Fluctuation-induced first-order phase transitions near mean-field tricritical points in solids

1993 J. Phys.: Condens. Matter 5 4419

(http://iopscience.iop.org/0953-8984/5/26/013)

J. Phys.: Condens. Matter 5 (1993) 4419–4428. Printed in the UK

Fluctuation-induced first-order phase transitions near mean-field tricritical points in solids

A P Levanyuk†‡, S A Minyukov‡ and M Vallade†

† Université Joseph Fourier, Laboratoire de Spectrometrie Physique, Boite Postale 87, 38402 Saint-Martin-d'Hères Cédex, France

‡ Institute of Crystallography, Russian Academy of Sciences, 117333 Moscow, Russia

Received 4 January 1993

Abstract. We consider displacive phase transitions with a one-component order parameter near what would be a tricritical point (TCP) in the mean-field approximation. As the system in question is a solid, a continuous phase transition is generally impossible. It is shown that, along a fairly large portion of the phase transition line, a fluctuation-induced first-order phase transition occurs within the region of applicability of the perturbation theory. Close to the mean-field TCP the first-order phase transition proves to be strong, i.e. the discontinuity of the order parameter is of the same order of magnitude as the order parameter at $T = 0$. Below T_c the temperature dependence of the order parameter is given by an equation containing a non-analytical term related to the critical fluctuations, and the other thermodynamic anomalies are governed by this (renormalized) temperature dependence of the order parameter. The present theory shows that first-order transitions which are accompanied by strong precursor anomalies in the symmetrical phase, as is the case for ammonium chloride and quartz, would very likely be second order in the mean-field approximation.

1. Introduction

It has been recognized for a long time that the condition of applicability of the Landau theory near a tricritical point (TCP) deserves special discussion [1]. If the phase transition under consideration occurs in a liquid, the situation is relatively simple; the classical (mean-field) picture is correct (up to logarithmic corrections [2]). This result is fairly natural. The coefficient of the quartic term in the order parameter expansion of the thermodynamic potential is zero at the TCP and it is precisely this term which is responsible for the interaction between the order-parameter fluctuations, leading to the non-classical behaviour in three-dimensional space. The situation is not so simple, however, when the phase transition occurs in a solid. In this case the medium has a non-zero shear modulus μ, and the homogeneous and inhomogeneous strains are governed by different elastic moduli. This has two main consequences.

(i) The order-parameter fluctuations renormalize the bulk elastic modulus K, so that macroscopic elastic instability and a first-order transition can occur before the continuous transition point of the 'ideal' (incompressible) system is reached [3, 4]. This happens as soon as the specific heat of the 'ideal' system diverges (a continuous transition could only occur at a very high pressure in this case [5]). At $d = 3$, divergence of the specific heat is expected for a one-component order-parameter second-order phase transition (in the absence of long-range interactions) and for TCPs, whatever the number of components of the order parameter. In this latter case the specific heat is strongly divergent (proportional

0953-8984/93/264419+10$07.50

to $(T - T_c)^{-1/2}$) so that a more pronounced discontinuous character of the transition is expected.

(ii) The lowest-order interaction between the order-parameter fluctuations does not disappear close to the 'mean-field TCP' (i.e. the TCP which would correspond to $\mu = 0$).

Therefore, the question arises of the self-consistency of the perturbation approach when μ is different from zero; does the fluctuation-induced first-order transition occur at a point where the criterion of smallness of the critical fluctuation effects is fulfilled [6]? How far from the mean-field TCP is this true? This problem has been already considered by Bruno and Sak [7], in the framework of a general analysis of a compressible Ising system by group renormalization techniques.

The purpose of the present paper is to give a more detailed analysis of the specific problem of the vicinity of the TCP, using what we think to be a simpler formulation which has already been used but for transitions which are far from the TCP [8]. Furthermore the role of the displacive character of the transition, which is known to be important in determining the range of applicability of the perturbation theory, is emphasized, and our results are expressed as functions of the two small parameters which control the perturbation expansion: T_c/T_{at} (where T_{at} is an 'atomic' temperature of about 10^4–10^5 K) and μ/K. An order of magnitude of the importance of fluctuations in two typical materials which exhibit a structural phase transition is estimated, with the conclusion that these fluctuations are sufficiently large to account for the observed first-order character of these transitions.

The paper is organized as follows. In section 2 we derive the perturbation theory close to the mean-field TCP. In section 3, the role of fluctuation in ammonium chloride and quartz is estimated through their contribution to the elastic constant in the symmetrical phase, and in section 4 we summarize our results and we make some additional remarks about possible extensions of the perturbation theory to multi-component order-parameter systems.

2. Perturbation theory

The effective continuous-media Hamiltonian has the form of the Landau thermodynamic potential

$$\Phi(\eta, u_{ik}) = \int [\varphi_\eta(\eta) + \varphi_u(\eta, u)]\,\mathrm{d}v \tag{1}$$

with

$$\varphi_\eta(\eta) = \tfrac{1}{2}A\eta^2 + \tfrac{1}{4}B\eta^4 + \tfrac{1}{6}C\eta^6 + \tfrac{1}{2}D\nabla\eta^2 \tag{2}$$

and

$$\varphi_u(\eta, u) = r\eta^2 u_{11} + \tfrac{1}{2}Ku_{11}^2 + \mu(u_{ik} - \tfrac{1}{3}u_{11}\delta_{ik})^2 \tag{3}$$

where η is the order parameter and u_{ik} is the strain tensor. We shall assume that the coefficient A in equation (2) is the only temperature-dependent coefficient: $A = A'(T - T_0)$. The other coefficients do not depend on temperature but may depend, for example, on pressure. This assumption is made for simplicity only and the results given below can easily be generalized.

It is assumed that the effective Hamiltonian is obtained as the result of a partial integration of the partition function over all the degrees of freedom but the long-wave

Fourier components of $\eta(r)$ and $u_{ik}(r)$, i.e. these two functions contain Fourier components with $k < k_m$ only, where k_m is the cut-off vector (which does not enter the real results of the theory). To find the thermodynamic quantities, one has to integrate over all the degrees of freedom but those probed in the experiment. For our purpose it will be enough to leave unintegrated the zero Fourier component of the order parameter (η_0) only. As the effective Hamiltonian (1) is quadratic in the strain components, it is possible to minimize over the elastic degrees of freedom instead of the integration if one is interested in the phase transition anomalies but not in the normal (background) parts of the quantities. At this minimization, one has to discriminate between spatially homogeneous and inhomogeneous strains:

$$u_{ij}(r) = u_{ij}^0 + \tfrac{1}{2}\sum_{k\neq 0}[ik_j u_i(k) + ik_i u_j(k)]\exp(ik\cdot r) \tag{4}$$

where u_{ij}^0 is the homogeneous strain and $u_i(r)$ is the displacement vector. One has to minimize with respect to u_{ij}^0 and $u_i(k)$ separately [3]. As a result, one obtains

$$\int \varphi_u(\eta, u)\,dV = -\frac{r^2}{2K}\left(\sum_k \eta_k\eta_{-k}\right)^2 - \frac{r^2}{2\lambda}\sum_{k\neq 0}\sum_{k_1,k_2}\eta_{k_1}\eta_{-k_1-k}\eta_{-k_2}\eta_{k_2+k} \tag{5}$$

where $\lambda = K + \frac{4}{3}\mu$ and we put the volume of the system equal to unity.

It is convenient to single out in the effective Hamiltonian the terms F_0 depending on η_0 only, the harmonic terms F_h depending on η_0 and η_k and the anharmonic terms F_a. One has

$$F_0 = \tfrac{1}{2}A\eta_0^2 + \tfrac{1}{4}\tilde{B}\eta_0^4 + \tfrac{1}{6}C\eta_0^6 \tag{6}$$

where

$$\begin{aligned} A &= A'(T - T_0) \\ \tilde{B} &= B - 2r^2/K \end{aligned} \tag{7}$$

and

$$F_h = \tfrac{1}{2}\sum_{k\neq 0}(A + 3B_1\eta_0^2 + 5C\eta_0^4 + Dk^2)\eta_k\eta_{-k} \tag{8}$$

where

$$B_1 = B - \tfrac{2}{3}r^2/K - \tfrac{4}{3}r^2/\lambda = \tilde{B} + \tfrac{16}{9}r^2\mu/K\lambda \equiv \tilde{B} + \Delta \tag{9}$$

and

$$F_a = \tfrac{1}{4}\hat{B}\sum_{k\neq 0}\eta_{k_1}\eta_{k_2}\eta_{k_3}\eta_{-k_1-k_2-k_3} - \frac{r^2}{2K}\left(\sum_{k\neq 0}\eta_k\eta_{-k}\right)^2 + \dots \tag{10}$$

where

$$\hat{B} = B - 2r^2/\lambda = \tilde{B} + \tfrac{3}{2}\Delta. \tag{11}$$

The ellipsis (...) in equation (10) represents terms which will not be taken into account explicitly.

Within the perturbation theory, one calculates the terms of the series

$$\Phi(\eta_0) = F(\eta_0) - T\log\left[\int \exp\left(-\frac{F_h(\eta_0,\eta_k)}{T}\right)\prod_k d\eta_k\right] + \langle F_a\rangle - \frac{1}{2T}(\langle F_a^2\rangle - \langle F_a\rangle^2) + \ldots \tag{12}$$

where $\langle\rangle$ designate averaging with the help of F_h. The first fluctuation correction to the Landau mean-field theory arises from the second term in equation (12). The integration over the Gaussian variables η_k can be readily performed and, assuming that $Dk_m^2 \gg A + 3B_1\eta_0^2 + 5C\eta_0^4$, one obtains

$$\Phi(\eta_0) = \tfrac{1}{2}[A + (T/2\pi^2)(k_m/D)3B_1]\eta_0^2 + \tfrac{1}{4}[\widetilde{B} + (Tk_m/\pi^2 D)5C]\eta_0^4 - \tfrac{1}{6}C\eta_0^6 - (T/12\pi D^{3/2})(A + 3B_1\eta_0^2 + 5C\eta_0^4)^{3/2}. \tag{13}$$

From the first two terms, one sees that there is a trivial renormalization of the coefficients A and $\widetilde{B}$ due to fluctuations. In fact, renormalization also takes place for the coefficients A and $3B_1$ in the last term of equation (13), as can be seen from the calculation of the higher-order terms in equation (12). Since this renormalization is of no interest within the phenomenological theory, we shall assume in the following that A, $\widetilde{B}$ and B_1 correspond to the renormalized quantities.

For the subsequent discussion, we have found it convenient to introduce the following dimensionless quantities:

$$t = (T - T_0)/T_0 \qquad b = \widetilde{B}/B_1 \qquad c = CA'T_0/B_1^2$$
$$g = TB_1/4\pi(A'T_0D^3)^{1/2} \qquad x = \sqrt{B_1/A'T_0}\,\eta_0 \qquad \varphi = \Phi B_1/(A'T_0)^2. \tag{14}$$

The orders of magnitude of some of these quantities can be found in a way which is conventional for displacive transitions [6] by taking

$$A' \simeq 1 \qquad D \simeq T_{at}d^2 \qquad B \simeq T_{at}d^3 \qquad C \simeq T_{at}d^6$$

where T_{at} is a typical 'atomic temperature' ($T_{at} \simeq 10^4$–10^5 K) and d is the lattice spacing. Close to the TCP, $\widetilde{B} \simeq 0$ and $B_1 \simeq \Delta \simeq (\mu/K)(r^2/\lambda)$. B_1 is then expected to be of the order of $B\mu/K \simeq T_{at}d^3\mu/K$. Then one obtains

$$g \simeq (1/4\pi)\sqrt{T_0/T_{at}}(\mu/K) \qquad c \simeq (T_0/T_{at})(K/\mu)^2. \tag{15}$$

Both these quantities are small for displacive transitions.

Using reduced units, equation (13) can be rewritten

$$\varphi(x) = \tfrac{1}{2}x^2 + \tfrac{1}{4}bx^4 + \tfrac{1}{6}cx^6 - \tfrac{1}{3}g(t + 3x^2 + 5cx^4)^{3/2}. \tag{16}$$

At first sight, it seems that $\varphi(x)$ would be negative at large x as soon as $g\sqrt{c} \gtrsim 0.04$. Let us note, however, that, at very large x, equation (16) is no longer correct because the assumptions made to deduce equation (13) from equation (12) are no longer valid. A closer

investigation indeed shows that the fluctuation correction becomes negligible at large x, as expected. For small x, one has

$$\varphi(x) \simeq \tfrac{1}{3}gt^{3/2} + \tfrac{1}{2}(t - 3g\sqrt{t})x^2 + \dots.$$

The fluctuation correction to the coefficient of the quadratic term is small as long as

$$t > 9g^2 = \bar{t}. \tag{17}$$

This condition corresponds to the range of applicability of the perturbation theory [8]. The equilibrium condition deduced from equation (16) is

$$x[t + bx^2 + cx^4 - g(3 + 10cx^2)(t + 3x^2 + 5cx^4)^{1/2}] = 0. \tag{18}$$

The two main consequences which follow from the resolution of equation (18) are the following.

(i) A first-order phase transition is driven by the fluctuation term, even for $b > 0$.

(ii) For sufficiently small b the first-order transition temperature falls in the range of validity of perturbation theory, which ensures the self-consistency of the method.

These two points have been checked using numerical calculation (figure 1), but they can also be understood using simple considerations. Let us assume that close to the transition temperature T_c the order parameter is such that

$$3x^2 \gg |t| \qquad 3x^2 \gg 5cx^4. \tag{19}$$

(The validity of these assumptions will be checked below.) Then, there is a cubic term of approximately $g\sqrt{3}|x|^3$ in the free energy (equation (16)), which obviously leads to the occurrence of a first-order transition.

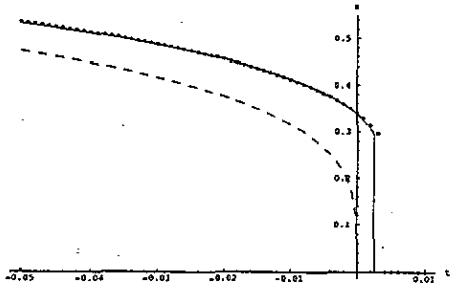

Figure 1. Temperature dependence of the order parameter: ●, solution of equation (18) with $b = 0$, $c = 1$ and $g = 0.005$; – – –, mean-field curve at the tricritical point ($b = 0$, $c = 1$, $g = 0$); ——, fit of the perturbation theory by an 'effective' mean-field theory ($b = -0.119$, $c = 1.041$, $g = 0$).

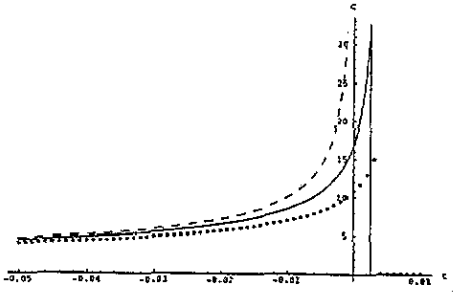

Figure 2. Temperature dependence of the specific heat C: ●, perturbation theory with $b = 0$, $c = 1$ and $g = 0.005$; – – –, tricritical mean-field curve ($b = 0$, $c = 1$, $g = 0$); ——, 'effective' mean-field theory ($b = -0.119$, $c = 1.041$, $g = 0$) as deduced from the fit shown in figure 1. (We note that it is not possible to obtain good fits for both the order parameter and the specific heat with the same set of parameters.)

Let us first consider the case when the transition is approached along the line $b = 0$. The order-parameter jump and the transition temperature can be calculated from the two equations

$$\varphi(x_c) = x_c^2(\tfrac{1}{2}t_c + \tfrac{1}{6}cx_c^4 - \sqrt{3}g|x_c|) = 0$$
$$(\partial\varphi/\partial x)_{x_c} = t_c + cx_c^4 - 3\sqrt{3}g|x_c| = 0. \tag{20}$$

One finds that

$$x_c = (3\sqrt{3}/2)(g/c)^{1/3} \simeq (T_{at}/T_0)^{1/6}(\mu/K)$$
$$|t_c| = [(3\sqrt{3}/2)g]^{4/3}(1/c)^{1/3} \simeq (T_0/T_{at})^{1/3}(\mu/K)^2. \tag{21}$$

The jump x_c has to be compared with the order parameter far below T_c, where $x_0 \simeq (1/c)^{1/4}$:

$$x_c/x_0 \simeq (T_0/T_{at})^{1/12}(\mu/K)^{1/2}. \tag{22}$$

Owing to the small exponent $1/12$, this ratio is usually not small and the first-order character of the transition is found to be quite strong. On the other hand, comparing equations (21) and (17) gives

$$|t_c|/\tilde{t} \simeq 1/3(g^2c)^{1/3} \simeq (T_{at}/T_0)^{2/3} \gg 1. \tag{23}$$

This means that the first-order transition is expected to occur in the region of applicability of perturbation theory. Using equation (21), one can check that

$$3x_c^2/|t_c| \simeq 3x_c^2/5cx_c^4 \simeq 1/(g^2c)^{1/3} \gg 1 \tag{24}$$

which is consistent with the assumption made in equation (19). Thus we come to the conclusion that critical fluctuations are strong enough to trigger a first-order transition well before the (mean-field) TCP is reached.

The strength of the fluctuations is reflected in the precursor increase in the specific heat above T_c (figure 2). The anomalous part ΔC has its maximum at T_c and, at this point,

$$\Delta C \simeq (A'^2T_0/B_1)(g/4\sqrt{|t_c|}) \simeq (T_0/T_{at})^{4/3}(K/\mu)C_{at} \simeq (T_0/T_{at})^{1/3}(K/\mu)\Delta C_L \tag{25}$$

where C_{at} is the 'atomic' (Dulong and Petit) specific heat and ΔC_L is the jump in the specific heat within the Landau theory of the second-order phase transition (far from the TCP).

The thermal expansion and the elastic constants are also expected to show the same type of behaviour as the specific heat, and anomalies are easier to observe experimentally in the case of the displacive phase transition because the relative changes are usually larger than for the specific heat.

In the low-temperature (asymmetrical) phase the entropy change is found to be

$$\Delta S = -\tfrac{1}{2}(A'^2T_0/B_1)[x^2 - g(t + 3x^2 + 5cx^4)^{1/2}]. \tag{26}$$

Close to T_c,

$$\Delta S \simeq -\tfrac{1}{2}(A'^2T_0/B_1)(x_c^2 - \sqrt{3}g|x_c|). \tag{27}$$

The second term is smaller than the first by a factor $\sqrt{3}g/x_c \simeq (g^2c)^{1/3} \simeq (T_0/T_{at})^{2/3}$, so that the fluctuation contribution to the entropy appears essentially through the renormalization of the order parameter x_c. The same result also holds for other quantities proportional to $\langle\eta^2\rangle$ such as the volume change or the optical indices.

Let us now consider what happens when the coefficient b is positive. As long as b is sufficiently small, all the above considerations still hold. The influence of b becomes noticeable only when $bx_c^2 > cx_c^4$ (see equation (18)), i.e. when

$$b > (g^2c)^{1/3} \simeq (T_0/T_{at})^{2/3}. \tag{28}$$

In this latter case, one finds that equation (21) has to be replaced by

$$\begin{aligned} x_c &\simeq 2\sqrt{3}g/b \\ |t_c| &\approx 6g^2/b. \end{aligned} \tag{29}$$

By comparing equation (29) with equation (17), one can see that the first-order transition falls within the range of applicability of the perturbation theory as long as $b < \frac{2}{3}$. Thus, over rather a large range of $\widetilde{B}$ ($\widetilde{B} \leqslant (\mu/K)B$), we expect a fluctuation-induced first-order transition outside the scaling region ('incipient second-order phase transition'). At the upper limit of the range of applicability of the theory ($b \simeq \frac{2}{3}$) the relative jump is

$$x_c/x_0 \simeq 3\sqrt{3}g/\sqrt{b} \simeq (9/\sqrt{2})g \simeq \sqrt{T_0/T_{at}}(\mu/K) \ll 1. \tag{30}$$

The transition is then close to a second-order transition. For larger b, one can guess that the jump becomes almost unobservable, but a quantitative estimate cannot be derived from the present theory.

Bruno and Sak [7] reached essentially the same qualitative conclusions, although they make a cruder approximation in calculating the fluctuation correction to the free energy (compare their equation (6-49) and our equation (13)).

3. Comparison with experimental results

The present discussion is relevant for one-component order-parameter systems without long-range interactions (proper ferroelectrics or ferrelastics are excluded). A good candidate for testing the theory described in the preceding section is an ammonium chloride crystal which exhibits a first-order structural phase transition at room pressure. The importance of critical fluctuations in this material is clearly demonstrated by the strong temperature dependence of the static elastic constant C_{11} in the high-symmetry phase. An accurate quantitative estimate of the fluctuation contribution to this elastic constant can be deduced in this case, from the comparison of hypersonic and ultrasonic measurements [9, 10]; in the former case the order parameter is 'clamped' whereas in the latter case it is 'free'. The difference ΔC_{11} between the high frequency (C_{11}^{∞}) and the low frequency (C_{11}^{0}) is directly related to the fluctuations of the order parameter [6]:

$$\Delta C_{11} = r^2T/\left(4\pi\sqrt{A'(T-T_0)D^3}\right) = (r^2/B_1)(g/\sqrt{t}). \tag{31}$$

Using the data reported in [9], the temperature dependence of $\Delta C_{11}/C_{11}^{\infty}$ can actually be fitted by equation (31) over a range of temperatures of about 80 K above the transition temperature (figure 3). The temperature T_0 is found to be 236.1 K ($T_c - T_0 \simeq 7$ K) and

$$(r^2/B_1C_{11}^{\infty})g \simeq 2.5 \times 10^{-2}. \tag{32}$$

From equations (9) and (14), one has

$$(B_1 - \widetilde{B})/B_1 = 1 - b = \tfrac{16}{9}(\mu/K)(r^2/B_1\lambda) \simeq \tfrac{8}{3}[(C_{11} - C_{12})/(C_{11} + 2C_{12})](r^2/B_1)C_{11} \tag{33}$$

(neglecting elastic anisotropy).

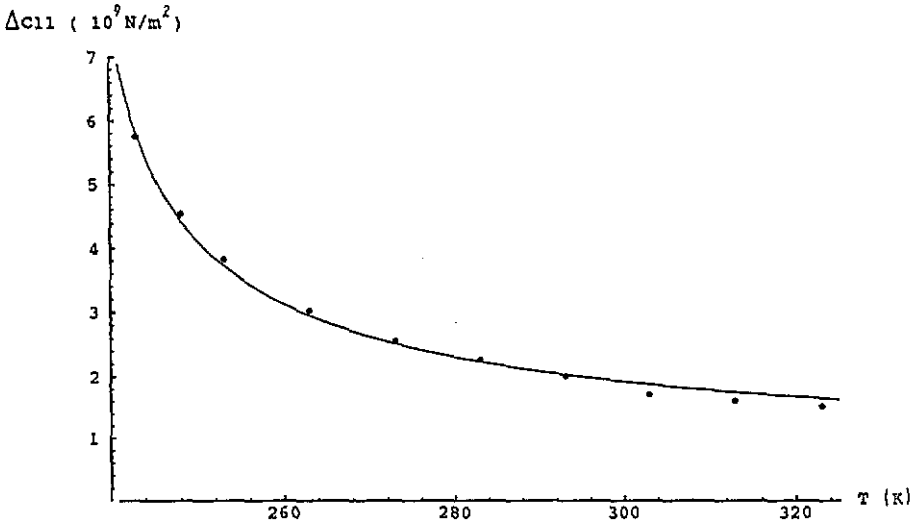

Figure 3. Temperature dependence of the difference ΔC_{11} between hypersonic and ultrasonic elastic constants of ammonium chloride, in the high-temperature phase: ●, experimental data reported in [9, 10]; ——, fit using the formula $\Delta C_{11} = 15.25/\sqrt{T - 236.1}$ (with ΔC_{11} in 10^9 N m^{-2} and T in kelvins).

From equations (32) and (33) and the experimental values of the elastic constants, one obtains

$$g(1 - b) \simeq 0.03. \tag{34}$$

There is also some evidence of strong elastic constant anomalies in the symmetrical phase of quartz [11]. In this case the situation is complicated by the occurrence of an incommensurate phase between the high-temperature β-phase and the low-temperature α-phase [12]. The critical fluctuations related to the incommensurate ordering, however, are important only over a very limited range of temperatures above the transition. It is then possible to extract the contribution of the fluctuations of the α–β order parameter to the elastic constants which extends over a larger range of temperatures. The estimate for this contribution is less accurately determined than for ammonium chloride; the result leads to an expression very similar to equation (34):

$$g(1 - b) \simeq 0.04. \tag{35}$$

We conclude that for both compounds the coefficient g which measures the strength of the fluctuations has an order of magnitude of several 10^{-2}, which is enough to induce the

strong first-order transition tractable within perturbation theory even if b is positive (see figure 1). Therefore it would be interesting to re-analyse the thermodynamic anomalies in these materials within the framework of the perturbation theory. A quantitative comparison, however, would require a careful analysis of the whole set of experimental data (order parameter, thermal expansion, specific heat, etc) and it would be necessary first to prove that these materials are close enough to the mean-field TCP (b sufficiently small). Furthermore it is clear that anisotropy of both the correlations and the elasticity have to be considered [13] in a quantitative analysis. We also note that equation (13) is only valid when Dk_m^2 is sufficiently large; far from T_0 some corrections to equation (13) have to be taken into account, and the temperature dependence of the coefficient of the Landau expansion can also become important. A more detailed analysis of experimental data will be published in a separate paper.

4. Conclusion

The widespread, almost standard way to interpret experimental data concerning first-order structural phase transitions is to use the Landau thermodynamic potential with a negative quartic term coefficient. We have shown that such an interpretation may be highly questionable, at least for systems for which there is no dramatic suppression of critical fluctuations due to long-range interactions. Indeed we have shown that, for systems which are close to the mean-field tricritical condition, the critical fluctuations are large enough to induce a first-order transition when the solid state elasticity is taken into account (rigidity modulus different from zero). This fact was recognized a long time ago [3, 4, 7] but it was usually thought that the first-order character was a small effect. The important specific feature of the mean-field tricritical region which is pointed out in this paper is that the transition has a strong first-order character and that it occurs at a temperature where the system can be self-consistently described by perturbation theory, at least for displacive systems. Let us note that the term 'displacive' should not be understood too literally in this case. In fact we mean only that we are considering systems for which there is a region where the fluctuation corrections to the mean-field theory can be treated perturbatively; that is typically the case for displacive systems, but it can also be the case for some order–disorder systems (when there is a strong temperature dependence of the double-well parameters due to phonon renormalization or when there are strong next-nearest-neighbour interactions). The vicinity of the mean-field TCP where the perturbation theory is self-consistent is found to be fairly broad and one may expect that the present theory is at least qualitatively correct for many structural phase transitions where strong precursor phenomena are observed in the symmetrical phase. It is very likely that ammonium chloride and quartz fall into this category.

In this paper we have restricted ourselves to the case of a one-component order parameter. It is of interest of course to discuss phase transitions with a multi-component order parameter in the same way, but this problem deserves separate considerations. There is one case which is simple to treat: the normal-to-incommensurate transition ($n = 2$ and no anisotropy in the order-parameter space). It is straightforward to show that the results of this paper are also valid for such a transition and a first-order transition is also expected to occur close to the mean-field TCP. This seems to be rather surprising since most observed normal-to-incommensurate transitions are found to be continuous. To explain this observation one has to assume either that these transitions are far from the TCP or that imperfections of the crystal should be considered. The latter explanation seems to be more likely because

the 'random field' (phase pinning in this case) defects are known to destroy the long-range order in an incommensurate phase, i.e. to smear the second-order phase transition. It is natural to believe that they may also have a drastic effect on the first-order transition. A preliminary consideration shows that it is indeed the case, even when the defects are of the 'random transition temperature' type. A thorough discussion of the role of defects will be reported in a forthcoming paper.

References

[1] Bausch R 1972 *Z. Phys.* **254** 81

[2] Wegner F J and Riedel E K 1973 *Phys. Rev.* B **7** 248

[3] Larkin A J and Pikin S A 1969 *Zh. Eksp. Teor. Fiz.* **56** 1664 (Engl. Transl. *Sov. Phys.–JETP* **29** 891)

[4] Sak J 1974 *Phys. Rev.* B **10** 3957
De Moura M A, Lubensky J L, Imry Y and Aharony A 1976 *Phys. Rev.* B **13** 2176
Bergman D J and Halperin B I 1976 *Phys. Rev.* B **13** 2145

[5] Imry Y 1974 *Phys. Rev. Lett.* **33** 1304

[6] Landau L D and Lifschitz E M 1981 *Statistical Physics* 3rd edn (Oxford: Pergamon)

[7] Bruno J and Sak J 1980 *Phys. Rev.* B **22** 3302

[8] Vaks V G 1968 *Zh. Eksp. Teor. Fiz.* **54** 910 (Engl. Transl. *Sov. Phys.–JETP* **27** 486); 1970 *Zh. Eksp. Teor. Fiz.* **58** 296 (Engl. Transl. *Sov. Phys.–JETP* **31** 161)

[9] Lunacek J H 1968 *PhD Thesis* Department of Physics Massachusetts Institute of Technology

[10] Garland C W and Pollina R J 1973 *J. Chem. Phys.* **58** 5002

[11] Kammer E W, Pardue T E and Frissel H F 1947 *J. Appl. Phys.* **19** 265

[12] Dolino G 1986 *Incommensurate Phases in Dielectrics* vol II ed R Blinc and A P Levanyuk (Amsterdam: North-Holland) ch 16

[13] Khmel'nitskii D E and Shneerson V L 1975 *Zh. Eksp. Teor. Fiz.* **69** 1100 (Engl. Transl. *Sov. Phys.–JETP* **42** 560)
Lyuksyutov I F 1977 *Zh. Eksp. Teor. Fiz.* **73** 7332 (Engl. Transl. *Sov. Phys.–JETP* **46** 383)