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On the intrinsic mechanism of the central-peak phenomena near ferroelectric phase transitions

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Abstract. A new microscopic analysis of the central-peak phenomena caused by thermal fluctuations near the order–disorder phase transitions is given. This is based on new results obtained recently in the dynamics of the disordered phase of ferroelectrics in the framework of the three-dimensional spin-$\frac{1}{2}$ Ising model in a transverse field and performed by the Green function method. A microscopic description for all the parameters of a phenomenological model adopted in the central-peak problem is given. In particular, the central-peak observation conditions are formulated. A new critical behaviour of the central relaxation-type mode, namely $\gamma_c \sim (T - T_c)^{5/4}$ is found. A minimum of the soft mode is predicted above the critical temperature T_c.

1. Introduction

The dynamic behaviour of crystals undergoing a structural phase transition can be described in terms of instability of the collective Goldstone-type *soft mode*, which vanishes at the transition temperature T_c, namely $\omega_0^2(T) \sim |T - T_c|^\gamma$ (γ is the susceptibility exponent). The soft-mode picture based on the ideas of Anderson and Cochran was established in the 1960s. It is remarkable that it follows from the mean-field approximation ($\gamma = 1$), which is in qualitative agreement with experiment [1] and, on the other hand, is also capable of describing critical fluctuations.

A new feature of the structural phase transitions is characterized by a new distinct time scale, related to the central-peak (CP) phenomenon, instead of a single peak suggested by the soft-mode theory. This was first predicted by Cowley [2] in 1970 and later discovered [3] in the elastic neutron-scattering spectra of strontium titanate. The CP phenomenon seems to be attributed to all structural phase transitions [4]. During the following decade it has been intensively studied by a great variety of experimental techniques, namely by neutron, light and Mössbauer scattering, electron and nuclear paramagnetic resonances, dielectric dispersion and ultrasound (see reviews in [5–7]). The main features of the CP phenomenon can be summarized here as follows:

(i) A diffuse-type *central-mode* ($\omega_c \approx 0$) peak appears in the fluctuation spectrum of the order parameter below and above the phase transition temperature besides the renormalized soft-mode ($\pm\omega_s$) side-band peaks (figure 1).

(ii) The CP (or the central-mode) intensity diverges but that of the overdamped soft mode remains finite as $T \to T_c$.

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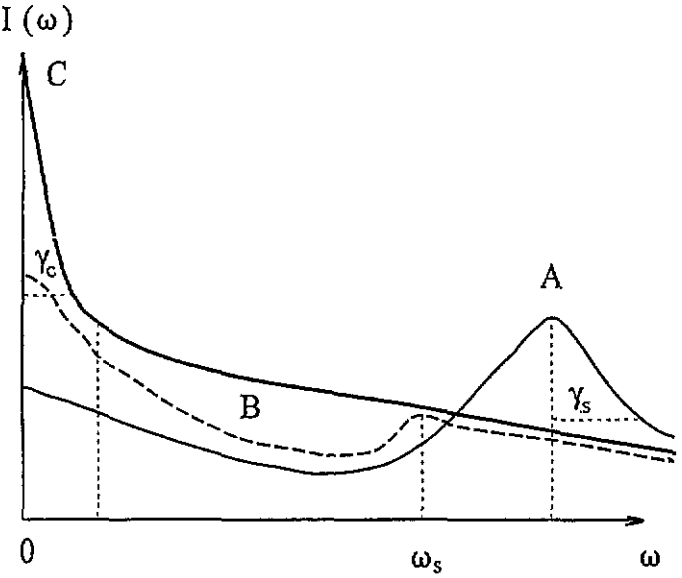

Figure 1. Schematic presentation of the order-parameter fluctuation spectrum in terms of the CP observable parameters introduced for the resonant-type soft mode (ω_s, γ_s) and the relaxation-type central mode ($\omega_c = 0$, γ_c). One can distinguish three temperature regimes: A, $T - T_c > T_c$, $\omega_s \simeq \omega_0 \gg \gamma_s$; B, $T - T_c \leqslant T_c$, $\omega_s \simeq \gamma_s \simeq \gamma_c$; C, $T - T_c \ll T_c$, $\omega_s \simeq \gamma_s \gg \gamma_c$.

As achieved in experiment, the *central-mode width* γ_c is at least three orders of magnitude smaller than the *soft-mode width* γ_s. The critical narrowing of the CP, which is observed close to T_c, gives evidence of a very slow regime of motion, which in most cases could not be resolved because the characteristic measurement frequency exceeds γ_c.

Besides the *dynamic CP effects* under discussion a completely static (elastic) CP component has been revealed in light-scattering experiments [8] in the paraelectric phase of KH_2PO_4 (KDP)-type crystals. As shown by Chaves and Blinc [9] this effect is due to long-range strain interactions produced by dislocations and can be strongly suppressed by annealing [10].

By means of parametrizing the experimental data for the spectral profiles $I(\omega, T)$ in different materials a *CP phenomenological model* has been proposed [6, 7, 11], namely

$$I(\omega, T) \sim \frac{1}{\omega} \operatorname{Im}[G_0(\omega, T)] \qquad G_0(\omega, T) \sim \left[\omega_0^2(T) - \omega^2 - i\omega \frac{\delta^2(T)}{\nu(T) - i\omega}\right]^{-1}. \tag{1a}$$

The *CP auxiliary parameters* δ and ν of unknown nature have been suggested to describe the interaction of a trial undamped soft mode ω_0 with some unspecified degree of freedom (relaxation mode) in terms of the coupling strength δ and Debye relaxation time $1/\nu$. The fitting of energy fluctuation spectra with equations (1*a*) led to the CP description in terms of *observable parameters* γ_c, γ_s and ω_s discussed above as well as to the formulation of *CP observation conditions* imposed on the auxiliary parameters in the critical region [6, 7, 11], namely

$$\gamma_c \to \nu \frac{\omega_0^2}{\omega_\infty^2}, \quad \omega_s^2 \to \omega_\infty^2 = \omega_0^2 + \delta^2 \qquad \text{as } T \to T_c \qquad \text{with } \delta, \nu \gg \omega_0. \tag{1b}$$

One can see that the phenomenological description (1*b*) based on the analysis of $I(\omega, T)$ given in (1*a*) is far from complete. It does not include a description of the soft-mode parameters and leaves the CP observation conditions unspecified. The first can be completed by the Green-function-poles analysis but the second needs the CP microscopic mechanisms to be clarified.

There were a number of attempts to identify on a microscopic level a CP mechanism and thus to analyze the origin of the relaxation mode mentioned above. It is remarkable that the first theoretical analyses were focused on the effects of the local order-parameter thermodynamic fluctuations (*intrinsic* mechanism). The role of these fluctuations driven by intrinsic dynamics was first demonstrated by Feder [13, 15] in the framework of the anharmonic phonon model† [12]. The importance of including short-range effects in the dynamics of ferroelectric transitions had also been pointed out earlier by Houston and Bolton [16]. Blinc and Žekš [14] have proposed a phenomenological stochastic description of the local order polarization effects. Probably the first microscopic version for the CP intrinsic mechanism was given by Takada *et al* [17] in terms of the local fluctuating molecular field (as a microscopic analogue of the stochastic field [14]) in the framework of the perturbation theory applied to the Green function used by Matsubara.

Another theoretical description of the CP intrinsic mechanism in the ordered phase has been proposed by Kühnel *et al* [18]. This is based on the generalized Hartree–Fock approximation to the Green function used by Zubarev and developed in terms of long-range pseudo-spin (spin-wave (SW)) excitations. It was shown in particular that the relaxation mode is due to the following three kinds of interaction of the collective excitations: two SW excitation scattering processes; direct decay processes of one SW excitation to two SW excitations; back-generation processes. These results, being formally extended to the disordered (paraelectric) phase, leave only direct decay processes, which in turn disappear in the critical long-wave limit [18]. This means that SW interactions should be revised above the critical temperature in view of the overdamping (short-lived) character of the soft-mode excitations. In other words, short-range (or long-wave) effects should be taken into account in the description of the decay of the local order parameter fluctuations. From this point of view, Binder's [19] approach to the description of thermal fluctuations in terms of compact clusters, as correlated regions of the local order parameter, looks more suitable for the CP intrinsic mechanism problem.

A major disadvantage of the theoretical approach based on Mori's continued-fraction representation [20] is due to the necessity (caused by fraction truncation) of introducing a semiphenomenological description for the relaxation mode. Within this approach the extremely narrow CP can be predicted for the highly anisotropic short-range interaction [21], which is qualitatively equivalent to one-dimensional results obtained in terms of non-linear solitons [22] and are more suitable for quasi-one-dimensional $PbHPO_4$ (see, for example, the analysis given by De Carvalho and Salinas [23]).

Another problem arises in regard to the adequacy of the Ising model in a transverse field for describing dynamical problems near the transition temperature. The CP problem analyses in the scope of the three-dimensional model under discussion but extended by forth-order pseudo-spin interactions [24] and interactions with an external anharmonic acoustic phonon branch [25] have been given by Wesselinowa. In the framework of the approach [19] it was shown [24] that higher-order pseudo-spin interactions can be effectively included in the model exchange interaction and, therefore, do not change the CP intrinsic mechanism.

† The Ising model in a transverse field is more appropriate for the analysis of the order–disorder structure phase transitions [1]. All theoretical papers referenced below employ this model.

In the second case [25], in contrast, the external anharmonic phonon branches have become responsible for the origin of the relaxation mode, such that its width has the same order of magnitude as that for the anharmonic phonons. Qualitatively, the same result has been obtained early in the scope of the phonon anharmonic model [12]. It has also been noted [5] that this is not the case for the observed CP phenomenon.

Fluctuations caused by *extrinsic mechanisms* (produced by defects, impurities, surfaces, etc), which can also contribute to the CP effects, have been estimated [26]. As in the case of the external acoustic mode, they lead to a broad relaxation mode and, thus, to a too broad central mode, which is not observed in the CP critical narrowing.

Some experiments give clear evidence for the occurrence of a CP phenomenon as ideal crystal behaviour [6]. Moreover, an EPR study [27] of CP fluctuations in ADA–ADP mixed crystals as well as a direct estimation [28] of the order-parameter fluctuation spectra for deuterated KDP crystals also give clear evidence for dynamic fluctuation–cluster effects [19] rather than relaxation defect effects [26].

Recently new results on the dynamics of the paraelectric phase have been obtained [29]. These are based on Green function analysis by Zubarev which was developed for a three-dimensional Ising model in a transverse field within a self-consistent cluster scheme avoiding the perturbation theory approximation. The main goal of the current paper is to give a further microscopic description of the CP intrinsic mechanism in view of recent results in the dynamics of order–disorder phase transitions.

2. Central-peak parameters

Before performing a microscopic analysis let us first extend equations (1*b*) to all observable parameters. The fluctuation energy spectrum excitations are determined by the poles of the Green function (1*a*), namely

$$z^3 - \nu z^2 + \omega_\infty^2 z - \nu\omega_0^2 = 0 \qquad \text{with } z = \mathrm{i}\omega. \tag{2a}$$

Because the determinant of the third-degree equation with real coefficients is positive, one can parametrize its solutions in the following way:

$$z_1 = \gamma_c \qquad z_2 = z_3^* = \tfrac{1}{2}\gamma_s + \mathrm{i}\omega_s \qquad \text{or } \omega_1 = -\mathrm{i}\gamma_c \qquad \omega_{2,3} = \pm\omega_s - \mathrm{i}\tfrac{1}{2}\gamma_s \tag{2b}$$

where the CP observable parameters γ_c, γ_s and ω_s have been introduced above (see also figure 1). Exact solutions for poles (1*a*) have been obtained by Cardan's formula known for the cubic equation and these are represented in figure 2. They have also been approximated in different ranges (denoted A and C; see also definition in figure 1) of the auxiliary parameters:

$$\text{A}: \ \gamma_c \simeq \nu\frac{\omega_0^2+\nu^2}{\omega_\infty^2+\nu^2} \qquad \gamma_s \simeq \nu\frac{\delta^2}{\omega_\infty^2+\nu^2} \qquad \omega_s^2 \simeq \omega_\infty^2 - \delta^2\frac{\nu^2}{\omega_\infty^2+\nu^2} \quad \text{with } \delta < \omega_0, \nu \tag{3a}$$

$$\text{C}: \ \gamma_c \simeq \nu\frac{\omega_0^2}{\omega_0^2+\delta^2} \qquad \gamma_s \simeq \nu\frac{\delta^2}{\omega_0^2+\delta^2} \qquad \omega_s^2 \simeq \omega_0^2+\delta^2-\frac{\delta^4\nu^2}{4(\omega_0^2+\delta^2)^2} \quad \text{with } \delta > \omega_0, \nu. \tag{3b}$$

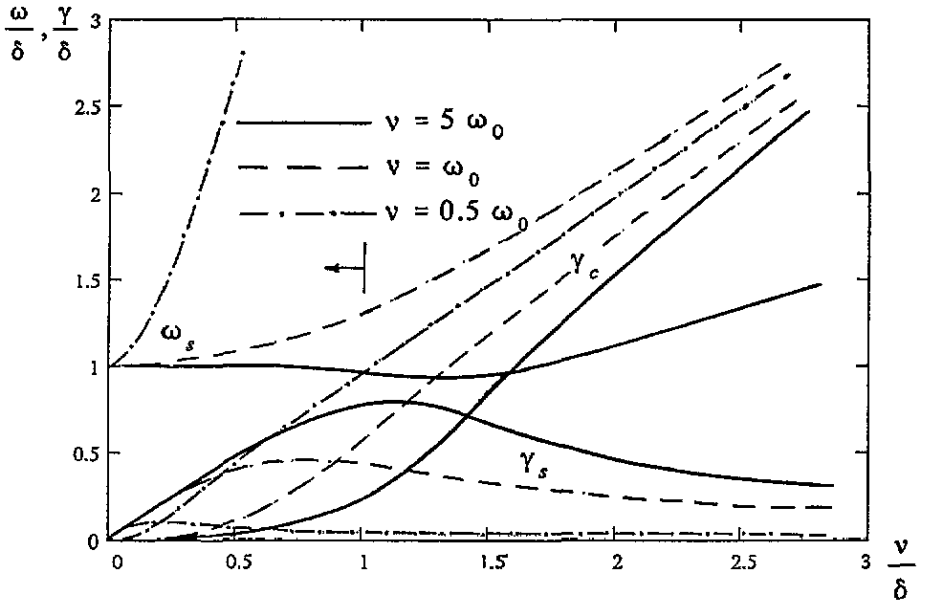

Figure 2. Excitation frequencies (or energies) of the fluctuation spectrum versus the CP auxiliary parameters within the phenomenological model (1), where ω_s is the renormalized soft-mode frequency, γ_s is the renormalized soft-mode width and γ_c is the central-mode width. The lines represent the Green function poles (2). The arrow indicates the critical regime range (see also figure 1).

The CP observable parameters of the phenomenological model in the critical region (3*b*) complete those given in (1*b*) and, on the other hand, are common to the different microscopic theories mentioned in the introduction. Nevertheless, the question of whether the CP observation conditions, approximately given in (3*b*), will correspond to (1*b*) suggested in [11], has different answers within different microscopic considerations, which, in particular, give different descriptions of the relaxation mode. In the case of $\nu > \omega_0$ our analysis also predicts the existence of a soft-mode minimum just above the critical region (figure 2).

3. Microscopic analysis

In the displacive-type crystals, one deals with phonon condensation at T_c and certain atomic displacements, which play the role of the order parameter. In the case of order–disorder-type crystals the order parameter, spontaneous macroscopic polarization, describes a rearrangement (or rotation) of a small group of atoms in the ferroelectric unit cell whereas other atoms remain unchanged [1]. In the particular case of hydrogen-bonded ferroelectrics a microscopic description is as follows. Each proton moves between two equilibrium states in the double-well potential with the quantum tunnelling frequency Γ and interacts with the nearest neighbour with energy $J_{ff'}$. Thus, the (pseudo-spin $S = \frac{1}{2}$) Ising model in the transverse field can be successfully employed for order–disorder ferroelectrics [1, 14, 21, 28]:

$$\mathcal{H} = -\Gamma \sum_{f}^{N} S_{xf} - \tfrac{1}{2} \sum_{ff'} J_{ff'} S_{zf} S_{zf'}. \tag{4}$$

In the *paraelectric phase*, N spins precess independently with the frequency Γ and are subject to the effective exchange $J_{ff'}$, which results in some local ordering effects, which can been discussed in terms of stochastic [14] or fluctuating molecular [17] fields. To describe these effects we introduce the two-site double-time retarded Green function

$$G_{ff'}(t) = -i\Theta(t)\langle[S_{zf}(t), S_{zf'}(0)]\rangle_T \equiv \langle\langle S_{zf}(t)||S_{zf'}(0)\rangle\rangle \tag{5}$$

with

$$\langle S_{yf}\rangle_T = \langle S_{zf}\rangle_T = 0 \qquad \langle S_{xf}\rangle_T \equiv \sigma(T) = \tfrac{1}{2}\tanh\left(\frac{\Gamma}{2T}\right) \qquad \text{at } T > T_c$$

where $\langle\ldots\rangle_T$ means a statistical average with Hamiltonian (7) and $\Theta(t)$ is the theta function. Developing the Heisenberg equations for the Fourier-time transformed Green function we have [29] after double-time differentiation

$$(\Gamma^2 - \omega^2)G_{ff'}(\omega^2) = \pi^{-1}\sigma(T)\Gamma\delta_{ff'} + \sigma(T)\Gamma\sum_{f''} J_{ff''}G_{f''f'}(\omega^2) - \Gamma\sum_{f''} J_{ff''}F_{ff''f'}(\omega^2) \tag{6}$$

$$F_{ff''f'}(t) = \langle\langle \delta S_{xf}(t)S_{zf''}(t)||S_{zf'}(0)\rangle\rangle \qquad \delta S_{xf} = S_{xf} - \langle S_{xf}\rangle_T$$

where a new irreducible Green function $F_{ff''f'}$ describes fluctuations of local polarizations in terms of three-site clusters. The canonical mean-field (MF) approximation ignores these fluctuations, namely

$$G_q^{(MF)}(\omega^2, T) = \pi^{-1}\Gamma\sigma(T)[\omega^2 - \omega_q^2(T)]^{-1} \qquad \omega_q^2(T) = \Gamma[\Gamma - J_q\sigma(T)] \tag{7}$$

with

$$J_q = J_0\gamma_q \qquad \gamma_q = \tfrac{1}{3}[\cos(q_z a) + \cos(q_y a) + \cos(q_x a)] \tag{8}$$

and leads to the undamped SW spectrum ω_q:

$$\omega_0(T) \leqslant \omega_q(T) \leqslant \omega_M(T) \qquad \omega_M(T) = \sqrt{\Gamma[\Gamma + J_0\sigma(T)]} \tag{9a}$$

which is unstable at the critical wavenumber $q = 0$ and critical temperature T_c:

$$\omega_0(T_c) = 0, \text{ where } T_c = \Gamma\ln^{-1}\left(\frac{J_0 + 2\Gamma}{J_0 - 2\Gamma}\right). \tag{9b}$$

If one includes a high-order Green function in equation (6), its solution can be represented in a general form, namely

$$G_q(\omega^2, T) = \pi^{-1}\Gamma\sigma(T)[\omega^2 - \omega_q^2(T) - \Delta_q(\omega^2, T)]^{-1} \tag{10a}$$

which comparatively with (7) can be treated as a MF solution improved by correlation effects. The explicit form for the polarization operator

$$\Delta_q(\omega^2, T) = \frac{\omega^2\langle S_z^2\rangle_T}{N}\sum_{q'}\frac{J_{q'}^2}{\omega^2 - \omega_{q'}^2(T)} - \frac{\Gamma^2\langle S_x\rangle_T^2}{N}J_q\sum_{q'}\frac{J_{q'}}{\omega^2 - \omega_{q'}^2(T)} \tag{10b}$$

has been obtained [29] for the particular case of a four-site-cluster approximation. The closed system of equations of motion for the four-site fluctuation Green functions, generalized from that given in (6), have been obtained within the standard Tyablikov scheme [30] and then exactly solved. Even the solution (10) is given in the wavenumber representation; a complete analysis of the equations of motion (6) has been done in the site representation which gives a major difference between the current cluster consideration and the others mentioned in the introduction. The first term in (10*b*) describes longitudinal fluctuations of the local parameter order and dominates at high frequencies. The second term dominates at low frequencies and characterizes reaction–polarization effects.

Now we can give a microscopic description of all the parameters of the CP phenomenological model (1). From a comparison of the results (10) with (1) we have, for the particular case $q = 0$,

$$\begin{aligned} &\mathrm{Re}[\Delta_0(\omega^2, T) - \delta_0^2(T)] \to \delta^2(T)\frac{\omega^2}{\omega^2 + \nu^2(T)} \qquad \text{as } \omega \to 0 \\ &\mathrm{Im}[\Delta_0(\omega^2, T)] \to \delta^2(T)\frac{\nu(T)\omega}{\omega^2 + \nu^2(T)} \qquad \text{as } \omega \to 0. \end{aligned} \tag{11}$$

Here we assume the existence of a low-frequency range $\omega \sim \omega_0 \ll \nu$ near $T \simeq T_c$ where the microscopic analogue of the CP auxiliary parameters δ and ν (equations (1)) can be introduced by means of relations following from (11), namely

$$\delta_0^2(T) = J_0\Gamma\sigma(T)\left(\left\langle\frac{\Gamma^2}{\omega_q^2}\right\rangle_{\mathrm{SW}} - 1\right) \qquad \delta_\infty^2(T) = \langle S_z^2\rangle_T\langle J_q^2\rangle_{\mathrm{SW}} = \frac{J_0^2}{24} \tag{12a}$$

$$\nu_0^2(T) = \delta_0^2(T)\left[\left\langle\frac{\Gamma^4}{\omega_q^4}\right\rangle_{\mathrm{SW}}\frac{J_0\sigma(T)}{\Gamma} - \left\langle\frac{\Gamma^2}{\omega_q^2}\right\rangle_{\mathrm{SW}}\left(\frac{J_0\sigma(T)}{\Gamma} + \frac{1}{4\sigma(T)^2}\right) + \frac{1}{4\sigma(T)^2}\right]^{-1}. \tag{12b}$$

Consequently, we have introduced the low-frequency δ_0 and infinite-frequency δ_∞ limiting coupling strengths of the effective fluctuating molecular field. One can see that the reaction and molecular local order field effects dominate at low and high frequencies, respectively. The high-frequency limit δ_∞ corresponds to the exact high-temperature limit result discussed in [20,31] in view of the high-temperature dynamics of the model (4); the low-frequency behaviour of the relaxation mode given in (12*b*) includes both reaction (first two terms) and molecular-field effects. The notation $\langle\ldots\rangle_{\mathrm{SW}}$ stands for the summation over the SW spectrum given in (10*b*). Summation has been performed here as integration with the SW spectral density

$$g_{\mathrm{SW}}(\omega^2) = \frac{8}{\pi}\frac{\sqrt{(\omega^2 - \omega_0^2)(\omega_{\mathrm{M}}^2 - \omega^2)}}{(\omega_0^2 + \omega_{\mathrm{M}}^2)^2} \tag{13a}$$

adopted for the cubic lattice taking into account the symmetry of interaction (8); the SW boundary frequencies are given in (9). The results of summation are

$$\langle\omega_q^{-2}\rangle_{\mathrm{SW}} = 8\frac{\Gamma^2 - \omega_0\omega_{\mathrm{M}}}{(\omega_0^2 + \omega_{\mathrm{M}}^2)^2} \qquad \langle\omega_q^{-4}\rangle_{\mathrm{SW}} = \frac{\langle\omega_q^{-2}\rangle_{\mathrm{SW}}}{\omega_0\omega_{\mathrm{M}}}. \tag{13b}$$

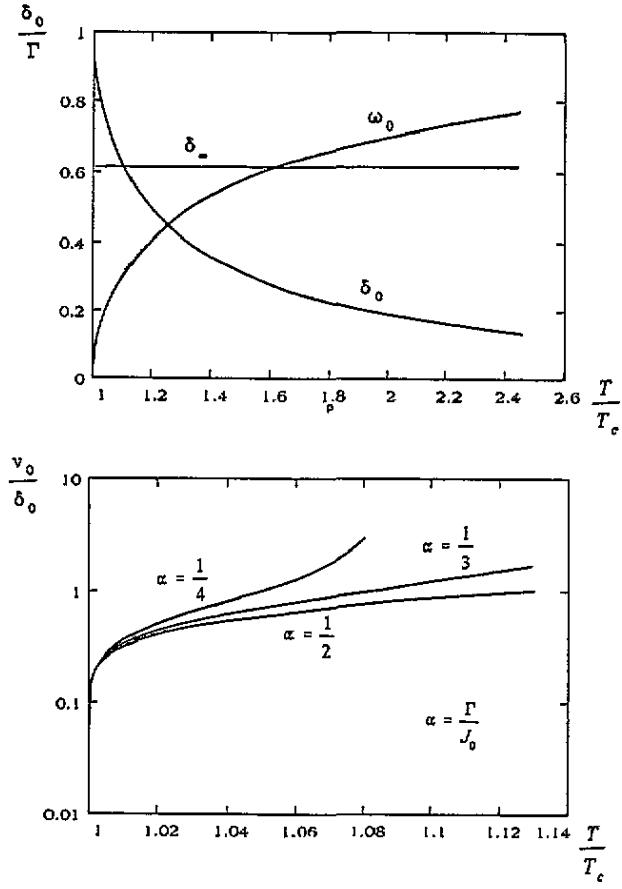

Figure 3. CP auxiliary parameters (12) versus reduced temperature within the microscopic model (4), where T_c is the critical temperature (9), ω_0 is the trial soft-mode frequency (9), δ_0 and δ_∞ are the coupling strengths (12*a*), ν_0 is the low-frequency limit for the relaxation mode (12*b*), Γ is the tunnelling frequency (4) and J_0 is the effective interaction (8).

One can see that the fourth-order high-frequency momentum $\langle\omega_q^{-4}\rangle_{SW}$ of the SW spectrum diverges at the critical temperature unlike the second-order momentum. Therefore, as follows from (12) and (13) in the critical regime the CP auxiliary parameters are

$$\nu_0(T) \to \left(\frac{\Gamma\omega_0(T)}{\sqrt{2}}\right)^{1/2} \qquad \delta_0(T) \to \Gamma \qquad \omega_0(T) \to \Gamma\sqrt{\frac{T}{T_c}-1} \qquad \text{as } T \to T_c. \tag{14}$$

Their behaviour in the whole temperature range is illustrated in figure 3. The CP observable parameters in turn follow from (3) and (13):

$$T \to T_c \qquad \gamma_c \to \Gamma\left(\frac{T}{T_c}-1\right)^{5/4} \qquad \gamma_s \to \Gamma\left(\frac{T}{T_c}-1\right)^{1/4}$$
$$\omega_s \to \Gamma \qquad \text{with } \delta_0 \gg \nu_0 \gg \omega_0 \tag{15}$$

and are shown in figure 4 for the particular case of a KDP crystal ($T_c = 123$ K; $J_0 = 3\Gamma$). Now the CP observation conditions (15) are given unambiguously.

4. Summary and discussion

Investigations of the CP phenomena, which accompany structure phase transitions, lead to deep insight into the dynamical mechanisms of phase transitions in complex crystals. Analytical results, even obtained within the simplest phase transition models, may serve as bases for further microscopic description of certain universal features of the structure phase transitions.

As already mentioned in the introduction, in the low-temperature ordered phase of crystals the CP intrinsic mechanism describes the process of order-parameter destruction in terms of decay and scattering processes of long-range excitations [18]. In the high-temperature disordered phase this mechanism drives the embryonic formation of the ordered phase and can be characterized, in general, in terms of the parameters of the CP phenomenological model (1). The short-range correlations lead to the origin of compact clusters due to fluctuations of the local order parameter. The relaxation mode describes a local motion of clusters as a whole and is characterized by the mean thermal relaxation time $1/\nu$. Because the mean cluster size increases to infinity as the temperature goes to the critical temperature, one should expect a divergence of the mean relaxation time. Delocalized excitations of atoms included in clusters are characterized by the trial soft mode. Their dynamical interaction, characterized by the coupling strength δ with the relaxation mode leads to the observable central and soft modes found in experiment (figure 1) and described within the phenomenological model adopted in the CP problem (figure 2).

Different microscopic approaches to the CP intrinsic-mechanism problem based on the same model (4) suggests a different description of δ and ν. By comparing the result for the coupling strength δ, given in figure 3, with those obtained within Mori's continued-fraction representation [20, 21] and the Green function perturbation approximation [17] used by Matsubara we note a general qualitative correspondence in the whole frequency range (see figure 1 in [29]) and only the low-frequency range for the first and second cases, respectively. All methods under discussion predict an enhancement in the correlation effects in the disordered phase with temperature decrease, i.e. $\delta \sim \langle \omega_q^{-2} \rangle_{SW}^{1/2}$ and, therefore, remains finite in the critical range. Critically different results have been obtained for the case of the relaxation mode. As follows from (12*b*) in the critical region it is characterized by $\nu \sim \langle \omega_q^{-4} \rangle_{SW}^{-1/2}$, in contrast with $\nu \sim \delta$ [17, 20, 21], which leads to a critical behaviour of the relaxation mode in the three-dimensional case and in turn to further critical narrowing of the central mode† (15), namely $\gamma_c \sim (T - T_c)^{5/4}$.

Both phenomenological and microscopic model analyses illustrated in figures 2 and 4 (inset), respectively, predict the existence of a soft-mode frequency minimum above T_c, which is caused by strong dynamic renormalization of the trial soft mode. This kind of temperature behaviour has been observed earlier for KDP-type crystals (see figure 13 from [32]).

The main advantage of the Ising model in a transverse field over anharmonic lattice models is that it effectively includes high anharmonic motion of a certain group of atoms, which are responsible for the transition, in terms of pseudo-spin variables. Nevertheless, the problems of taking into account other branches of phonons and of including their anharmonic natures in an estimation of the CP characteristics remain unsolved [17, 23, 24, 33, 34].

In real crystals of the KDP family there is a strong coupling of the ferroelectric soft mode with one optic and one acoustic transverses phonon branch [35]. The main effect of

† It is interesting to note that the same behaviour has been predicted for the central mode in the one-dimensional case (see (15c) from [21]).

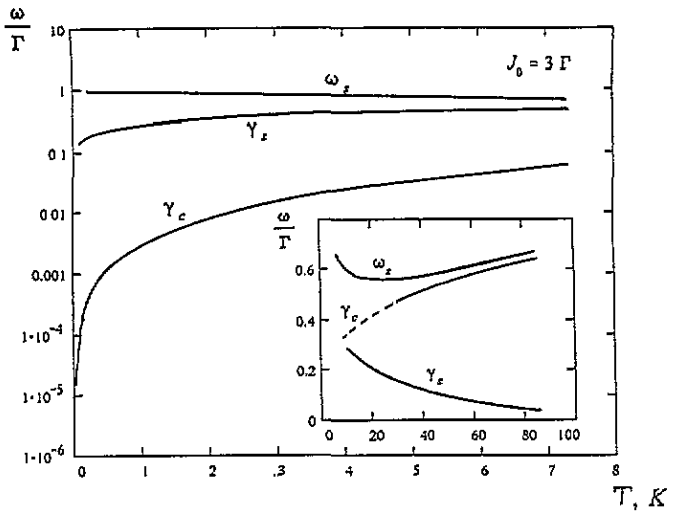

Figure 4. CP observable parameters versus temperature within the microscopic model (4) for the case of the KDP crystal (T_c = 123 K). The lines represent exact solutions of the cubic equation (2) for regime C (see figure 1) and approximate solutions (3*a*) for regime B (inset). The microscopic CP auxiliary parameters given in figure 3 were used for regime C. In the case of regime B (inset the relaxation time $1/\nu_0$ was approximated by $\nu_0 = \sqrt{\omega_0^2 + \delta_0^2}$) adopted in high-temperature dynamics [31]. The notation corresponds to that in figures 1 and 2.

the latter is to increase the transition temperature T_c^x from the 'clamped' value to the 'free' value, namely $T_c \simeq T_c^x + 4.3$ K. This shift was first derived by Lagakos and Cummins [8] from the Raman scattering experiments. According to our theoretical estimation given in the appendix and based on piezoelectric effect, the shift is 3.3 K.

As to coupling with optical phonons, phenomenological coupled-oscillator models were widely adopted (see, e.g., [8], and references therein) and much discussion has appeared concerning the choice of the phase of the complex coupling (as fitting) parameters. For the analysis of light-scattering experiments, one can use arbitrary representations for the coupled mode system, connected to each other by a unitary transformation. However, when making experiments in the wavevector region of the polaritons, one can in fact determine uniquely the phase under discussion [36]; nevertheless, this has not been done, and so the uncertainty remains. As was pointed out in [8] the convenience of choosing a pure imaginary coupling was only based on the fact that it does not affect the static susceptibility. We guess that the pure imaginary coupling approximation is inconsequential. Even considering the same (imaginary) coupling, different investigators came to different conclusions. It was found by Lagakos and Cummins [8] for the KDP crystal that the soft-mode behaviour is $\omega_s^2(T) \sim (T - T_c^x)$, whereas Scarparo *et al* [32] have argued that KDP, RDP and RDA crystals have the non-linear behaviour mentioned above. The discrepancy could be due to a poor theoretical description of the coupled overdamped mode and has been discussed earlier [32, 35] in terms of strong 'correlation' between the frequency ω_s and its linewidth, both of which are used as fitting parameters in the Raman spectra analysis. In the overdamped regime, because of this correlation, the simultaneous determination of the frequency and linewidth based on scattering data is imprecise. Further theoretical consideration and more comprehensive analysis of experiments on this point would be needed.

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Appendix. Piezoelectric shift of the transition temperature

Within the framework of the Landau theory of the second-order structural phase transitions [1] we expand the Gibbs free energy of the paraelectric phase in the electric displacement D_3 (up to the fourth order) and strain X_6 (up to the second order), namely

$$G = \frac{(T - T_c^x)}{2C} D_3^2 + \frac{b}{4} D_3^4 + \frac{C_{66}^{T,D}}{2} X_6^2 - h_{36}^T D_3 X_6. \tag{A1}$$

Here C is the Curie constant, $C_{66}^{T,D}$ is an elastic coefficient, h_{36}^T is a piezoelectric coefficient and b is the non-linear electric susceptibility. The standard thermodynamic analysis leads to the free Curie temperature:

$$T_c = T_c^x + C\frac{(h_{36}^T)^2}{C_{66}^{T,D}} \tag{A2}$$

which in turn gives the shift $T_c - T_c^x = 3.3$ K if one employs the tabulated values [37] for the coefficients involved in (A2).

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