PHYSICAL REVIEW B VOLUME 21, NUMBER 7 1 APRIL 1980

^{35}Cl nuclear quadrupole resonance study of the ferroelectric transition in HCl and in the mixed crystals HCl-DCl

A. Rigamonti* and J. R. Brookeman
Department of Physics, University of Florida, Gainesville, Florida 32611

(Received 8 October 1979)

The order-disorder ferroelectric transition in HCl and in the mixed crystals HCl-DCl has been studied by means of ^{35}Cl ($I = \frac{3}{2}$) nuclear quadrupole resonance (NQR) pulse Fourier transform measurements. The NQR parameters are related to the static and dynamical quantities involved in the transition through a theoretical picture, which includes the librational motions around the equilibrium positions of the dipoles as well as their critical reorientations accompanying the polarization fluctuations. These reorientations are described by a kinematical Ising model, with the addition of a tunneling integral which is small for the HCl dipoles and goes to zero for the DCl dipoles. The experimental results for the quadrupole frequency, linewidth, intensity, and relaxation rates in the ferroelectric phase, including the effect of deuteration and of hydrostatic pressure, are analyzed. Besides providing a comprehensive consistency to the model, the analysis allows one to obtain interesting information on the temperature dependence of the order parameter, the correlation times for the reorientations of the dipoles, and on the mechanism of the transition. In a range of about 0.5 K around the transition, the results suggest the occurrence of heterophase fluctuations, with ferroelectric embryos of biased dipoles existing in a matrix of the paraelectric phase. In the framework of the droplet model, these heterophase fluctuations (apparently detected for the first time at a first-order phase transition in a crystal) should be ascribed to the lack of a structural change at the transition, with a negligible strain-energy contribution to the free energy of the metastable states. The temperature dependence of the concentration of the embryos is difficult to justify quantitatively by the droplet model in q space for the heterophase fluctuations. Careful neutron scattering measurements for the possible detection of a temperature-divergent central peak are urged.

I. INTRODUCTION

The study of the ferroelectric transition in solid hydrogen chloride is worthy of great attention. In fact, besides the simple structure of the crystal (perhaps the simplest ferroelectric discovered so far), the transition is characterized by several interesting features. It is a classical order-disorder transition, associated with the critical reorientational fluctuations of the HCl dipole moment. No appreciable change in the structure at the transition was detected in detailed x-ray and neutron-diffraction studies.[1] The lack of a sizeable volume and shape change is one of the conditions for the occurrence of heterophase fluctuations[2] at a first-order phase transition in crystals. For most of the order-disorder transitions a kinematical Ising model, possibly with a transverse field,[3] depending on the importance of the tunneling integral in the pseudospin Hamiltonian, can provide a suitable starting point for the description of the critical dynamics. The driving interactions are expected to be short-range and long-range dipole-dipole interactions and under certain approximations the Hamiltonian of the dipoles can be cast[4] in the form of a two-dimensional anisotropic Ising model. Finally, HCl-DCl mixed crystals seemingly are the simplest and most appealing cases of isotopically disordered ferroelectrics, which can be considered the analog of random ferromagnets or of other random systems, for which a growing interest has been witnessed in recent years.[5]

An ideal tool for the microscopic study of several features of the phase transition in HCl and HCl-DCl, is the ^{35}Cl($I = \frac{3}{2}$) quadrupole moment. The reorientations of the dipoles, as well as their angular oscillations around the equilibrium positions, cause fluctuations in the electric-field-gradient (EFG) components at the Cl site. These fluctuations affect the nuclear quadrupole resonance (NQR) frequency ν_Q, the linewidth, and the quadrupole relaxation time T_1. For the ferroelectric transition in NaNO$_2$, it has recently been pointed out[6] that precise evaluation of the NQR parameters allows one to study in detail the local short-range order as well as the dynamics of the ferroelectric dipoles.

Cl NQR has been already performed[7,8] in the low-temperature ferroelectric phase of HCl, providing some useful insight. In particular, recent high-

©1980 The American Physical Society

resolution Fourier transform (FT) NQR measurements[9] revealed fine structure related to the intramolecular spin-spin interactions and the motional averaging of the intramolecular dipolar splitting. The interpretation of the temperature dependence of ν_Q and T_1 has been attempted only through rather crude models,[7,8,10,11] disregarding the critical reorientational fluctuations[7,8] or the molecular torsional motions.[10] O'Reilly[11] approximately took into account the molecular jumps with superimposed modulations due to the torsional oscillations in the framework of a single-particle model. The actual cooperativity in the molecular jumps was not considered, so no direct connection with the critical dynamics could be achieved.

In this paper high-resolution FT ^{35}Cl NQR frequency and T_1 measurements in HCl and in HCl-DCl mixed crystals, around the phase transitions, are presented and discussed in the light of a theoretical picture which allows a fruitful analysis of the experimental results. In Sec. II a theory is described to relate the NQR quantities to the local order parameter, to the mean-square amplitude of the fluctuations as well as to their correlation times. This theory is applied to pure HCl and to the mixed crystals HCl-DCl in the framework of a kinematical Ising model with the addition of a small tunneling integral. The results for ν_0, T_1, linewidth, and intensity around the transition are presented in Sec. III, with a few experimental details. A thorough discussion of these results, including the effect of hydrostatic pressure on the resonance frequency around the transition up to about 2 kilobars, is given in Sec. IV. From the analysis of the data the temperature dependence of the local order parameter and of the fluctuation times in the ferroelectric phase are derived. It is pointed out how the results for the line intensity suggest the occurrence of heterophase fluctuations in a narrow temperature range around the transition, with embryos of fluctuating biased HCl dipoles in the matrix of the paraelectric phase of unbiased dipoles. This seems to be, in the author's knowledge, the first detection of heterophase fluctuations at a first-order phase transition in crystals. The effect of deuteration on the static and dynamical quantities are discussed in the light of a simple picture in which the deuteration is assumed to reduce almost to zero the tunneling matrix element for the reorientation of the electrical dipoles. The effect of hydrostatic pressure is shown to support such a picture, and some information about the pressure dependence of the critical parameters is obtained. Finally, since no Cl NQR resonance was detected in the disordered paraelectric phase, it is conjectured that the disorder could involve 12-fold orientations of the dipoles with orthorhombic symmetry. In Sec. V the comprehensive consistency of this picture and the main conclusions are summarized.

II. THEORY

A. NQR quantities and reorientational dynamics

The appropriate analysis of the experimental data requires a detailed description for the effects of the reorientational dynamics as well as the out-of-plane and in-plane vibrational motions of the HCl dipoles on the NQR quantities.

As will be shown later on, there is experimental evidence that for $T \gtrsim 70$ K the reorientational fluctuations of the dipoles are fast compared to the NQR frequency ν_Q. In spite of the expected slowing down of the fluctuations, this is also true around the transition temperature ($T_0 \sim 99$ K), due to the first-order character of the transition, already indicated by dielectric measurements.[12]

For fast motions the resonance frequency, the linewidth, and the relaxation rates can be derived by writing, for the EFG components

$$V_{jk}(t) = \langle V_{jk} \rangle + V_{jk}(t) - \langle V_{jk} \rangle = \langle V_{jk} \rangle + V^{f}_{jk} \ , \tag{1}$$

where $\langle V_{jk} \rangle$ are the time-average components which give the NQR frequency, while the fluctuating components V^f_{jk} cause line broadening and nuclear relaxation. We will assume that the effect of the motions is simply to rotate a rigid EFG tensor with respect to a crystalline frame of reference coinciding with the average position of the principal axes frame of reference ($\bar{x} \parallel \bar{c}$; $\bar{z} \parallel \bar{b}$). This assumption is supported by the intramolecular character of the EFG at the Cl site. For the rigid-lattice principal axes V_{JK} components one has $V_{ZZ} = eq$ with Z along the H$-$Cl bond and $V_{XX} = V_{YY} = -\frac{1}{2}eq$. The possible effect of deuteration on V_{JK}, as well as the effect of the high-frequency stretching motion, can be taken into account *a posteriori* by modifying the effective rigid-lattice component of the EFG tensor.

Let $\phi_\parallel$ and $\phi_\perp$ indicate the angular displacements of the H$-$Cl bond parallel and perpendicular to the *ab* plane. The critical reorientations of the molecules will be described on the basis of a kinematical Ising model, which has been fruitful for the interpretation of the NQR and dielectric measurements around the ferroelectric transition[6,13] in $NaNO_2$, as well as in several other crystals undergoing order-disorder phase transitions.[14] It can be mentioned that a double-minimum potential in HCl is also supported by a theoretical calculation,[15] based on the zigzag chain structure.

Therefore, the angle of rotation of the HCl molecule around the *c* axis will be written

$$\alpha(t) = \tfrac{1}{2}\pi - \tfrac{1}{2}\pi s(t) + \phi_\parallel(t) \ , \tag{2}$$

where $s(t)$ is a local order-disorder variable which assumes the values $+1$ or -1 according to the sign of the projection of the dipole moment on the *a* ferroelectric axis. According to Eq. (2), the reorientation jump is assumed to be $\frac{1}{2}\pi$. Only minor numerical corrections would be present if the actual value (93°) for the planar zigzag HCl segments should be considered. Moreover, it can be observed that, in principle, due to the finite width of the potential well, the molecular reorientations could involve an angle which differs from $\frac{1}{2}\pi$, at random, by a value ϕ^* of the order of $\langle\phi_\parallel^2\rangle^{1/2}$. It is of crucial importance[6] for Ising-type reorientations of angle π to take this latter effect into account, while for a $\frac{1}{2}\pi$ jump the different symmetry conditions cause the critical dynamics to affect the NQR parameters more directly, as it will be shown later on. Therefore, for the sake of simplicity, the classical Ising model, i.e., $\phi^*=0$, has been assumed in writing Eq. (2).

Taking into account Eq. (2) and the out-of-plane librational motion by an angle $\phi_\perp$, a straightforward tensor transformation gives for the time average $\langle V_{jk}\rangle$ components

$$\begin{aligned}\langle V_{xx}\rangle &= \langle V_{yy}\rangle = -\tfrac{1}{2}\langle V_{zz}\rangle\\ &= (\tfrac{1}{4}eq)(1-3\langle\phi_\perp^2\rangle)\ ,\\ \langle V_{xy}\rangle &= (\tfrac{3}{4}eq)\langle s\rangle(1-2\langle\phi_\parallel^2\rangle-\langle\phi_\perp^2\rangle)\ ,\\ \langle V_{xz}\rangle &= \langle V_{yz}\rangle = 0\ ,\end{aligned}\tag{3}$$

while the fluctuating components can be written

$$\begin{aligned}V_{xx}^f(t) &= A[\phi_\perp^2(t)-s(t)\phi_\parallel(t)]\ ,\\ V_{yy}^f(t) &= A[\phi_\perp^2(t)+s(t)\phi_\parallel(t)]\ ,\\ V_{zz}^f(t) &= 2A[\phi_\perp^2(t)]\ ,\\ V_{xy}^f(t) &= A\{s(t)[1-2\phi_\parallel^2(t)-\phi_\perp^2(t)]\\ &\qquad -\langle s\rangle(1-2\langle\phi_\parallel^2\rangle\langle\phi_\perp^2\rangle)\}\ ,\\ V_{xz}^f(t) &= -(2A/\sqrt{2})[s(t)\phi_\perp+\phi_\perp\phi_\parallel]\ ,\\ V_{yz}^f(t) &= (2A/\sqrt{2})[s(t)\phi_\parallel\phi_\perp-\phi_\perp]\ ,\end{aligned}\tag{4}$$

with $A=\frac{3}{4}eq$.

From Eq. (3), after the diagonalization of the tensor, the ^{35}Cl NQR frequency

$$\nu_Q=(eQ\langle V_{zz}\rangle/2h)(1+\tfrac{1}{3}\eta^2)^{1/2}\ ,$$

with $\eta=(\langle V_{xx}\rangle-\langle V_{yy}\rangle)/\langle V_{zz}\rangle$, is given by

$$\begin{aligned}\nu_Q(T) &= (\tfrac{1}{2}\nu_Q^0)[(1-3\langle\phi_\perp^2\rangle)^2\\ &\quad +3\langle s\rangle^2(1-2\langle\phi_\parallel^2\rangle-\langle\phi_\perp^2\rangle)^2]^{1/2}\ ,\end{aligned}\tag{5}$$

where $\nu_Q^0=eq^0Q/2h$ is the "rigid-lattice" quadrupole frequency. Equation (5) shows how the ^{35}Cl NQR frequency is affected by the temperature behavior of the local order parameter $\langle s\rangle$, and indicates how the effect of the oscillations cannot simply be included in an "effective" value of ν_Q^0. It can be noted that for $\langle s\rangle=1$ the usual Bayer-type[4] expression for $\nu_Q(T)$ is obtained from Eq. (5). For $\langle s\rangle=0$ (disordered phase) one has

$$\nu_Q(T)=(\tfrac{1}{2}\nu_Q^0)(1-3\langle\phi_\perp^2\rangle)\ ;\tag{6}$$

i.e., the effect of the in-plane motion is quenched by the $\frac{1}{2}\pi$ jumps.

For the Cl-NQR spin-lattice relaxation time T_1, starting from

$$T_1^{-1}=(e^2Q^2/6h^2)(\mathcal{J}_1+\mathcal{J}_2)\ ,\tag{7}$$

where $\mathcal{J}_1$ and $\mathcal{J}_2$ are the spectral densities at the resonance frequency of the well-known EFG functions V_1 and V_2, by taking into account Eqs. (4) the contribution to the relaxation rate related to the critical reorientational variable $s(t)$ is given by

$$T_1^{-1}=\tfrac{3}{4}(\omega_Q^0)^2\int e^{-i\omega_Q t}(g_1+g_2+g_3+g_4)\,dt\ ,\tag{8}$$

with

$$g_1=\tfrac{1}{2}\langle s(0)s(t)\rangle\ ,\tag{8a}$$

$$g_2=\langle s(0)\phi_\perp(0)s(t)\phi_\perp(t)\rangle\ ,\tag{8b}$$

$$g_3=2\langle s(0)\phi_\parallel^2(0)s(t)\phi_\parallel^2(t)\rangle\ ,\tag{8c}$$

$$g_4=\tfrac{1}{2}\langle s(0)\phi_\perp^2(0)s(t)\phi_\perp^2(t)\rangle\ ,\tag{8d}$$

where $\langle\ \ \rangle$ means the ensemble average for the correlation function.

By referring to a kinematical Ising model,[3] the correlation function for the collective critical variable can be written

$$\langle s_{\vec{q}}(0)s_{-\vec{q}}(t)\rangle=\langle|s_{\vec{q}}|^2\rangle\exp(-t/\tau_{\vec{q}})+\delta_{\vec{q},0}\langle s\rangle^2\ .\tag{9}$$

This expression can be expected to apply quite well to the critical dynamics in HCl if the tunneling integral Ω between the two equilibrium positions for H is small compared to the interaction energy between the dipoles, and when polarization fluctuations related to the exchange of energy with the thermal bath occur. Even in the presence of a sizeable tunneling effect Eq. (9) would be used if strong damping affects the pseudospin waves.[16] In this case the relaxation time for the polarization fluctuation should be written.

$$\tau_{\vec{q}}=2\gamma_{\vec{q}}/\omega_{\vec{q}}^2\ ,\tag{10}$$

where $\omega_{\vec{q}}$ is the soft-mode frequency, related to Ω, and $\gamma_{\vec{q}}$ the damping factor. Moreover, Eq. (9) could be used to describe a possible low-frequency part of the spectral density of the excitations in HCl, as a "central-peak" tail of resonant pseudo-spin-wave modes.[16]

To make explicit the correlation functions in Eqs. (8b)–(8d), we will assume for $\phi_\perp$ and $\phi_\parallel$ classical damped-harmonic-oscillator equations, with average frequencies $\omega_\perp$ and $\omega_\parallel$. A straightforward calculation, in the random-phase approximation, for the damping factor $\Gamma \lesssim \tau_{\vec{q}}^{-1}$, gives

$$g_2(t) = \langle \phi_\perp^2 \rangle \frac{1}{N} \sum_{\vec{q}} \langle |s_{\vec{q}}|^2 \rangle e^{-t/\tau_{\vec{q}}} \cos\omega_\perp t \quad , \tag{11a}$$

$$g_3(t) = 4(\langle \phi_\parallel^2 \rangle)^2 \frac{1}{N} \sum_{\vec{q}} \langle |s_{\vec{q}}|^2 \rangle e^{-t/\tau_{\vec{q}}} \cos^2\omega_\parallel t \quad , \tag{11b}$$

while $g_4(t) = \frac{1}{4} g_3(t)$, with $\phi_\perp$ and $\omega_\perp$ instead of $\phi_\parallel$ and $\omega_\parallel$. For strong damping, i.e., $\Gamma >> \tau_{\vec{q}}^{-1}$, the fluctuations due to $s(t)$ can be neglected and the usual correlation functions for the damped harmonic oscillator are obtained for Eqs. (8b)–(8d).

From Eq. (8), taking into account Eqs. (9) and (11), and by considering that the reorientational fluctuations are slow compared to the oscillational motions, the relaxation rate is written

$$T_1^{-1} = \frac{3}{4}(\omega_Q^0)^2 \frac{1}{N} \sum_{\vec{q}} \langle |s_{\vec{q}}|^2 \rangle \left(\frac{\tau_{\vec{q}}}{1 + \omega_Q^2 \tau_{\vec{q}}^2} + 4\langle \phi_\parallel^2 \rangle^2 \tau_{\vec{q}} + \langle \phi_\perp^2 \rangle^2 \tau_{\vec{q}} \right) \tag{12}$$

for negligible damping. For strong damping, i.e., $\Gamma_\parallel$, $\Gamma_\perp >> \tau_{\vec{q}}^{-1}$ the above equation modifies to

$$T_1^{-1} = \frac{3}{4}(\omega_Q^0)^2 \frac{1}{N} \sum_{\vec{q}} \left[\left(\frac{\langle |s_{\vec{q}}|^2 \rangle \tau_{\vec{q}}}{(1 + \omega_Q^2 \tau_{\vec{q}}^2)} \right) + \frac{\Gamma_\perp}{\omega_\perp^2} \left[4\langle \phi_\perp^2 \rangle + \frac{1}{4} \langle \phi_\perp^2 \rangle^2 \right] + \frac{\Gamma_\parallel}{\omega_\parallel^2} (\langle \phi_\parallel^2 \rangle)^2 + \frac{(\langle \phi_\parallel^2 \rangle)^2}{\Gamma_\parallel} + \frac{(\langle \phi_\perp^2 \rangle)^2}{4\Gamma_\perp} \right] \tag{13}$$

which is only slightly different, in view of the dominant role of the first term in the summation.

For the $\vec{q}$ dependence of $\langle |s_{\vec{q}}|^2 \rangle$ and $\tau_{\vec{q}}$ we will use the mean-field approximation (MFA) results for the compressible Ising model[17]

$$\langle |s_{\vec{q}}|^2 \rangle = (1 - \langle s \rangle^2)/[1 - I(\vec{q})(1 - \langle s \rangle^2)/kT] \quad , \tag{14a}$$

$$\tau_{\vec{q}} = \tau_0/[1 - I(\vec{q})(1 - \langle s \rangle^2)/kT] \quad , \tag{14b}$$

where τ_0 is the fluctuation time in the absence of interactions between the dipoles and $I(\vec{q})$ the Fourier transform of the interaction. For $I(\vec{q})$ we will write

$$I(\vec{q}) = I(q=0)[1 - (q^2/\kappa_0^2) - \delta\cos^2\theta] \quad , \tag{15}$$

where κ_0 is the inverse correlation length in the absence of interactions, while the term $\delta\cos^2\theta$ (θ the angle with the polar axis) takes into account the anisotropy of the dipolar part of the interaction, related to the depolarizing electric field.[18]

B. HCl-DCl mixed crystals

HCl-DCl mixed crystals represent perhaps the simplest example of isotopically disordered ferroelectrics, and can be considered the electric analog of random ferromagnets. The analysis of their static and dynamical properties may be attempted by applying some theoretical treatments already developed for the above mentioned systems. A suitable approach is the coherent potential method[5] (CPA), while another often more convenient approximate method is the virtual crystal approximation (VCA), developed by Tahir-Kheli.[19] VCA corresponds to the MFA for nonrandom systems and it is expected to hold for infinite-range interactions. Although VCA breaks in the dilute limit, nevertheless it appears to be quantitatively valuable at higher concentrations, where all CPA treatments have difficulties.[5]

The VCA approach has already been used for the study of the static,[20] as well as of the dynamical properties[21] of partially deuterated potassium dihydrogen phosphate (KDP) crystals. We will apply these approaches to HCl-DCl crystals, with slight modifications and some assumptions which, although rather crude, should allow one to obtain a suitable physical picture while preserving the essential validity of the description.

Since the effect of deuteration on T_c is small (about 7% in HCl, compared to 80% in KDP) and the dielectric measurements indicate a Debye-type relaxation mode, we can assume, in the framework of the pseudospin formalism,[16] that the tunneling integral Ω is small for H, compared to the interaction energy, while it can be neglected for D. In addition we will assume that the I_{ij} interaction between the ith and the jth dipoles is not mass dependent (this is not true in KDP-type crystals, since the coupling with the O—O lattice vibrations may cause a renormalization of I_{ij}).[21]

With these assumptions the single-particle Hamiltonians can be written

$$\mathcal{H}_{\mathrm{H}} = -\Omega S_x^{\mathrm{H}} - I_0(\langle S_z^{\mathrm{H}} \rangle C_{\mathrm{H}} + \langle S_z^{\mathrm{D}} \rangle C_{\mathrm{D}}) S_z^{\mathrm{H}} \quad , \tag{16a}$$

$$\mathcal{H}_{\mathrm{D}} = -I_0(\langle S_z^{\mathrm{D}} \rangle C_{\mathrm{D}} + \langle S_z^{\mathrm{H}} \rangle C_{\mathrm{H}}) S_z^{\mathrm{D}} \quad , \tag{16b}$$

where $I_0 = \sum_j I_{ij}$, and $S_\alpha^{\mathrm{H,D}}$ are the usual Pauli spin matrices, and the expectation values $\langle\ \rangle$ include a configurational average, and C_{H} and C_{D} are the concentrations. In writing Eqs. (16) it has been assumed that the Hamiltonian depends on the particle type only and not on its position. In this case, for instance $\langle S_{z,j}^{\mathrm{H}} C_{\mathrm{H},j}\rangle = C_{\mathrm{H}}\langle S_z^{\mathrm{H}}\rangle$ (where $C_{\mathrm{H},j}=1$ if a proton is at the jth position, and zero otherwise). A partial support of this VCA assumption can be considered the fact that in HCl-DCl mixed crystals close to T_c, no broadening or structure in the ^{35}Cl NQR line has been observed, indicating that the local order parameter, i.e., $\langle S_z\rangle$ is not a sensible function of the position (see Sec. IV).

From Eqs. (16) the self-consistency equations for the thermal expectation values of the z component of the pseudospin operators are

$$\langle S_z^{\mathrm{H}}\rangle = \tfrac{1}{2} I_0 (C_{\mathrm{H}}\langle S_z^{\mathrm{H}}\rangle + C_{\mathrm{D}}\langle S_z^{\mathrm{D}}\rangle)\tanh\alpha/2kT\alpha^{-1} \ , \tag{17a}$$

$$\langle S_z^{\mathrm{D}}\rangle = \tfrac{1}{2}\tanh\frac{I_0(C_{\mathrm{H}}\langle S_z^{\mathrm{H}}\rangle + C_{\mathrm{D}}\langle S_z^{\mathrm{D}}\rangle)}{2kT} \ , \tag{17b}$$

where $\alpha = [\Omega^2 + I_0^2(C_{\mathrm{H}}\langle S_z^{\mathrm{H}}\rangle + C_{\mathrm{D}}\langle S_z^{\mathrm{D}}\rangle)^2]^{1/2}$.

From Eqs. (17) the transition temperature T_0^M in HCl-DCl crystals is given by the equation

$$1 = C_{\mathrm{H}}\frac{I_0}{2\Omega}\tanh\frac{\Omega}{2kT_0^M} + C_{\mathrm{D}}\frac{I_0}{4kT_0^M} \ . \tag{18}$$

By expanding tanh up to the second term, one derives for the tunneling integral

$$\Omega \simeq 2kT_0^{\mathrm{H}}(3\Delta T/T_0^{\mathrm{D}})^{1/2} \ , \tag{19}$$

with

$$\Delta T = T_0^{\mathrm{D}} - T_0^{\mathrm{H}} \ ,$$

while

$$I_0 \simeq 4kT_0^{\mathrm{D}} \ . \tag{20}$$

Then from Eq. (18) one can obtain for the transition temperature the simplified form

$$T_0^M \simeq C_{\mathrm{H}}T_0^{\mathrm{H}} + C_{\mathrm{D}}T_0^{\mathrm{D}} \ . \tag{21}$$

From Eqs. (17) the temperature dependence of the order parameter in the two subsystems can be derived. If one assumes for $T \lesssim T_0$ $\langle S_z^{\mathrm{H}}\rangle \simeq \langle S_z^{\mathrm{D}}\rangle \rightarrow 0$ then by expanding tanh one obtains

$$\langle S_z^{\mathrm{D}}\rangle \simeq \langle S_z^{\mathrm{H}}\rangle\frac{1+AC_{\mathrm{H}}}{1-AC_{\mathrm{D}}} \ , \tag{22}$$

where $A = I_0\Omega^2/48(kT)^3$. In discussing the results for HCl-DCl crystals it will turn out useful to consider the case for which $\langle S_z^{\mathrm{D}}\rangle \simeq \langle S_z^{\mathrm{H}}\rangle \simeq 1$. Then, from Eqs. (17), taking into account that $I_0^2 \gg \Omega^2$ and $(\Omega^2/4I_0kT) \ll 1$, one derives

$$\langle S_z^{\mathrm{D}}\rangle \simeq \langle S_z^{\mathrm{H}}\rangle(1+\Omega^2/2I_0^2) \times [1+(\Omega^2/2kTI_0)\exp(-I_0/kT)]^{-1} \ . \tag{23}$$

As regards the reorientational dynamics, by dividing the expectation values of the pseudospin operators into a static and a fluctuating part, from Heisenberg equation the fluctuation around the VCA solution can be found by means of a standard random-phase approximation (RPA) linearization procedure.[16,22] Under the above mentioned assumption about Ω, one can derive the following. There is one ferroelectric ω_1 mode corresponding to the in-phase motion of the HCl and DCl subsystems and there is one antiferroelectric ω_2 mode corresponding to the out-of-phase motion of the two subsystems. Above the transition the $q=0$ frequency of the ω_2 mode is given by

$$\omega_2^2 = \Omega^2\{1 - C_{\mathrm{H}}[\tanh(\Omega/2kT)/\tanh(\Omega/2kT_0^{\mathrm{H}})]\} \ . \tag{24}$$

Again expanding tanh and taking into account Eq. (10), the effective relaxation time can be written

$$\tau_{q=0} = (2\gamma/\Omega^2)(1 - C_{\mathrm{H}}T_0^{\mathrm{H}}/T)^{-1} \ . \tag{25}$$

Since the instability limiting temperature is $C_{\mathrm{H}}T_0^{\mathrm{H}}$, according to Eq. (25) for $T \simeq T_0^M$, $\tau_{q=0}$ is unlikely to contribute to the quadrupole Cl relaxation [see Eq. (12)]. For the ferroelectric ω_1 mode the real part of the eigenfrequency is zero. Therefore, the reorientational fluctuations of the HCl or DCl dipoles are of completely relaxational character.

Below the transition temperature the ω_1 and ω_2 frequencies can be written

$$\omega_1^2 = (C_{\mathrm{D}}\langle S_z^{\mathrm{D}}\rangle + C_{\mathrm{H}}\langle S_z^{\mathrm{H}}\rangle)^2 I_0^2 \ , \tag{26a}$$

$$\omega_2^2 = \omega_1^2 + \Omega(\Omega - \langle S_x^{\mathrm{H}}\rangle I_0 C_{\mathrm{H}}) \simeq \omega_1^2 \ . \tag{26b}$$

Therefore, a kinematical Ising model, as used in the previous Sec. II A, retains its essential validity also in the HCl-DCl mixed crystal. The effective relaxational time $\tau_{q=0}$ for HCl is indirectly determined by the tunneling integral and one can crudely expect that the relaxation time in the absence of the interactions [see Eq. (14b)] is inversely proportional to Ω.

III. EXPERIMENTAL RESULTS

The ^{35}Cl NQR measurements have been performed by means of a pulse spectrometer with quadrature detection and Fourier transform (FT) capability, achieved by means of a Nicolet 1180 data-processor system. Quadrature detection, with on resonance irradiation, allowed us to reduce line-shape distortion and/or broadening, thus improving resolution and accuracy. Furthermore, quadrature detection was essential for reliable T_1 measurements, due to short T_1's and the relatively large linewidths. For the NQR frequency and linewidth measurements accumulations of up to 10^4 free-induction decays (FID) after $\sim\frac{1}{2}\pi$ pulses were averaged, particularly around the transition. The T_1 measurements have been performed through a standard $\frac{1}{2}\pi$-t-$\frac{1}{2}\pi$ sequence, with FT-quadrature detection of the FID following the second pulse.

Automatic temperature control was provided by a properly designed cryostat,[23] and the temperature was measured with a standardized Pt. resistance thermometer. Temperature resolution was about 10^{-2} K, and the temperature gradients on the sample were estimated to be negligible ($\lesssim 10^{-2}$ K). The measurements of ν_Q under hydrostatic pressure were performed with less frequency and temperature resolution, using a beryllium-copper pressure vessel, and details will be published elsewhere.[24]

In Fig. 1 the results for the ^{35}Cl NQR frequency, linewidth, and intensity in pure HCl are shown. Figures 2 and 3 are the analogous results for HCl-DCl, for the ^{35}Cl resonance in the HCl molecules and in the DCl molecules, respectively. It should be stressed that the results pertain only to the ferroelectric phase. In the disordered high-temperature phase no NQR signal was detected, a significant point which is discussed later (Sec. IV).

The ^{35}Cl NQR T_1 are shown in Fig. 4. In the temperature range 80–90 K, T_1 in pure HCl is too short to be measured with good accuracy. However, an estimate of ^{35}Cl NQR T_1 can be obtained in that temperature range, for the proton $T_{1\rho}^{H}$ data.[25,26] In fact $T_{1\rho}^{H}$ is dominated by the intermolecular dipolar relaxation of the second kind and is given by

$$T_{1\rho}^{H} = [1 + (\omega_1 T_1^{Cl})^2]/\gamma_H^2 M_2 T_1^{Cl} \ , \qquad (27)$$

where M_2 is the contribution to the proton second moment due to the chlorine nuclei. Although T_1^{Cl} may differ from the pure NQR T_1, because of the presence of a sizeable magnetic field for the $T_{1\rho}^{H}$ measurements, the data derived through Eq. (27) satisfactorily match with the result at 77 K (see Fig. 4). The small discrepancy at higher temperatures is probably related to the fact that for $T \sim 100$ K other mechanisms[25] of relaxation for proton $T_{1\rho}$ increase their effectiveness. Further ^{35}Cl NQR T_1 measurements for HCl-DCl 75:25 gave $T_1^{-1} \simeq 10^4$ sec^{-1} almost temperature independent in the range 78–96 K, with no measurable difference for the HCl and the DCl molecules (data not reported in Fig. 4). Other results for ν_Q, $\delta\nu$, and T_1, not shown in Figs. 1–4, will be referred to in the discussion (Sec. IV).

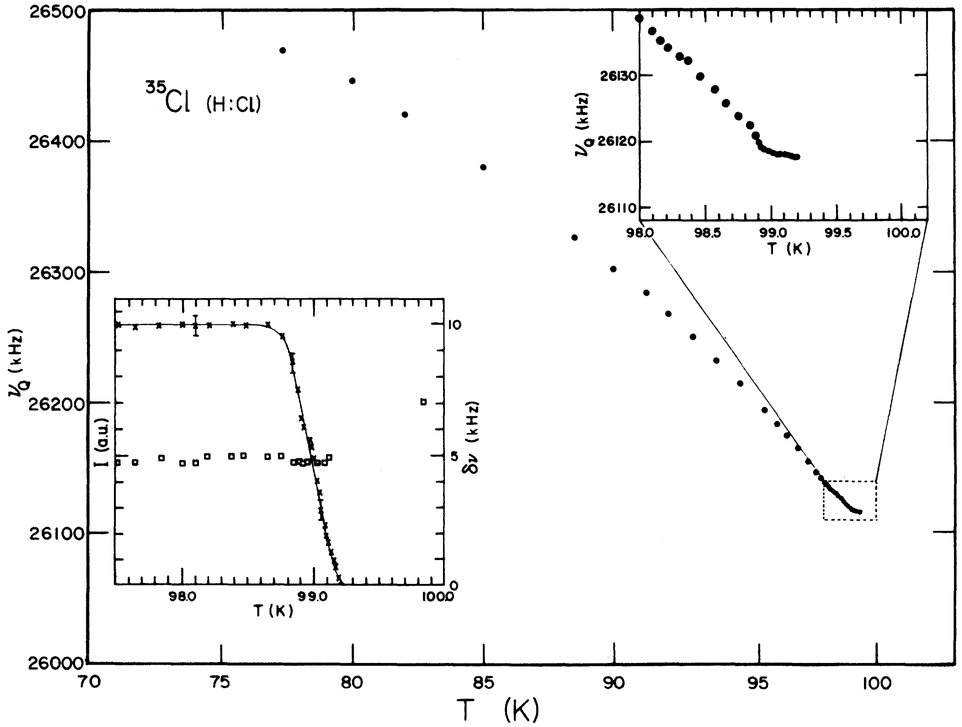

FIG. 1. ^{35}Cl NQR frequency (●), linewidth $\delta\nu$(□) (half width at half intensity), and intensity I of the absorption line (×) for pure HCl vs temperature.

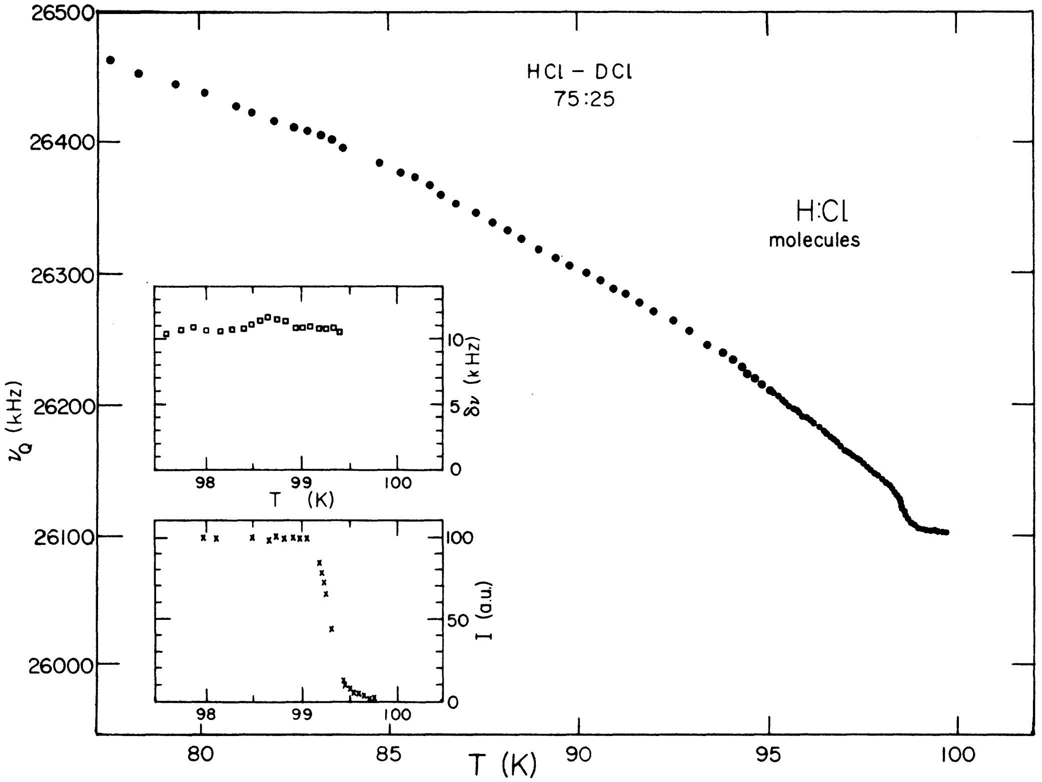

FIG. 2. ^{35}Cl NQR frequency, linewidth $\delta\nu$(□) (half width at half intensity) and intensity I of the absorption line for the HCl molecules in the mixed crystal HCl:DCl = 75:25 vs temperature.

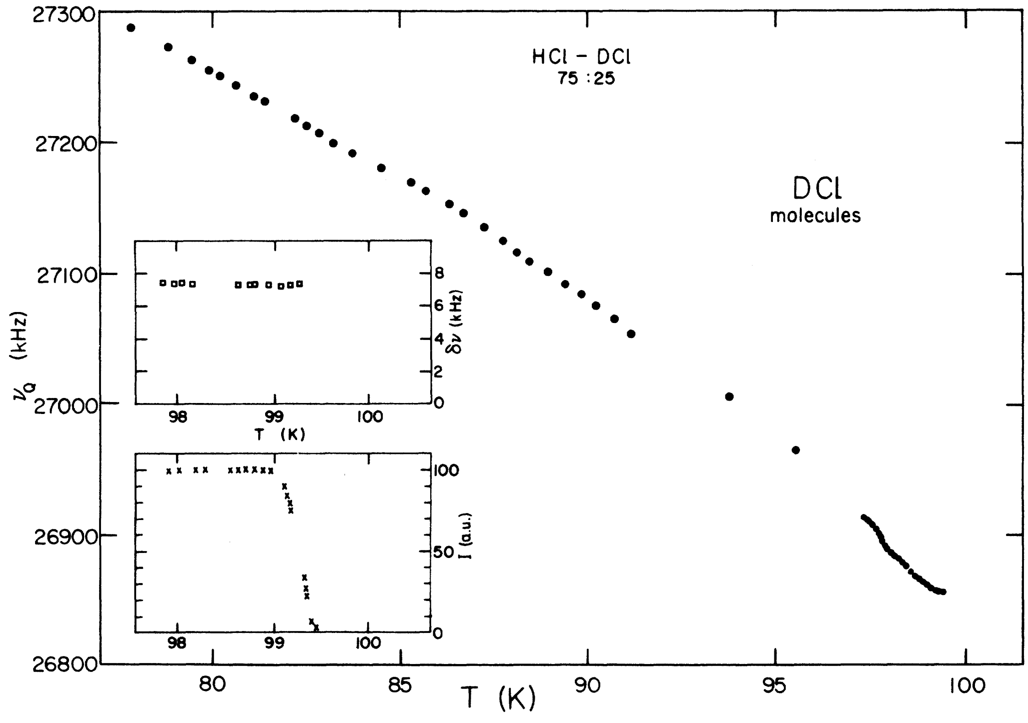

FIG. 3. ^{35}Cl NQR frequency, linewidth $\delta\nu$(□) (half width at half intensity) and intensity I of the absorption line for the DCl molecules in the mixed crystal HCl:DCl = 75:25 vs temperature.

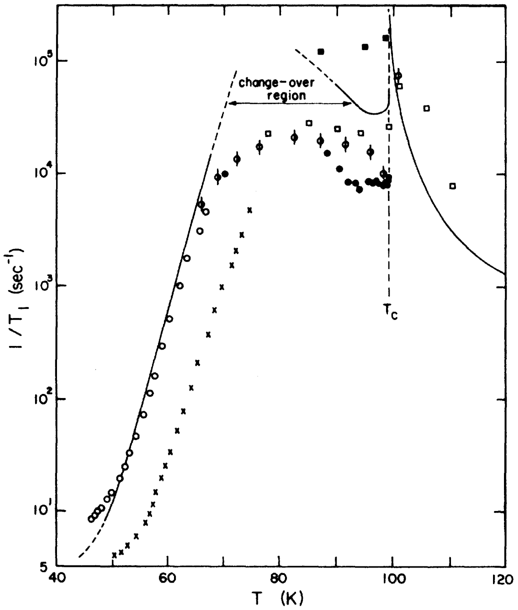

FIG. 4. ^{35}Cl NQR spin-lattice relaxation rates in HCl, HCl:DCl = 50:50 and DCl vs temperature [pure HCl: (●), present work; (○), data from Ref. 7; (□), deduced from proton $T_{1\rho}$, according to Eq. (27) in the text, from the data in Ref. 25 and (ϕ), from the data in Ref. 26; pure DCl: (×), data from Ref. 7 HCl:DCl = 50:50, for the HCl molecule: (■) deduced from the proton $T_{1\rho}$ according to Eq. (27) in the text, from the data in Ref. 25]. The solid lines are the theoretically derived relaxation rates, without adjustable parameters, as explained in the text (Sec. IV B).

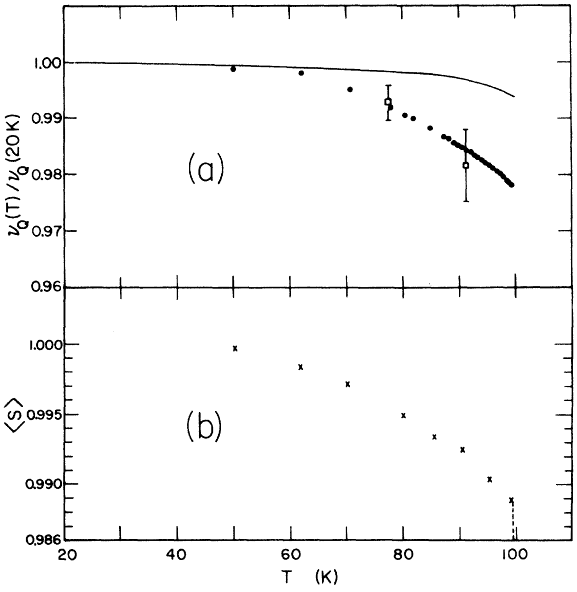

FIG. 5. (a) Temperature dependence of the NQR frequency $\nu_Q(T)$ (normalized to the value at 20 K) expected from Eq. (5) in the text, for no reorientational motions of the dipoles (solid lines). (●) Representative of actual results, as derived from the data in Fig. 1 for HCl. (ϕ) expected results by taking into account for $\langle \phi_\parallel^2 \rangle$ the values indicated by neutron scattering (Ref. 28). (b) Local order parameter $\langle s \rangle$ vs T derived from Eq. (5), as explained in the text.

IV. DISCUSSION

A. Temperature dependence of ν_Q and the order parameter

Equation (5) gives the expected temperature dependence of the NQR frequency ν_Q due to the angular oscillations and by the reorientations of the dipoles.

Neutron-diffraction measurements[27] in DCl provide the values of $\langle \phi_\parallel^2 \rangle$ and $\langle \phi_\perp^2 \rangle$ at three temperatures in the low-temperature phase. At 4.2 K $\langle \phi_\perp^2 \rangle \simeq 40$ deg^2 and $\langle \phi_\parallel^2 \rangle \simeq 32$ deg^2. The temperature dependence of these quantities, in the harmonic approximation, has been calculated.[4] Taking into account only the temperature dependence of $\langle \phi_\perp^2 \rangle$ and $\langle \phi_\parallel^2 \rangle$ (i.e., by setting $\langle s \rangle = 1$) one derives, for $\nu_Q(T)/\nu_Q(20\text{ K})$ the solid line plotted in Fig. 5. The comparison with the experimental values puts in evidence a significant departure, already noted[8] and later[10] qualitatively associated with the effect of $\langle s \rangle$. As shown in Fig. 5 a possible explanation for the departure could be found in the anomalous increase of $\langle \phi_\parallel^2 \rangle$ estimated[27] for DCl, particularly at 92.4 K. Some facts, however, do not support such an interpretation. Crudely speaking, $\langle \phi_\parallel^2 \rangle$ is inversely proportional to the frequency of the lattice mode which causes the in-plane librations. Raman scattering measurements[28] do not show any anomalous temperature dependence of the zone-center in-plane librations. A self-consistent phonon theory derivation of the $k = 0$ frequency spectrum of HCl corroborates the absence of any soft-mode behavior on approaching the transition temperature from below. Moreover, our T_1 measurements (see Sec. IV B), as well as dielectric measurements, definitely indicate the occurrence, for $T \gtrsim 80$ K, of fast reorientations of the dipoles, which must have some effect on averaging the quadrupole interaction. A possible explanation is that the increase in $\langle \phi_\parallel^2 \rangle$ estimated from neutron diffraction indirectly reflects the starting of the reorientational motions, while the amplitude of the oscillations around the equilibrium positions still remains almost constant. A superposition of ordinary, nonsoft, oscillatory modes and of critical reorientational fluctuations is known to occur in other ferroelectric crystals.[29]

If one assumes for $\langle \phi_\parallel^2 \rangle$ and $\langle \phi_\perp^2 \rangle$ the temperature dependence suggested by the Raman frequencies,[28] from the experimental data for $\nu_Q(T)$ (see Fig. 1), through Eq. (5), one can derive the value of $\langle s \rangle$ shown in Fig. 5. The first-order character of the transition is apparent. It has to be stressed here that in the transition region, namely, 98.7–99.2 K for HCl and 99.2–99.6 K for HCl:DCl 75:25, the local order parameter $\langle s \rangle$ remains almost constant, while the intensity of the absorption line drops continuously to zero (see Figs. 1–3). This fact is important in elucidating the mechanism of the transition and it will be discussed in more detail below.

The quadrupole frequencies in mixed crystals would allow one to derive, in principle, $\langle s \rangle$ for the two subsystems of the HCl and DCl dipoles. This has not been carried out in detail, since the vibrational dynamics of the mixed crystals is complicated and the effect of deuteration on $\langle s \rangle$ appears small. As far as the vibrational dynamics is concerned, in fact, the mixed systems can be considered[30] as a series of oligomers of HCl linked in a zigzag chain embedded in a lattice of DCl or vice versa. The infrared spectra[30,31] show a structure with many lines of different intensities, depending on the length of the oligomer and the probability distribution. This distribution in the vibrational frequencies can explain the extra broadening of the NQR lines. At $\tilde{T} \simeq 48$ K we measured, for the half width at half intensity, $\delta\nu \simeq 5$ kHz for pure HCl and $\delta\nu \simeq 8$ kHz in HCl:DCl 75:25.

Close to the transition no further broadening or structure of the lines has been observed, and this can be considered a support of the VCA used in Sec. II B. The effects of the deuteration on the local order parameter do not appear to be dramatic, at least from a qualitative analysis of the data in Figs. 2 and 3. This is in agreement with the main conclusion of the theoretical picture in Sec. II B. In fact, if the crude values derived in Eqs. (19) and (20) are used for Ω and I_0, one would have for the correction factor A in Eq. (22) $A \simeq \Delta T (T_0^{\mathrm{H}})^2 4/T^3 \simeq 10^{-2}$ while, for S_z^{D}, $S_z^{\mathrm{H}} \simeq 1$, Eq. (23) gives $S_z^{\mathrm{D}} \simeq S_z^{\mathrm{H}}\, 1.02$.

B. Relaxation times and reorientational dynamics

The results for the ^{35}Cl NQR relaxation rates shown in Fig. 4 indicate that in the low-temperature phase there are three different regions. For $T \gtrsim 90$ K (region a) the motions are fast, namely, the effective correlation time is shorter than ω_Q^{-1}, and the relaxation rates for the DCl dipoles are greater than those for the HCl ones. For $T \lesssim 70$ K (region b), the relaxation rates decrease on cooling, the motions are slow compared to ω_Q^{-1} and the relaxation rate for DCl dipoles is smaller than the one for HCl dipoles by a factor around 14. For $70 \lesssim T \lesssim 90$ K (region c) the changeover from the slow- to the fast-motions condition occurs, and more complicated relations between the relaxation rates for HCl and DCl dipoles are present.

The above-mentioned features, which have caused some confusion in the interpretation of previous results[7,8,25,26] can be consistently justified in the light of the theoretical picture presented in Sec. II. Furthermore, their analysis can provide enlightening information on the dynamical properties of the systems.

In region b, from Eq. (12) taking into account Eqs. (14) under the condition $\omega_Q \tau_q >> 1$ for any $\vec{q}$, one obtains

$$T_1^{-1} \simeq \tfrac{3}{4}(1-\langle s \rangle^2)\tau_0^{-1} \ . \tag{28}$$

It can be mentioned that for reorientational times less than ω_Q^{-1} the perturbation-theory approach implicit in the derivation of Eq. (28) would be more appropriately substituted by a picture based on the time evolution equations for the populations under the sudden rotation of the eigenkets of the quadrupole Hamiltonian.[32] This picture would give, for independent motions (namely, without taking into account biasing effects related to the transition), $T_1^{-1} \simeq \frac{3}{2}\tau_0^{-1}$. Therefore, we can refer to Eq. (28) for some discussion in the slow-motion regime.

It should be mentioned that in the slow-motion regime the averaging of the quadrupole resonance frequency is provided only by the fast oscillations around the equilibrium positions. Moreover the fact that one single NQR line is observed in this region supports the assumption that the EFG at the Cl site is almost completely of intramolecular origin.

In the region a one has $\omega_Q \tau_q << 1$ in Eq. (12). By means of Eqs. (14) and (15) one derives

$$T_1^{-1} = C(1-\langle s \rangle^2)\tau_0 \ , \tag{29}$$

where the constant C is given by

$$C = \frac{3(\omega_Q^0)^2}{8\pi^2 N}\left\{\frac{\kappa_0^3 T_0''^2}{2T_0^{3/2}\Delta^{1/2}}\tan^{-1}\left[\frac{q_{\mathrm{D}}}{\kappa_0}\left(\frac{T_0}{\Delta}\right)^{1/2}\right] - \frac{q_{\mathrm{D}}\kappa_0^2 T_0''^2}{2T_0\Delta + 2(q_{\mathrm{D}}/\kappa_0)^2 T_0^2}\right\} \tag{30}$$

for isotropic interaction [$\delta = 0$ in Eq. (15)]. For $\delta \neq 0$ a more complicated expression holds, the leading term being

$$C = \frac{3(\omega_Q^0)^2}{64\pi}\kappa_0^3\left(\frac{T_0''}{T_0}\right)^2 \delta^{-1/2}\ln\left(\frac{\Delta}{T_0}\right)^{-1} \ . \tag{31}$$

It must be stressed that in order to derive Eqs. (29) and (30) one has to take into account in the q integration in Eq. (12) that the local order parameter $\langle s \rangle$ is discontinuous at the transition, for example by setting

$$\langle s \rangle^2 = \frac{T_0'' - T}{T_0''} = \frac{T_0 + \Delta - T}{T_0 + \Delta} \ . \tag{32}$$

The condition of discontinuity at the transition temperature T_0 (see Fig. 5), allows one to keep the MFA and the fast motion conditions, which otherwise would give inconsistent results for $T \simeq T_0$. In Eq. (30) q_D is the Debye wave vector.

Equations (28) and (29) show how, in the low-temperature phase, the relaxation rates are affected by the biasing of the dipoles. Furthermore, the effective correlation time is given by the time each dipole spends in the "wrong" position with respect to the polarization, and its order of magnitude is around the correlation time in the absence of the interactions. In the region b one has $\tau_0 \lesssim \omega_Q^{-1} \simeq 6 \times 10^{-9}$. An activated temperature behavior, i.e.,

$$\tau_0 \sim T^{-1} e^{E_A/kT} \tag{33}$$

can be expected for τ_0. On cooling, this causes the changeover to the slow motion conditions.

For $T \simeq 82$ K where the maximum in the relaxation rate occurs, one should have $\tau_0 \sim \omega_Q^{-1}$. For the activation energy E_A in Eq. (33) the value $E_A = 0.113$ eV, indicated by dielectric dispersion in the temperature range about 63–100 K, can be used. Therefore, by means of Eqs. (28) and (30), and by taking for $\langle s \rangle$ the values in Fig. 5, a quantitative determination of the ^{35}Cl NQR relaxation rate can be attempted, without adjustable parameters, in the whole temperature range. The result of such a calculation for pure HCl is shown as a solid line in Fig. 4. For the value of C in the region a, Eq. (30), we have set $\kappa_0 \sim a^{-1}$ with an average value of the lattice parameter $a = 5.4$ Å, while Δ has been taken equal to T_0 (only modifications of some units can be expected by reasonably changing the above parameters).

As appears from Fig. 4, the agreement of the theoretical prediction with the experimental data is gratifying and allows one to draw some conclusions about the validity of the model assumed for the theoretical picture. It can be noted in particular, that the effect of the biasing, through the terms $(1 - \langle s \rangle^2)$, typical of the cooperative compressible Ising model, is essential in giving the correct order of magnitude of T_1 (typically for $T \simeq 70$ K, without the effect of the biasing a factor of about 1.7×10^2 would be present). The effect of deuteration on the Cl relaxation rate can be justified along the following lines. Since it is affected by the tunneling matrix element, which is strongly reduced for the deuterium atom (see Sec. II B), the ratio between the relaxation rates for HCl and DCl in the region b is much greater than the value 1.4 that one would expect for classical reorientations, in view of the different moments of inertia.[7,33] In the region a the changeover to fast motions causes $(T_1^{-1})_{\mathrm{DCl}} > (T_1^{-1})_{\mathrm{HCl}}$, which also explains the proton $T_{1\rho}$ measurements[25] in HCl:DCl 50:50 [see Eq. (27)].

C. Mechanism of the transition

As it appears from the behavior of $\langle s \rangle$ (see Fig. 5), the transition is of first-order character. In the temperature range of about 98.7–99.2 K for HCl and 99.2–99.7 K for HCl:DCl 75:25, while $\langle s \rangle$ is almost constant, the intensity I of the absorption line drops rapidly, but continuously towards zero (see Figs. 1–3). Since the linewidth remains practically constant, I can be considered proportional to the fraction of dipoles which are biased, i.e., with $\langle s \rangle \neq 0$.

Furthermore, as it appears from Fig. 4, in the transition region the fraction of ^{35}Cl nuclei whose resonance is detected have $T_1 \simeq 10^{-4}$ sec, practically constant.

The qualitative conclusion from the above mentioned results is that in the transition region two phases are simultaneously present. The ferroelectric phase, for which $\langle s \rangle \simeq 0.988$ and with characteristic correlation time of the order of 10^{-9} sec, and the paraelectric phase for which $\langle s \rangle \simeq 0$, which cannot be detected because of the large shift of the quadrupole frequency [see Eq. (6) and discussion below]. The number of dipoles belonging to the ferroelectric phase decreases on heating as I does. Such a situation can be discussed on the basis of the droplet model for heterophase fluctuations.

The picture of heterophase fluctuations, early proposed[34] on the basis of thermodynamical arguments for the two phases of a fluid, has recently been applied by Cook[35] to the phase transitions in crystals, in an attempt to explain the existence of the intrinsic central peak in the dynamical structure factor $S(\vec{q}, \omega)$. In such a picture the fluctuations occurring around the transition temperature T_0 are related to the formation of embryos, or clusters, of the low temperature when, on cooling, the free energy of the high-temperature phase F_H approached the free energy of the metastable low-temperature phase F_L. The order parameter inside an embryo jumps from zero to the value of the metastable state. The average size of the clusters, which should be related to the correlation length, changes rapidly around the transition. The frequency width of the central peak is controlled by the time required for the formation and collapse of the embryos.

For first-order transitions in crystals the volume and the shape changes associated with the transition cause a strain-energy contribution to the free energy F_L, which is likely to suppress the heterophase fluctuations. Since in HCl no appreciable change in the structure occurs at the transition,[1] the strain-energy contribution to the free energy should be small, allowing some persistence of the metastable state in the disordered phase, around the transition temperature.

In the framework of the thermodynamical droplet model in q space, the concentration of atoms within an embryo is given by the transcendental equation[35]

$$c = 4\pi kT\left[\frac{q_m}{\beta} - \frac{\alpha^{1/2}}{\beta^{3/2}}\tan^{-1}\left(\frac{q_m\beta^{1/2}}{\alpha^{1/2}}\right)\right] , \quad (34)$$

where α and β are coefficients related to the pairwise contributions to the free energy, to the average elastic free energy associated to the coherency strains and to the gradient-free-energy coefficient. α depends on c, and q_m is a maximum wave vector playing the role of the Debye wave vector, which is equal to $0.62a^{-1}$ in the droplet model for cubic lattices. For the free energy one has $F(q) \simeq \alpha + \beta q^2$. $F(q)$ is inversely proportional to the generalized static susceptibility $\chi(q,0)$ and from fluctuation-dissipation theorem $\chi(q,0) \propto F(q)^{-1} \simeq (N/kT)S(q)$, where $S(q)$ is the static structure factor for a variable taking value one if a site is within an embryo and zero if not. Then, by recalling the classical Ornstein-Zernike expression for the static structure factor, which defines the inverse correlation length, we can write

$$\alpha/\beta = \kappa^2 \ . \quad (35)$$

For a first-order phase transition κ (as well as α in the thermodynamical description) goes to zero at a temperature $T_0' < T_0$, T_0 being the transition temperature at which the free energies of the two phases are equal, $F_H = F_L$. T_0' is the temperature at which the central peak in $S(\vec{q},\omega)$ should diverge.

Then we can write

$$\kappa^2 = \kappa_0^2(T - T_0')/T \quad (36)$$

and from Eqs. (33) and (34), the concentration of the heterophase fluctuations results

$$\begin{aligned} c &= (4\pi kT/\beta)[q_m - \kappa\tan^{-1}(q_m/\kappa)] \\ &= c_0'[1-(\kappa/q_m)\tan^{-1}(q_m/\kappa)] \ , \end{aligned} \quad (37)$$

where c_0' is the concentration at T_0', on cooling from above. The interpretation of the experimental results for I on the basis of Eq. (37) is made uncertain by the lack of knowledge of parameters like κ_0, T_0', and c_0'. If one assumes $\kappa_0 \sim a^{-1}$, no reasonable values can be found for T_0', and c_0' to give a satisfactory reproduction of the behavior of I in the transition region.[36] In fact, the marked increase of I from zero in a few tenths of degree seems hard to justify by means of a cusped-shaped function as the one in Eq. (37), with Eq. (36). An attempt to take approximately into account the effect of the short-range order by modifying the Orstein-Zernike form of $S(q)$ in $S(q) \propto (q^2+\kappa^2+\delta^2)^{-1}$, where δ is a term slightly temperature dependent, such that $(\alpha/\beta) \simeq \kappa^2+\delta^2$, does not give a significant modification of the predicted temperature behavior of $\langle c \rangle$.

In spite of the partial failure of the droplet model in fitting quantitatively the temperature dependence of I (at least for our choices of the parameters involved) it appears that the general features of the heterophase fluctuations around the ferroelectric transition HCl are correctly described. Refinements in the theory could lead to a better agreement. A possible further support for the occurrence in HCl of heterophase fluctuations, as well as of the general validity of a droplet model approach, could be envisaged in the temperature behavior of the spontaneous polarization P_s. P_s, in fact, as measured from the pyroelectric current,[37] shows a behavior roughly similar to I in Fig. 1, which would not be compatible with a first-order phase transition without the occurrence of heterophase fluctuations.[38]

Although the measurements for mixed crystals are not conclusive, it would appear from the results for I in HCl:DCl 75:25 (see Figs. 2 and 3) that the deuteration does not change the width of the temperature range, around the transition, in which heterophase fluctuations occur.

As regards the lifetime of the embryos, the present measurements allow us to conclude only that it should be longer than the inverse of the difference in the NQR frequency for the paraelectric and the ferroelectric phase, namely, longer than about 10^{-7} sec.

Regarding the paraelectric phase of HCl, while a dynamical structure seems necessary to account for the x-ray results,[1] one unambiguous disordered model has not yet been established. Our measurements definitely rule out the occurrence of the antiferroelectric ordering as well as of any other kind of static disordered structure. In fact, a simple rearrangement of the dipoles above T_0 would only slightly affect the NQR frequency. At the same time, the extension above T_0 of the dynamical model for the ferroelectric phase, i.e., reorientations of the dipoles involving the two positions along the zigzag chain with no biasing, is not supported by the experimental results. According to Eq. (6), this model for the dynamical disorder would cause the ^{35}Cl NQR frequency to shift to about 13 MHz at the transition. An attempt to detect the ^{35}Cl NQR resonance in the range 11–26 MHz, at $T \simeq 105$ and 115 K was unsuccessful. A very short T_1 could prevent the detection of the resonance. As shown in Fig. 4, the straightforward extension in the paraelectric phase of the theoretical calculations for T_1 (solid line) is roughly supported by the data derived by proton $T_{1\rho}$. For $T \simeq 110$ K the value $T_1 \sim 10^{-4}$ sec is likely to allow the detection of the resonance. Furthermore, it must be stressed that ^{35}Cl NMR quadrupole perturbed spectra have been detected[8] at two temperatures in the paraelectric phase of HCl. Although incomplete, and not confirmed for DCl, those spectra point out that $\nu_Q << \nu_L$, where ν_L is the ^{35}Cl Larmor frequency 4.1 MHz.

A marked decrease of the ^{35}Cl quadrupole frequency in the paraelectric phase can be explained only with the occurrence of fast reorientational motions of the dipoles among more than two positions. A possibility is that the disorder mechanism above T_0 involves 12 $\langle 110\rangle$ directions, through 60° and 90° flipping processes, the crystal structure being orthorhombic for HCl and cubic for DCl. This conjecture would give consistency to a recent incoherent neutron scattering study[39] of the proton motions in HCl, since the scattering cross sections have been interpreted on the basis of that dynamical model. Unfortunately, the authors seem unaware of the occurrence of the cubic-orthorhombic phase transition at about 120 K.

Detailed studies of the quadrupole perturbed Cl NMR spectra and T_1 could give useful insights into the disorder mechanism of the dipoles in the paraelectric phase of HCl. Only minor modifications to the theoretical picture would be necessary.

D. Effect of pressure

The experimental results for the NQR frequencies in HCl as a function of temperature for various hydrostatic pressures[24] can be summarized as follows. The quadrupole frequency at the transition temperature $\nu_Q(T_0,P)$ decreases almost linearly for P up to 2.3 kilobars with

$$\left|\frac{d\nu_Q(T_0P)}{dP}\right|_{P\to 0} \simeq -36 \text{ kHz kbar}^{-1} \ . \tag{38}$$

The dependence of the transition temperature T_0 on the pressure is well described by the equation

$$T_0(P) \simeq 99 + bP \text{ K} \ , \tag{39}$$

with $b \simeq 3$ K/kbar. Further experimental data will be published elsewhere.[24]

It should be mentioned that while some uncertainty is present in defining the transition temperature T_0, this does not affect the main conclusions of the following discussion.

It is known that ν_Q, is, in general, a complicated function of P, through the effects of various microscopic quantities. Around T_0, for low P, one can tentatively assume that the dominant effect on ν_Q is through the effect on the order parameter $\langle s\rangle$. Under this assumption, from Eq.(5), Eq. (38) gives

$$\left|\frac{d\langle s\rangle T_0}{dP}\right|_{P\to 0} \simeq -1.8\times 10^{-3} \text{ kbar}^{-1} \ . \tag{40}$$

The law of corresponding states, proposed for magnetic systems,[40,41] states that whenever an additional thermodynamical variable P is involved, the variation of the order parameter with P will be dominated by the dependence of the transition temperature on P. For a first-order phase transition no reliable expression for the dependence of $\langle s\rangle\,(T,0)$ on T is known. One can tenatively use Eq. (32), whose purpose was just to take into account the discontinuity in $\langle s\rangle$ at T_0. By assuming Δ independent of P, and by using for $T_0(P)$ Eq. (39), one has

$$\left|\frac{d\langle s\rangle T_0}{dP}\right|_{P\to 0} = -\Delta^{1/2} b/2[T_0(0)+\Delta]^{3/2} \ . \tag{41}$$

If for Δ we use an indicative value of the order of T_0 (as for the theoretical derivation of T_1, see Sec. IV B). Equation (41) gives

$$\left|\frac{d\langle s\rangle T_0}{dP}\right|_{P\to 0} \sim -5\times 10^{-3} \text{ kbar}^{-1} \ .$$

Considering the crudeness of some of the assumptions, the comparison of this evaluation with Eq. (40) is not discouraging and seems to support the hypothesis that the major effect of P is on the order parameter. This could also be considered indirect and perhaps naive support for the application of the law of corresponding states.

The dependence of the transition temperature on P [Eq. (39)] can be discussed in terms of the microscopic quantities by writing

$$b = \frac{\partial T_0}{\partial \Omega}\frac{d\Omega}{dP} + \frac{\partial T_0}{\partial I_0}\frac{dI_0}{dP} \ , \tag{42}$$

$d\Omega/dP$ is known to be negative[42,43] and is most likely to cause $T_0(P) < T_0(0)$ in KDP crystals and other hydrogen-bonded ferroelectrics.[44] The positive sign of b in HCl points out that the second term in Eq. (42) dominates, consistent with our assumption of a small Ω (see Sec. II). Another order-disorder ferroelectric crystal[45] for which $b > 0$ is $NaNO_2$. In this crystal the critical dynamics is also of the relaxational type, and Ω is supposed to be very small, and where it is the increase of the interaction energy between dipoles under compression which causes $b > 0$.[44]

If for I_0 and Ω expressions (19) and (20) used, from Eq. (42) and the experimental value for b [Eq. (39)] one derives

$$\frac{dI_0}{dP} \simeq 10^{-3} \text{ eV/kbar} \ .$$

Detailed studies of the effect of pressure on the NQR parameters in HCl and DCl can be expected to permit a more comprehensive analysis of the data and to provide more elucidating insights. Here we only emphasize that the effect of pressure is consistent with the model for the phase transition on which the theoretical picture developed in Sec. II rests, as well as with the main conclusions outlined in this section.

V. CONCLUSIONS

HCl and $(HCl)_{1-x}$-$(DCl)_x$ are interesting ferroelectric crystals. They are essentially an assembly of simple electrical dipoles which at the transitions temperature reorient cooperatively without any appreciable change in the lattice structure. Furthermore, the mixed crystals represent probably the simplest example of isotopically disordered ferroelectrics.

The ^{35}Cl nuclear quadrupole moment is an ideal tool to study the static and dynamical effects around the transitions. In fact, through the coupling with the intramolecular electric field gradients, the quadrupole interaction is directly affected by the biasing of the dipoles and by their critical reorientations.

Detailed results, obtained from NQR pulse measurements, with FT in quadrature detection, and with high resolution and accuracy, for the ^{35}Cl resonance frequency, linewidth, line intensity and T_1 around the transition have been presented in this paper. The analysis of these results has been carried out in the light of a theoretical treatment which takes into account the effects of the librational motions of the dipoles around the equilibrium positions as their reorientations related to the polarization fluctuations. On the basis of previous neutron diffraction and dielectric relaxation measurements, the reorientational fluctuations of the dipoles have been described by means of a simple kinematical Ising model with the addition of a tunneling integral which is small for the HCl dipole and goes to zero for the DCl dipole.

A thorough discussion of the experimental results, including the effect of hydrostatic pressure on the resonance frequency at the transition, has given comprehensive support to this model for the critical dynamics. It has also permitted a consistent explanation of some controversial points in early interpretations of data on HCl, and has provided interesting information on the static properties and the dynamical mechanism of the transition.

The temperature dependence of the local order parameter $\langle s \rangle$, which measures the biasing of the dipoles, has been obtained. The transition is confirmed as a classical first-order one with $\langle s \rangle \simeq 0.988$ at the transition. The correlation times for the fluctuations of the dipoles, roughly the time each dipole spends in the wrong position with respect to the polarization, have been derived in the ferroelectric phase. The correlation times are of the order of the fluctuation time τ_0 in the absence of the interaction. The activated temperature dependence of τ_0 causes the changeover, on cooling, from a region of fast motions with the time scale $(2\pi\nu_Q)^{-1} \simeq (2\pi 26\text{ MHz})^{-1}$, to a region of slow motions (below about 70 K). The activation energy for τ_0 is approximately the same as is indicated by dielectric absorption and dispersion measurements, namely about 0.11 eV. Deuteration turns out to affect drastically the correlation time, ruling out the occurrence of classical motions, while it can be qualitatively explained through the effect on the tunneling matrix element for the reorientation of the protons. The leading effect of the pressure is to increase the interaction energy between dipoles, such that the transition temperature is increased.

In the temperature range 98.7–99.3 K for HCl and 99.2–99.8 K for $HCl_{0.75}$-$DCl_{0.25}$ the NQR line intensity drops to zero continuously, while the resonance frequency, the linewidth, and the relaxation rate stay practically constant. This seems to indicate the occurrence in these temperature ranges of heterophase fluctuations. These fluctuations cause the progressive appearance (on cooling) of polarized clusters, or ferroelectric embryos, in the matrix of the paraelectric phase. Inside an embryo the order parameter as well as the correlation times are the ones typical of the ferroelectric phase just below the transition. The lifetime of the clusters should be at least 10^{-7} sec, or greater. According to a picture based on the droplet model, the reason the embryos are allowed to exist in the metastable state should be related to the very small change of shape and volume at the transition in HCl, thus reducing the coherency strain energy, which is thought usually to suppress the heterophase fluctuations at a first-order phase transition in crystals. The temperature dependence of the concentration of the embryos seems hard to be quantitatively justified in the framework of the droplet model in q space. Careful neutron inelastic scattering in the transition region of HCl could give a direct corroboration of the occurrence of heterophase fluctuations, through the detection of a temperature diverging central peak in the dynamical structure factor.

Finally it has to be mentioned that evidence of static low-temperature clusters above the phase transition obtained by means of high-resolution ^{13}C NMR spectroscopy in the two-dimensional antiferroelectric squaric acid has been very recently reported.[46] Some significant differences seem to be present in squaric acid compared to HCl (as to the nature of the transitions, the role of the impurities, the dimensionality). However, the temperature dependence of the concentration of the clusters appears roughly similar to the behavior of I in HCl although extending over a wider temperature range, i.e., about 2 K.

ACKNOWLEDGMENTS

One of us (A.R.) wishes to acknowledge illuminating discussions with J. Dufty and the hospitality of the Department of Physics of the University of Florida kindly provided by the chairman Professor F. E. Dunnam and by the solid-state physics group headed by Professor T. A. Scott. Acknowledgments are also due to Paul Canepa for valuable technical assistance and to Dr. K. Krynicki for careful preparation of the HCl-DCl mixed sample. This research was supported by the NSF under Grant No. DMR-77-08658.

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

[1] N. Niimura, K. Shimaoka, H. Motegi, and S. Hoshino, J. Phys. Soc. Jpn. 32, 1019 (1972).

[2] H. E. Cook, Phys. Rev. B 15, 1477 (1977).

[3] See, K. Kawasaki, in *Phase Transitions and Critical Phenomens,* edited by C. Domb and M. S. Green (Academic, New York, 1972); R. Blinc and B. Žekš, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam, 1974).

[4] P. N. Yi and A. T. Gavrielides, J. Chem. Phys. 56, 3777 (1971).

[5] See, R. J. Elliot, J. A. Krumhansl, and P. L. Leath, Rev. Mod. Phys. 46, 465 (1976).

[6] R. Ambrosetti, A. Colligiani, and A. Rigamonti, Phys. Rev. B 15, 4318 (1977).

[7] E. P. Marram and J. L. Ragle, J. Chem. Phys. 41, 3546 (1964).

[8] H. Okuma, N. Nakamura, and H. Chihara, J. Phys. Soc. Jpn. 24, 452 (1968).

[9] M. Mackowiak and J. R. Brookeman, Acta Phys. Pol. A 52, 281 (1977).

[10] S. Zumer (private communication); in Proceedings of the Conference on Magnetic Resonance and Related Phenomena, Bucharest, 1971, edited by I. Ursu, p. 376.

[11] D. E. O'Reilly, J. Chem. Phys. 52, 2398 (1970).

[12] S. Hoshino, K. Shimaoka, and N. Niimura, Phys. Rev. Lett. 19, 1287 (1967).

[13] I. Hatta, J. Phys. Soc. Jpn. 38, 1430 (1976) and references therein.

[14] See various contributions in *Local Properties at Phase Transitions,* edited by K. A. Muller and A. Rigamonti (North-Holland, Amsterdam, 1976); see also A. Rigamonti, in *Structural Phase Transitions,* edited by H. Thomas and K. A. Muller (Springer-Verlag, New York, 1980); F. Borsa and A. Rigamonti, in *Magnetic Resonance at Phase Transitions,* edited by F. Owens, H. Farach, and C. Poole (Academic, New York, 1979).

[15] T. Tsang and E. L. Shaw, J. Chem. Phys. 55, 2337 (1971).

[16] R. Blinc and B. Žekš, Adv. Phys. 21, 693 (1972).

[17] See, K. Kawasaki in Ref. 3; M. Suzuki and R. Kubo, J. Phys. Soc. Jpn. 24, 51 (1968), see also S. Zumer, Phys. Rev. B 11, 1830 (1975).

[18] G. Bonera, F. Borsa, and A. Rigamonti, Phys. Rev. B 2, 2784 (1970). For a discussion of the effects of the depolarizing field, see M. Tokunaga and T. Mitsui, Ferroelectrics 11, 451 (1976).

[19] R. A. Tahir-Kheli, Phys. Rev. B 6, 2808, 2826, 2838 (1972).

[20] J. Holakovsky, Czech. J. Phys. B 22, 651 (1972).

[21] B. Žekš, Ferroelectrics 12, 91 (1976); R. Blinc, R. Pirc, and B. Žekš, Phys. Rev. B 13, 2943 (1976).

[22] A similar procedure, including also the assumption $\Omega \simeq 0$, for the deuterium atom, has been used by E. Courtens [Phys. Rev. Lett. 39, 561 (1977)] in order to justify the strength and the temperature dependence of the central peak in the Rayleigh scattering in KDP crystals, as related to the natural abundance of deuterium impurities.

[23] J. R. Brookeman and T. A. Scott, J. Low Temp. Phys. 12, 491 (1973).

[24] J. R. Brookeman and M. H. Mackowiak (unpublished).

[25] M. O. Norris, J. H. Strange, J. G. Powles, M. Rhodes, K. Marsden, and K. Krynicki, J. Phys. C 1, 445 (1968).

[26] D. J. Genin, D. E. O'Reilly, E. M. Peterson, and T. Tsang, J. Chem. Phys. 48, 4525 (1968).

[27] E. Sandor and R. F. C. Farrow, Discuss. Faraday Soc. 48, 78 (1969).

[28] T. S. Sun and A. Anderson, Chem. Phys. Lett. 17, 104 (1972).

[29] In NaNO$_2$, for example, no strongly temperature-dependent soft modes were found by means of various infrared and Raman-spectroscopy experiments, while neutron inelastic scattering [J. Sakurai, R. A. Cowley, and G. Dolling, J. Phys. Soc. Jpn. 28, 1426 (1970)], showed a quasielastic component, of relaxational character, related to ferroelectric fluctuations. For the superposition of reorientational fluctuations of permanent dipoles on the ordinary lattice dynamics see also, A. S. Barker, Jr., Phys. Rev. B. 12, 4071 (1975).

[30] M. Gussoni and G. Zerbi, J. Chem. Phys. 60, 4862 (1974).

[31] D. F. Hormig and G. L. Hiebert, J. Chem. Phys. 27, 752 (1957).

[32] S. Alexander and A. Tzalmona, Phys. Rev. 138, A865 (1965).

[33] T. P. Das, J. Chem. Phys. 25, 896, 27, 763 (1957).

[34] J. Frenkel, *Kinetic Theory of Liquids* (Clarendon, Oxford, 1946), p. 374.

[35] In Eq. (34) we have omitted the term $-c^2$ which is present in Ref. 2 [Eq. 40)]. In fact, since in the integration in the continuum limit the $q = 0$ term is included, it appears appropriate to take into account that $T(q = 0)$. $T(q = 0) = c^2$.

[36] J. Brookeman and A. Rigamonti (unpublished).

[37] T. Kobayashi, M. Ida, and S. Kawada, J. Phys. Soc. Jpn. 27, 1365 (1969).

[38] For a more detailed discussion see Ref. 36.

[39] Y. Fujii, S. Hoshino, and T. Sakuma, J. Phys. Soc. Jpn. 45, 175 (1978).

[40] G. B. Benedek and T. Kushida, Phys. Rev. 118, 46 (1960).

[41] P. Heller, Phys. Rev. 146, 403 (1966).

[42] R. Blinc, and B. Žekš, Helv. Phys. Acta 41, 700 (1968).

[43] V. S. Vikhnin and A. Ya Gordon, Sov. Phys. Solid State 17, 1433 (1976).

[44] G. A. Samara, Ferroelectrics 20, 87 (1978).

[45] K. Gesi, K. Ozawa, and Y. Takagi, J. Phys. Soc. Jpn. 20, 1773 (1965).

[46] M. Mehring and D. Suwelack, Phys. Rev. Lett. 42, 317 (1979).