of "RLF" defects on the phase diagram of a first-order phase transition with elasticity taken account. If the elasticity is neglected the same behaviour that in (a) is obtained. (c) Expected influence of "RLF" defects on the phase diagram of a N-IC first-order phase transition
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Fig. 1a PRB
--- Pure material
--.-- Material with defects

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Fig. 1b PRB
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Fig. 1c PRB