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Phase transition anomalies in crystals with defects: the contribution of non-equilibrium domain structures

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Abstract. We consider the defect contribution to phase transition anomalies in various physical quantities in the situation when the system is quenched from the high-symmetry phase. The main emphasis is placed on the contribution of the metastable domain structure arising at the time of quenching. It is found that the formation of the domain structure may cause a sharp change in the frequency dependence of the sound absorption coefficient as well as the emergence of a narrow non-Lorentzian central peak in the inelastic light scattering spectrum. The recent conclusion that the temperature dependence of the elastic light intensity during cooling from the high-symmetry phase through the phase transition temperature is monotonic is supported but also amended.

1. Introduction

One of the main achievements of the theory of phase transitions in crystals containing defects is the conclusion that long-range order is absent for a relatively long time in a crystal cooled to the low-symmetry phase (i.e. a random domain structure exists in the crystal, see, for example, Nattermann and Villain (1988)). However, long-range order does exist in equilibrium in a system with 'random local field' defects with sufficiently small 'power'. The metastable domain structure is expected to increase slowly but to disappear later on; however in reality such processes have proved to be so slow that they have not been discovered experimentally.

The presence of a metastable domain structure in a crystal cooled from the high-symmetry phase affects the anomalies in various physical quantities. This fact has not been taken into account in the majority of papers on the problem, including the book by two of the authors (Levanyuk and Sigov 1988). Levanyuk (1990) considered the anomaly in elastic light scattering at structural phase transitions in crystals with point defects, but attention was focused on the role of the non-equilibrium domain structure. It was shown (Levanyuk 1990) that the domain structure markedly changed the temperature dependence of the scattering intensity found for a single-domain crystal (Levanyk *et al* 1976, Levanyuk *et al* 1979, Levanyuk and Sigov 1988).

In the present paper we consider the influence of a non-equilibrium domain structure on anomalies in several physical quantities, including the intensity of the elastic

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light scattering (as there were some inaccuracies in the former analysis). We use here the continuous medium approximation and the Landau thermodynamic potential as in a number of our previous works (for a review see Levanyuk and Sigov (1988)). The structural phase transition in question is neither ferroelectric nor ferroelastic, i.e. the domain structure does not arise at the phase transition in a crystal without defects. The non-equilibrium domain structure is described using the theoretical results obtained by Nattermann and Villain (1988). These results are qualitative in nature, therefore we can only estimate the order of magnitude of the quantities examined.

The next section is devoted to a brief description of the temperature evolution of the non-equilibrium domain structure arising in crystals with defects after quenching from the high-symmetry phase. In section 3 we discuss the anomalies in the thermodynamic characteristics and elastic light scattering. In section 4 anomalies in the kinetic properties, the sound absorption coefficient and the soft-mode damping constant are considered. The central peak in the spectrum of the order-parameter fluctuations is also discussed in this section.

2. Non-equilibrium domain structure

We confine our discussion to 'random local field' (RLF) defects and the one-component order parameter. In this case the Landau thermodynamic potential is

$$F = \tfrac{1}{2}A\eta^2 + (\tfrac{1}{4})B\eta^4 + \tfrac{1}{2}D(\nabla\eta)^2 - h\eta \tag{1}$$

where

$$h(r) = \sum h_i \delta(r - r_i) \tag{2}$$

where $h_i = \pm h_1$; both signs have the same probability and the positions of the defects are taken to be fully random. We assume mean-field temperature dependences for the coefficient of the thermodynamic potential. In addition, the strength of the defects is supposed to be small, $h_1 \ll h_{1at}$, where h_{1at} is the characteristic (atomic) value of the local field.

If the defect concentration N is small long-range order persists at $T < T_c$ in spite of the presence of defects. It means that the ground state is a single-domain one. Nevertheless in a quenched crystal there is a domain structure with an initial characteristic size which expands slowly. We neglect this expansion, taking into account the fact that in the most studied systems it has never been observed (Belanger 1988).

According to Nattermann and Villain (1988) for the characteristic domain size R we have

$$R \simeq \xi/(N\xi^3 h_1^2 h_{1at}^{-2}) \tag{3}$$

where ξ is the domain wall width, or the order-parameter correlation length. In the mean-field approximation $\xi \propto (T_c - T)^{-1/2}$ i.e. $R \propto T_c - T$. Equation (3) is valid until $R > \xi$, because the domain size should be greater than the domain width. In other words, equation (3) is valid when $N\xi^3 h_1^2 h_{1at}^{-2} < 1$, which is also a condition for the applicability of perturbation theory of defect-induced anomalies at $T > T_c$ (Levanyuk and Sigov 1988). In the close vicinity of T_c where $Nh_1^2 h_{1at}^{-2} \geqslant 1$, little is known about the space distribution of the order parameter. It is considered that in this region the poly-domain (disordered) state is stable.

3. Anomalies in thermodynamic quantities and elastic light scattering

To estimate the domain contribution to the specific heat (C) it is convenient to use the formula

$$C = -\tfrac{1}{2}A_0\frac{\partial\langle\eta^2(r)\rangle}{\partial T} \tag{4}$$

where $A_0 = T_0(\partial A/\partial T)$, and the brackets denote the statistical average over the defect distributions. The domain structure contribution to $\langle\eta^2(r)\rangle$ is negative and can be estimated as $-\eta_0^2\xi R^{-1}$. Thus we have

$$C \simeq C_{\mathrm{L}}N\xi^3h_1^2h_{1\mathrm{at}} \propto (T_{\mathrm{c}} - T)^{-3/2} \tag{5}$$

where $\Delta C_{\mathrm{L}} = A_0^2/(2BT_{\mathrm{c}})$ is the specific heat jump in the Landau theory. Up to a numerical coefficient, which cannot be found using our approach, equation (5) coincides with the expression for the RLF defect contribution to the specific heat of a single-domain state (Levanyuk *et al* 1979, Levanyuk and Sigov 1988). Thus, the presence of the poly-domain structure does not change the temperature dependence of the specific heat qualitatively, but the difference between quenched and equilibrium crystals is of the same order of magnitude as the defect contribution itself.

Let us now consider elastic light scattering. This was calculated by Levanyuk (1990), but with an incorrect formula for the domain size R. The intensity of the elastic light scattering was found (Levanyuk 1990) in two cases: $qR \ll 1$ and $qR \gg 1$, where q is the difference between the wavevectors of the scattered and incident light waves. In the first case

$$I = VQ\epsilon_0^2R \tag{6}$$

where V is the scattering volume, $Q = q_0^4/(16\pi^2)$, q_0 is the wavevector of the incident wave, and ϵ_0 characterizes the change in the dielectric constant for optical frequencies (ϵ) induced by the domain wall. In our case the dielectric constant $\epsilon = \epsilon(T > T_{\mathrm{c}}) + a\eta^2$ and $\epsilon_0 = a\eta_0^2$. Since $\epsilon_0 \simeq (T_{\mathrm{c}} - T)^{1/2}$, the intensity has a temperature dependence of the form

$$I \propto (T_{\mathrm{c}} - T)^2. \tag{7}$$

For lower temperatures the condition $qR > 1$ is realized and we have (Levanyuk 1990)

$$I \simeq VQ\epsilon_0^2q^{-2}R^{-1}. \tag{8}$$

It can be seen that in this region the intensity is nearly independent of temperature. Note that in both cases the intensity appears to be much greater than the maximum light scattering intensity in the high-symmetry phase within the region of applicability of the perturbation theory (Levanyuk and Sigov 1988, Levanyuk 1990). Thus, when the crystal is cooled from the high-symmetry phase through the phase transition, the temperature dependence of the elastic light scattering intensity is expected to be monotonic.

4. Kinetic coefficient anomalies

We shall assume that for a perfect crystal the equation of motion for the order parameter has the form

$$m\ddot{\eta} + \gamma\dot{\eta} + \partial F/\partial\eta = 0. \tag{9}$$

Equation (9) can be used for both displacive and order–disorder systems. In the latter case one has to put $m = 0$. The coefficient γ is the order-parameter viscosity. It has been shown (Levanyuk *et al* 1979, Levanyuk and Sigov 1988) that if there is an inhomogeneity in the static value of the order parameter then an additional contribution to γ arises. This contribution is connected with the thermal conductivity: the order-parameter vibrations are accompanied by inhomogeneous space changes in temperature. The coupled equations of motion for the order parameter and temperature are (see, for example, Levanyuk *et al* 1979)

$$\begin{aligned} &m\ddot{\eta} + \gamma\dot{\eta} + A_0[(T - T_c)/T_c]\eta^2 + B\eta^3 - D\nabla^2\eta = h(r) + h_e(r,t) \\ &C_0\dot{T} - A_0\eta\dot{\eta} = \kappa\nabla^2 T \end{aligned} \tag{10}$$

where C_0 is the regular part of the specific heat, κ is the thermal conductivity coefficient, and $h_e(r,t)$ is the external perturbation field.

Taking into account the inhomogeneity of the order parameter created by the domain walls, we consider two cases: $\lambda_T \ll R$ and $\lambda_T \gg R$, where $\lambda_T = (\kappa/C_0\omega)^{1/2}$ represents the wavelength of the 'temperature wave' with frequency ω. In the later analysis we are only interested in the response to long-wave external perturbation, i.e. it becomes possible to consider the dependence of h_e on time, assuming it to be homogeneous in space. Then, if $\lambda_T \ll R$, the heat flow is nearly perpendicular to the domain-wall plane and the space distribution of temperature is one-dimensional.

In this case the contribution of the domain structure to the soft-mode damping constant equals the sum of the contributions from separate walls whose linear density is of the order of R^{-1}. Excluding temperature from coupled equations (10) and passing to the Fourier transform $\eta(\omega)$ one finds for a single-domain wall

$$[-m\omega^2 - i\omega(\gamma + \Delta\gamma_1(\omega)) + (A + 3B\eta_0^2)]\eta(\omega) = h_e(\omega) \tag{11}$$

where

$$\Delta\gamma_1(\omega) = (A_0^2/T_c)\int (dq/2\pi)(\kappa q^2|\eta'(q)|^2)/(C_0^2\omega^2 + \kappa^2 q^4) \tag{12}$$

and $\eta'(q) = -2i\eta_0/q$ is the space Fourier transform of the 'jump' induced by the wall. Calculating the integral given in equation (12) and multiplying it by R^{-1} gives the total domain structure contribution to the damping constant.

$$\Delta\gamma_w(\omega) = \Delta C_L C_0^{-3/2}\kappa^{1/2}\omega^{-3/2}(h_1/h_{1at})^2 ND. \tag{13}$$

It follows from equation (13) that in the case $\lambda_T \ll R$ the magnitude of γ_w is independent of temperature, and its dependence on frequency is of a somewhat unusual form ($\omega^{-3/2}$).

Consider the case $\lambda_T \ll R$, where the energy of the order-parameter vibrations is dissipated at inhomogeneous inclusions in the volume R^3. Using equation (10) one finds

$$\Delta\gamma_w = \Delta C_L \kappa^{-1} |A| (N(h_1/h_{1at})^2)^{-2} \xi^{-4} \tag{14}$$

Therefore $\Delta\gamma_w \propto (T_c - T)^3$.

It seems meaningful to compare the quantity $\Delta\gamma_w$ with the corresponding contribution of RLF point defects $\Delta\gamma$ (see, for example, Levanyuk *et al* (1979)):

$$\frac{\Delta\gamma_w}{\Delta\gamma} = \begin{cases} (\Omega/\omega)^{3/2} & \lambda_T \ll R \\ [(h_1/h_{1at})^2 N \xi^3]^{-3} & \lambda_T \gg R. \end{cases} \tag{15}$$

Here $\Omega \equiv \kappa/C_0\xi^2$. This frequency can be estimated as follows. By the order of magnitude $\kappa \simeq \omega_{at} C_0 a^2$ where ω_{at} is the characteristic phonon frequency, e.g. the Debye one, and a is the interatomic distance. Thus $\Omega \simeq \omega_{at} a^2/\xi^2$. For an order–disorder system this frequency is equal, in order of magnitude, to the relaxation rate ($\tau^{-1} = |A|/\gamma$) of the order parameter. For a displacive system $\xi^2 = a^2 T_{at}/|T - T_c|$ and $\Omega \simeq \omega_{at}(T - T_c)/T_{at}$, where T_{at} is the atomic temperature (10^4–10^5 K). For $(T - T_c) \simeq 1$ K, we find that in the latter case $\Omega \simeq 10^7$–10^8 s^{-1}. Thus in ultrasonic experiments one can expect that the condition $\omega < \Omega$ is fulfilled. If we also take the condition of applicability of the theory into account (see earlier and Levanyuk and Sigov (1988)) we come to the conclusion that for ultrasonic frequencies we can expect $\Delta\gamma_w$ to be bigger than $\Delta\gamma$.

Using this estimate we can express $\Delta\gamma_w$ as

$$\Delta\gamma_w \simeq (\Delta C_L/C_0)(\omega_{at}/\omega)^{3/2} N (h_i/h_{at})^2 a^3 \gamma_{at}. \tag{16}$$

We have estimated D as $A_{at} a^2$ and A_{at} as $\omega_{at}\gamma_{at}$. If we put $Na^3 \simeq 10^{-4}$, $h_1/h_{at} \simeq 10^{-1}$, $\Delta C_L/C_0 \simeq 10^{-1}$ and, bearing in mind ultrasonic wave frequencies with $\omega \simeq 10^7$, $\omega_{at}/\omega \simeq 10^6$ we find that $\Delta\gamma_w \simeq 10^2\gamma_{at}$. In spite of the inevitable uncertainty of such an estimate it is quite probable that $\Delta\gamma_w \gg \gamma$ for the ultrasonic frequencies, i.e. in this frequency region the order-parameter relaxation is fully determined by the domain structure.

To describe the sound attenuation anomaly the mean-field formula (Landau and Khalatnikov 1954) with $\Delta\gamma_w$ instead of γ can be used. For the low-frequency attenuation coefficient α one has

$$\alpha = (\Delta\lambda/\lambda)\omega^2 \Delta\gamma_w / 2vA \tag{17}$$

where λ is the bulk elastic modulus, $\Delta\lambda$ is the jump in the modulus at $T = T_c$, and v is the sound velocity. Taking into account the temperature dependence of R (see earlier) one can describe the temperature dependence of α as follows. At $T \ll T_c$ we expect that $\lambda_T \ll R$ and $\alpha \propto (T - T_c)^{-1}$, i.e. it has the same temperature dependence as that of a perfect crystal. However, the frequency dependence is different: $\alpha \propto \omega^{1/2}$. It is this frequency dependence which was found by Isakovich (1948) for sound absorption in a polycrystal with heat transfer between the crystallites being the main mechanism for the absorption. At the temperature at which $\lambda_T \simeq R$ the function $\alpha(T)$ exhibits a maximum ($T = T_m$) and at $T > T_m$ the coefficient α decreases and has the 'normal'

frequency dependence $\alpha \propto \omega^2(T - T_c)^2$. The temperature T_m depends on the sound frequency and the defect concentration

$$T_c - T_m \propto N/\omega^{1/2}. \tag{18}$$

A specific feature of the low-frequency behaviour of the damping constant for η may be observed in the spectrum of the inelastic light scattering in the low-symmetry phase: namely a narrow central peak of the non-Lorentzian shape may arise in the scattering spectrum far enough from the phase transition temperature. Close to this peak ($\omega \leqslant \kappa/C_0R^2$) the spectral intensity is constant and varies with temperature as $(T_c - T)^3$. However, at $\omega > \kappa/C_0R^2$ the intensity falls off as $\omega^{-3/2}$ and is independent of $(T_c - T)$.

5. Conclusions

It follows from these considerations that the domain structure is most clearly revealed in specific features of the kinetic properties. The contribution of the domain structure depends strongly on the probe frequency and on the domain size R.

Real systems, for example diluted anti-ferromagnets, exist in which the domain size R can be easily adjusted by both the external field and the concentration of the substitution impurities (Belanger 1988). Such systems are, probably, the most suitable for checking the results of this paper experimentally.

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