Pretransitional clusters and heterophase fluctuations at
first-order phase transitions in crystals

J. Brookeman and A. Rigamonti*

Department of Physics, University of Florida, Gainesville, Florida 32611

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^{35}Cl nuclear quadrupole resonance measurements around the order-disorder ferroelectric transition in HCl and HCl-DCl mixed crystals are analyzed for possible evidence of pretransitional clusters of biased ferroelectric dipoles in the matrix of the paraelectric phase. It is shown that the hypothesis of an *extrinsic* mechanism related to local freezing-in around the DCl molecules does not fit the temperature dependence of the concentration of clusters, or the effect of sizable deuteration. The hypothesis of an *intrinsic* mechanism related to heterophase fluctuations expected in the framework of the thermodynamical droplet model is supported by the negligible change of shape and volume at the transition, which reduces the coherency strain energy that is usually thought to suppress heterophase fluctuations at first-order phase transitions. However, in such a model, the temperature dependence of the concentration of clusters can only be justified by assuming a temperature dependence for the average size of the clusters different from that expected for the correlation length in the mean-field description of critical phenomena.

I. INTRODUCTION

In the classical thermodynamical approach to phase transitions the postulate of complete independence between two phases rules out the possibility of the occurrence of pretransitional phenomena. For a long time, however, the relevance of precursor effects has been considered for various kinds of phase transitions.[1,2] Statistical-mechanical theories of the kinetics of phase transitions have recently provided a comprehensive and rather general framework to describe the nucleation process of the metastable phase.[3] The difficulty in achieving experimental evidence of such a process has been emphasized,[3] particularly in view of the "explosive" character of the nucleation rate.

The early picture of heterophase fluctuations for two phases of a fluid[1] has recently been applied by Cook[4] to phase transitions in crystals, in an attempt to explain the existence in neutron and light scattering experiments of a central peak in the dynamical structure factor $S(\vec{q}, \omega)$. Although pretransitional clusters due to heterophase fluctuations are expected to give rise to a central peak, some care should be exercised in considering this central peak to be equivalent to the one observed in scattering experiments and/or in computer simulations. This latter peak can be ascribed either to an extrinsic, impurity-driven mechanism or to nonlinear terms in the Hamiltonian for the critical variables. This point deserves more attention and will be discussed later.

In the picture of heterophase fluctuations, the formation of clusters around the transition temperature T_0 occurs when, on cooling, the free energy of the high-temperature phase F_H approaches the free energy of the metastable low-temperature phase F_L. The order parameter inside an embryo when it forms jumps from zero to the value of the metastable state. The average size of the cluster changes rapidly around the transition. The width of the central peak is controlled by the time required for the formation and collapse of the clusters. Analogous to the gas-liquid change, at first-order transitions in crystals, the volume and shape change associated with the transition cause a strain energy contribution to the free energy F_L, which is likely to suppress the heterophase fluctuations. In fact, direct evidence of heterophase clustering at first-order phase transitions in crystals is still lacking.

In this addendum we will refer to the results of a ^{35}Cl nuclear quadrupole resonance (NQR) investigation around the ferroelectric transition in HCl and HCl-DCl mixed crystals. Most of these results have already been published[5] in the framework of a comprehensive theoretical and experimental study of the static and dynamical properties of the ferroelectric phase in HCl, including the effect of deuteration and of hydrostatic pressure. Our aim here is to focus attention just in the transition region and to analyze the results in the light of possible mechanisms, of extrinsic and of intrinsic character, which can cause the occurrence of pretransitional clusters.

II. EXPERIMENTAL RESULTS

The results for the ^{35}Cl quadrupole resonance frequency ν_Q, the linewidth $\delta\nu$, and the spin-lattice relaxation rate T_1^{-1} around the transition temperature in HCl are reported in Fig. 1.
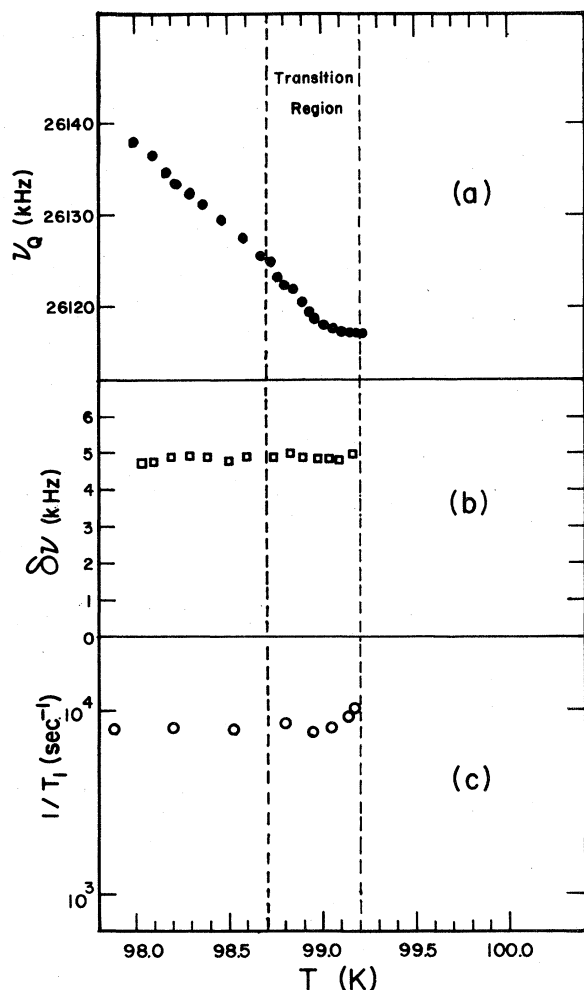
FIG. 1. (a) ^{35}Cl NQR frequency, (b) linewidth (half-width at half-intensity), and (c) spin-lattice relaxation rate around the ferroelectric transition in HCl, obtained by a Fourier transform pulse spectrometer with quadrature detection.

The sample was pure HCl provided by Matheson. The temperature was measured with a Pt resistance thermometer and the temperature gradients were carefully checked and found to be small ($\lesssim 10^{-2}$ K). The long-term temperature stability was about 10^{-2} K.

The ferroelectric transition is driven by the critical order-disorder dynamics of the HCl dipoles which, on cooling, cease their large-scale reorientational motions, through the effect of biasing along the direction of zigzag hydrogen-bonded chains, each dipole forming an angle of approximately 45° with the axis of polarization.

The NQR parameters can be related to the critical reorientational motions by relating the rigid electric-field gradient (EFG) tensor in its principal axis frame of reference to the crystalline frame of reference of

the polarization. The time average of the EFG gives ν_Q, while for T_1 one has $T_1^{-1} = e^2 Q^2 (\mathcal{I}_1 + \mathcal{I}_2)/6h^2$, $\mathcal{I}_{1,2}$ being the spectral densities at ω_Q of the well known V_1 and V_2 functions for the fluctuating part of the EFG components. For $\delta\nu$, besides a dynamical contribution of the order of T_1^{-1}, a static contribution due to defects, strains, etc., can be expected.

The reorientation of the dipoles can be taken into account through a local Ising-type variable $s(t)$ having the values $+1$ or -1, where $\langle s \rangle$ is the local order parameter to which the spontaneous polarization can be related. By neglecting for simplicity the torsional oscillations of the dipoles around the equilibrium positions, after a straightforward tensor transformation, one finds for the time average

$$\nu_Q(T) \simeq \frac{\nu_Q^0}{2}(1 + 3\langle s \rangle^2)^{1/2} , \qquad (1)$$

where ν_Q^0 is the "rigid-lattice" quadrupole frequency. It can be noted that when the order parameter drops to zero a drastic shift of the quadrupole resonance occurs.

The spectral densities $\mathcal{I}_{1,2}$ can easily be evaluated in the framework of the dynamical Ising model and RPA, to yield

$$T_1^{-1} \simeq 3(\nu_Q^0)^2(1 - \langle s \rangle^2)\tau_0 , \qquad (2)$$

where τ_0 is the correlation time for the dipole fluctuations in the absence of the interactions, which is of the order of time that the dipoles spend in the "wrong" position (with respect to the polarization) below the transition temperature. An expression similar to Eq. (2) can be derived for the intrinsic linewidth.

In a temperature range of about 0.5 K below the temperature at which the NQR signal disappears, a continuous decrease of the line intensity was noted. By storing the signals in different memory sections of the computer a quantitative analysis was performed. In Fig. 2 the results for the intensity I of the absorption lines are shown, for nominally pure HCl and for HCl-DCl 0.75/0.25.

From Eqs. (1) and (2) and the data in Fig. 1 approximate values for $\langle s \rangle$ and τ_0 can be derived. One obtains $\langle s \rangle \simeq 0.99$ at 97 K and $\langle s \rangle \simeq 0.988$ at 99.2 K, and $\tau_0 \simeq 10^{-9}$ sec. It should be mentioned that this value for τ_0 is also supported by the result derived from the condition $\tau_0 \simeq (2\pi\nu_Q)^{-1}$ at $T \simeq 82$ K, where the maximum in the relaxation rate is detected,[5] if one takes into account the activation energy for τ_0 as given by dielectric measurements.[6] What has to be stressed, however, is that $\langle s \rangle$ is close to 1 in the transition region, where the intensity of the line I decreases continuously. Since the linewidth is constant in this region, I can be considered proportional to the number of nuclei in the ferroelectric phase. Therefore the qualitative conclusion from the
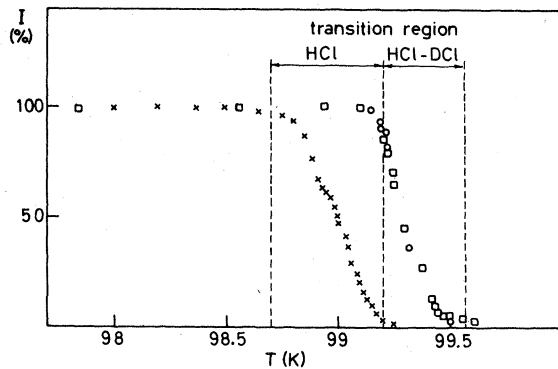
FIG. 2. Normalized intensity I of the ^{35}Cl NQR absorption line (from FT of quadrature pulse detection) around the ferroelectric transition in HCl ($\times$) and HCl-DCl 0.75/0.25 mixed crystals, ($\square$) HCl molecules, ($\circ$) DCl molecules.

data presented in Figs. 1 and 2 is that in the temperature range 98.7–99.2 K for HCl and 99.2–99.7 K for HCl-DCl 75/25, on heating, two phases are present: one for which $\langle s \rangle \simeq 0$, which cannot be detected because of the large shift of the quadrupole frequency,[5] and a second one with $\langle s \rangle$ almost equal to one and characteristic correlation time of the order of 10^{-9}, i.e. the ferroelectric phase for a temperature slightly less than the transition temperature. The number of dipoles in the ferroelectric-phase clusters decreases on heating as shown by the intensity I. The lifetime of the clusters is at least $(\nu_Q/2)^{-1}$, namely, 10^{-7} sec or greater.

III. ANALYSIS OF THE DATA AND DISCUSSION

A possible explanation of the experimental data presented in Sec. II could be the trivial rounding of the transition temperature due to the presence of impurities and/or defects which do not couple with the order parameter. This is somewhat reminiscent of the trivial premelting related to impurities not soluble in the crystal.[2] Indeed, in HCl, impurities and/or defects could cause strains which can locally shift the transition temperature T_0. However, a quantitative analysis of such a mechanism does not support this interpretation. NQR measurements as a function of pressure,[7] in fact, indicate that a shift of the transition temperature of about 0.5 K would also cause a shift of the quadrupole frequency of about 6 kHz. Since no broadening of the line is observed, the presence of sizable strains round T_0 can be ruled out. Any impurity or defect which shifts locally the transition temperature, without coupling to the critical dynamics, should induce extra broadening of the line. Another trivial rounding of the transition tempera-

ture that could be considered is the finite-size effect.[8] An order-of-magnitude estimate, on the basis of Eq. (2) in Ref. 8 and taking into account the transition entropy gives a negligible rounding of T_0 for our samples.

Local impurities or defects coupled to the critical dynamics can cause the occurrence of pretransitional clusters when the transition temperature of the matrix is approached.[9,10] The self-consistent, mean-field picture[10] suggests a local mode condensation at a temperature $T_0^{loc} > T_0$ with a critical correlation time $\tau_{loc} \propto (T - T_0^{loc})^{-1}$, provided that $dT_0/dc_D > 0$, c_D being the concentration of the defect. In the temperature range $T_0 \lesssim T \lesssim T_0^{loc}$ a local order occurs around the impurity, with a size related to the intrinsic correlation length of the matrix.

In HCl, deuterium impurities are present in natural abundance. In the following we will discuss this possible *extrinsic* mechanism for the occurrence of pretransitional clusters.

A. Extrinsic mechanism (deuterium impurities)

The critical reorientations of the dipoles between the two equilibrium positions can be described in the pseudospin formalism, namely, the kinematical Ising model in a transverse field. The tunneling integral Ω is considerably decreased for DCl dipoles. Thus deuterium impurities can cause local clusters above the transition temperature of the pure crystal. The possibility that the D impurities in potassium dihydrogen phosphate (KDP) can account for the central peak in $S(\vec{q}, \omega)$, observed in light scattering experiments, has already been considered by Courtens.[11] Furthermore, through T_1 measurements of the proton and deuteron in KDP, Blinc *et al.*[12] found evidence for a central peak that exhibits narrowing on deuteration.

For HCl-DCl mixed crystals, the pseudospin formalism, in the assumption of $\Omega \rightarrow 0$ for DCl and interaction energy between the dipoles $I = \sum_j I_{ij}$ not mass dependent, and in the framework of the virtual crystal approximation (VCA) (the equivalent of mean-field approximation MFA for random systems) leads[5] to

$$1 = (1 - c_D)\frac{I}{2\Omega} \tanh\frac{\Omega}{2kT_0M} + c_D\frac{I}{4kT_0^M} \quad (3)$$

for the transition temperature T_0^M of the mixed system (c_D deuterium concentration). It can be noted that by considering the two limiting cases $c_D = 0$ and $c_D = 1$ with $T_0^H \simeq 99$ K and $T_0^D \simeq 105$ K, from Eq. (3) one derives

$$I = 420 \text{ K and } \Omega = 84.94 \text{ K} \quad . \quad (4)$$

For $c_D \ll 1$, one has

$$\frac{d(\ln T_0)}{dc_D} \simeq \frac{4I}{I^2 - 4\Omega^2}\Delta T \simeq 6.8 \times 10^{-2} \ ,$$

with $\Delta T = (T_0^D - T_0^H)$.

For the concentration of pretransitional clusters around the deuterium dipoles one can define $c = 1/(1+x)$, where x is the ratio of the area of the Brillouin peak over the area of the central peak in $S(\bar{q}, \omega)$. The temperature dependence of x is given by[11] $x = (2\Omega\alpha/c_D I)\epsilon$, where $\alpha = (I/2\Omega) - (2\Omega/I)$ and $\epsilon \equiv (T - T_a)/T_a$, T_a being the free Curie temperature, i.e., the limiting instability temperature for the relaxational soft mode. Taking into account for I and Ω the numerical values given by Eqs. (4), the concentration of extrinsic clusters can be written

$$c = \frac{c_D}{c_D + 0.84\epsilon} \ . \tag{5}$$

As shown in Fig. 3, such a form does not adequately fit the results for the intensities of the NQR lines reported in Fig. 2.

B. Intrinsic mechanism (heterophase fluctuations)

In HCl, no appreciable change in the structure at the transition was detected in detailed x-ray and neutron-diffraction studies.[13] Therefore one expects that the strain energy contribution to the free energy is small, and this could favor the occurrence of heterophase fluctuations, according to the thermodynamical droplet theory.[1,4]

In order to analyze the data reported in Sec. II in such a light, let us refer to the expression for the average concentration c of atoms within a cluster, derived[4] in the framework of the thermodynamical

droplet model in q space

$$c = 4\pi kT\left[\frac{q_m}{\beta} - \frac{\alpha^{1/2}}{\beta^{3/2}} \tan^{-1}\frac{q_m\beta^{1/2}}{\alpha^{1/2}}\right] \ , \tag{6}$$

where α and β are coefficients related to the pairwise contribution to the free energy associated with the coherency strains and to the gradient of the free-energy coefficient, and q_m is the Debye wave vector. For the free energy one has $F(q) \simeq \alpha + \beta q^2$. $F(q)$ is inversely proportional to the generalized static susceptibility and from the fluctuation-dissipation theorem one can write $F(q)^{-1} \simeq (N/kT) S(q)$, where $S(q)$ is the structure factor for a variable taking the value one if a site is within a cluster and zero if not. In this way, by recalling the classical Orstein-Zernike expression for the static structure factor, α and β can be written in terms of a "correlation length" ξ which has the meaning of the average size of the clusters. One has $\alpha/\beta = \xi^{-2}$ and from Eq. (6) one obtains

$$c = (4\pi kT/\beta)(q_m - \xi^{-1}\tan^{-1}q_m\xi)$$

$$= c_0'[1 - (q_m\xi)^{-1}\tan^{-1}(q_m\xi)] \ , \tag{7}$$

where c_0' is the concentration of the clusters at the temperature T_0' at which ξ should diverge.

The interpretation of the experimental results on the basis of Eq. (7) is made uncertain by the lack of knowledge of parameters like T_0' and c_0' and of the temperature dependence of ξ. For the sake of illustration, in Fig. 4 the average concentration of ferroelectric clusters is reported for different choices of T_0' and c_0', having assumed $\xi^2 \propto (T - T_0')^{-1}$ as an extension of the classical result for the correlation length in the description of critical phenomena.
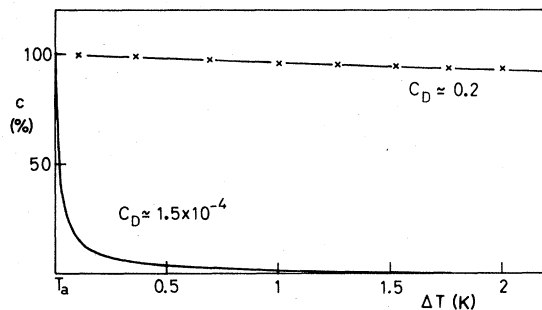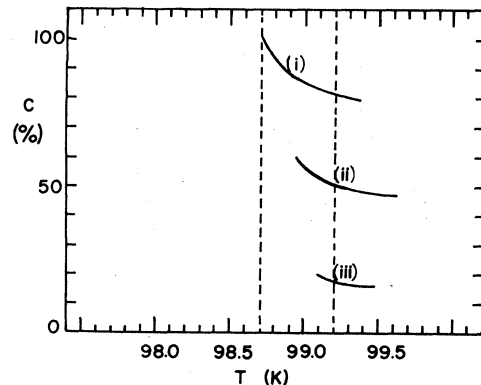

FIG. 3. Temperature behavior, above the limiting instability temperature T_a, of the concentration c of clusters for the extrinsic mechanism, for deuterium concentration c_D in natural abundance and for $c_D \simeq 0.2$, according to Eq. (5) in the text. It should be mentioned that the theory (Ref. 11) for the central peak in $S(\bar{q}, \omega)$, is expected to hold only for $c_D \ll 1$.

FIG. 4. Temperature dependence of the average concentration c of the ferroelectric clusters in the transition region, according to Eq. (7) in the text on the assumption $\xi^2 \propto (T - T_0')^{-1}$, for different choices of the parameter T_0' and c_0': (i) 98.7, 1, (ii) 98.85, 0.6, (iii) 99.1, 0.2, for all, for $T \gg T_0'$ $\xi \simeq a$, and $q_m = 0.62a^{-1}$.

From the figure it appears that no reasonable values for the parameters can be found giving a satisfactory reproduction of the behavior of I in the transition region (Fig. 2). An attempt to take into account the possible effect of short-range order according to the standard MFA procedure, by adding in the Orstein-Zernike form for $S(q)$ a further temperature-dependent term, gives a behavior of c not too different from the one in Eq. (7). Actually, if the temperature dependence $(T - T_0')^{-1/2}$ is assumed for ξ, it seems hard to justify a marked increase from zero of I in a few tenths of degree by means of a cusped-shape function like the one in Eq. (7).

It should be mentioned that ξ could indeed exhibit a temperature behavior different from the one assumed above. In fact the size of pretransitional clusters due to heterophase fluctuations, at first-order phase transitions, does not have to be directly related to the correlation length introduced in the theory of critical phenomena for second-order or quasi-second-order phase transitions. The fitting of the data for I according to Eq. (7) could be achieved by postulating an *ad hoc* temperature behavior for ξ which would turn out roughly of the form $\sim (1 - I)^{-1}$.

In conclusion, the interpretation of the ^{35}Cl NQR and relaxation data around the ferroelectric transitions in HCl and HCl-DCl mixed crystals seems to indicate the occurrence of pretransitional ferroelectric clusters in the matrix of the paraelectric phase, in a temperature range of approximately 0.5 K. The hypothesis of an extrinsic mechanism related to local freezing-in around deuterium impurities does not account for the temperature dependence of the concentration of the clusters, or for its dependence on the deuterium concentration. The negligible change of shape and volume at the transition, with a small coherency strain energy, supports the interpretation of the clusters as due to the intrinsic mechanism of heterophase fluctuations at a first-order phase transition, as expected in the framework of the thermodynamical droplet model. However, to fit quantitatively the temperature dependence of the concentration of clusters one should postulate a temperature dependence of the average size of the clusters different from that for the correlation length in the MFA theory for critical phenomena.

Finally we would like to conclude with the following remarks:

(i) Because of the occurrence of pretransitional clusters a macroscopic order parameter should exhibit a smooth temperature behavior. In particular, in spite of the first-order character of the transition, a discontinuous jump for the spontaneous polarization should not occur. This is precisely what appears through measurements of pyroelectric current,[14] from which a spontaneous polarization is detected that increases continuously over about 0.7−0.8 K.

(ii) Pretransitional clusters at first-order phase transitions have little to do with the central peak observed in the dynamical structure factor around the quasi-second-order phase transitions.[15] In this case, in fact, the nonlinear terms in the Hamiltonian for the soft modes cause "domain-wall" motions or solitons, with the occurrence of *short-range order* above the transition temperature. Such effects are not expected for strongly first-order transitions since the fluctuations do not increase too much. On the other hand, the thermodynamical heterophase fluctuations can occur, in principle, at first-order phase transitions; they involve in a crucial way the thermal bath which provides the energy for the thermal hopping in the metastable states; they cause the appearance of a *long-range order*.

(iii) The two pictures for the intrinsic and the extrinsic mechanisms generating the clusters are not necessarily in contrast. The presence of impurities, not directly coupled to the order parameter, could favor the intrinsic formation of the pretransitional clusters. This seems to be the case for the two-dimensional antiferroelectric squaric acid,[16] where the high-resolution ^{13}C NMR line shows a temperature dependence roughly similar to the behavior of I for HCl, although extending over a wider temperature range, i.e., about 2 K. In squaric acid the pretransitional clusters are probably pinned by impurities.[16] However it should be stressed that, according to the droplet model, only when a negligible strain energy contribution is present can the clusters persist as metastable states for a time sufficient for experimental detection.

(iv) In another NMR experiment, in RbCaF$_3$, the temperature dependence of the intensity of the ^{87}Rb absorption line in the cubic phase in a temperature range of about 20 K, has been interpreted as possible indication of pretransitional tetragonal domains.[17] This seems to be a different case from HCl. Apart from the fact that the cubic-to-tetragonal transition is almost second order, the temperature behavior of the NMR line is sample dependent[18] and most likely related to strains and/or defects.

(v) Careful neutron inelastic scattering measurements in the transition region of HCl could give a direct corroboration of the occurrence of pretransitional clusters, through the detection of a temperature-divergent central peak in $S(\vec{q}, \omega)$.

*On leave of absence from the Institute of Physics "A. Volta," University of Pavia, Pavia, Italy.

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