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Quantum tunneling effects in dipolar ferroelectrics: A nuclear-quadrupole-resonance study in HCl-DCl mixed crystals

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Static and dynamical effects from a quantum tunneling contribution to the dipole reorientations in the ferroelectric phases of the mixed crystals HCl-DCl have been studied through ^{35}Cl nuclear-quadrupole-resonance pulse Fourier-transform measurements. Experimental data for the transition temperatures T_c and the local correlation times τ, of both the HCl and DCl dipoles, for several percentages of deuteration are analyzed in the light of a dynamical Ising model in a transverse field which includes damping in a heuristic way. The virtual-crystal approximation (VCA) is used in deriving both the static properties (local order parameters and transition temperatures) and the reorientational dynamics (local correlation functions). Estimates of the interaction energy and the tunneling integrals are obtained from the dependence of T_c on deuteration. The behavior of the correlation times for the DCl dipoles as a function of deuteration, predicted within the framework of the VCA approach, is consistent with the experimental results. However, for the HCl dipoles this theoretical picture does not account for the correlation times in the dilute limit of almost-complete deuteration. Instead, the persistence of quantum tunneling (namely, short correlation times) is observed in spite of the interaction with the "classical" DCl dipoles (long correlation times). Possible sources for this phenomenon are discussed. The only hypothesis that appears suitable involves the effect of local phonon modes on the tunneling of the HCl dipoles.

I. INTRODUCTION

Most dipolar order-disorder ferroelectrics exhibit reorientational dynamics of a classical nature. In other words, in an assembly of permanent electric dipoles or flipping ions, polarization fluctuations are related to the exchange of energy with the thermal bath. The time dependence of the polarization as derived, for instance, from the Onsager irreversible thermodynamics, is characterized by diffusional relaxational modes, with a correlation time at a critical wave vector which diverges on approaching the transition temperature.[1] In the local representation classical fluctuations mean that the electric dipole can take the reverse position in a double-well—type potential only through thermally activated motion.

For an atom of small mass involved in the reorientation, a sizable contribution to the collective dynamics can come from quantum tunneling between the equilibrium positions. Several static and dynamical properties of the crystal (Curie constants, transition temperatures, spontaneous polarizations, relaxational times, as well as the nature of the dielectric response) can be affected by the quantum fluctuations. In practice, sizable effects can be expected only when hydrogen is the reorienting atom, because of the strong mass dependence of the tunneling integral. An analysis of the static effects in the crystals of the potassium dihydrogen phosphate (KDP) family has recently been carried out[2] in the framework of the square-well and double-well models for the local potential at the hydrogen site.

Because of several interesting features the ferroelectric HCl-DCl mixed crystals appear to be ideal systems for the study of quantum effects. Besides the simplicity of the structure, namely a mere assembly of electric dipoles, the reorientation involves motion of only the hydrogen atom, and direct access to the thermal average of the dipole, as well as to its fluctuations, is provided by ^{35}Cl nuclear-quadrupole-resonance (NQR) and relaxation measurements.[3] The relevance of quantum effects is indicated by a comparison of the correlation times in HCl and DCl: A decrease by a factor of about 14 in HCl with respect to DCl occurs.[3] As already observed,[4] only a factor of 1.4, corresponding to the different moments of inertia, should be present if the reorientations were classical.

Furthermore, it must be emphasized that the ^{35}Cl quadrupole frequency in HCl is different from that in DCl, so in the mixed crystal, *independent* measurements of the correlation times for the two kinds of dipoles can be performed.

This paper deals with a study, in the ferroelectric phase of the mixed crystals HCl-DCl, of the static and dynamical effects related to quantum tunneling through the analysis of the ^{35}Cl NQR frequencies, linewidths, and spin-lattice relaxation times.

In Sec. II the experimental results for the transition temperatures and the local correlations times of the HCl and DCl dipoles are reported for several percentages of deuteration. A theoretical picture for the properties of the mixed crystals is presented in Sec. III. This is based upon a dynamical Ising model in a transverse field with damping included in a crude and heuristic way. The data are then analyzed in light of the theoretical picture, and the relevant considerations are outlined.

II. EXPERIMENTAL DATA

The ^{35}Cl NQR and spin-lattice relaxation measurements have been performed with a heterodyne pulse spectrometer

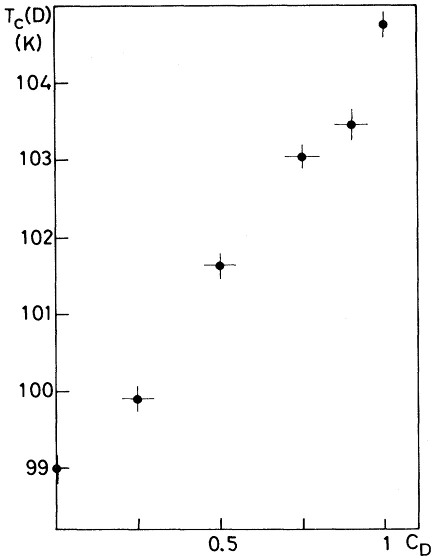

FIG. 1. Ferroelectric transition temperatures in the HCl-DCl crystals as a function of the DCl concentration c_D.

with quadrature detection of the rf free induction decay (FID). Gate pulse formation was accomplished by a Nicolet 293-A pulse programmer and a gated phase shifter. The pulse programmer was interfaced with a Nicolet 1180 computer. Under software control, using the program NTCFT, the following parameters could be set: the pulse sequences, the widths and phases of the individual pulses, and the repetition rate of the sequence. All frequencies were obtained from a PTS-160 frequency synthesizer. Quadrature detection, with on-resonance excitation, was particularly important for reliable T_1 measurements, because of the relatively large linewidths. These measurements were made with a standard $\frac{1}{2}\pi$-t-$\frac{1}{2}\pi$ sequence, with subsequent Fourier transform of the quadrature-detected FID's. Up to 10^4 FID's were averaged. NTCFT permitted the averaged FID to be the accumulation of a phase-alternating pulse sequence which significantly reduced noise not coherent in phase with the rf pulse.

A cryostat system, with automatic temperature control (provided by a Scientific Instruments cryogenic temperature controller) and calibrated platinum resistors, permitted a temperature resolution of about 0.01 K, with negligible temperature gradients over the sample. The temperature was stable during the longest periods of measurements to within 0.1 K.

The mixed crystals of HCl-DCl were obtained by mixing the gases under controlled pressure in a suitable manifold device. The HCl gas (provided by Matheson Gas) had a stated purity of 99.99 vol % while the DCl gas (provided by Merck Chemical Co.) was stated to contain 99 vol % DCl. Taking into account the accuracy of the gauge used to measure the pressure in the manifold and the possible occurrence of exchange of hydrogen in the whole system, the worst error in concentration percentages could be around 5%. Further experimental details can be found elsewhere.[5]

The transition temperatures from the ferroelectric to the paraelectric phase have been measured by monitoring, upon heating, the intensity of the ^{35}Cl NQR signal from the HCl and/or DCl dipoles. The first-order character of the transition implies a sudden, marked shift of the NQR frequency.[3] However, pretransitional phenomena[6] cause a smooth decrease of the intensity of the ^{35}Cl NQR line as a function of temperature, at practically constant resonance frequency, in a transition region of a few tenths of a degree. The transition temperature was located where the intensity of the line was about 50% of the value at the beginning of the transition region (this is the main source of the experimental uncertainty in the transition temperatures indicated in Fig. 1). For a given sample, the same transition temperature was observed from both the ^{35}Cl NQR of the HCl dipoles and the DCl dipoles, thus supporting the homogeneity of the deuteration of the sample. In Fig. 1 the transition temperatures in the mixed crystals HCl-DCl are reported.

In order to study the tunneling effects on the correlation times for the polarization fluctuations, the NQR T_1 measurements were performed in the temperature region of slow fluctuations, namely, when the reorientational times are slow compared to the inverse quadrupole frequency $\omega_Q^{-1}=(2\pi e^2qQ/2h)^{-1}$, and the relaxation rates are decreasing upon cooling.[3] Then the relaxation rate can be written[3]

$$T_1^{-1}=A(1-\langle s\rangle^2)\frac{1}{\tau_e}\ , \tag{1}$$

where $\langle s\rangle$ is a local order parameter (to which the spontaneous polarization can be related) resulting from the time averaging of a biased order-disorder variable describing the reorientations of the dipole; τ_e is the local correlation time for the dipole fluctuations, which is of the order of the time the dipole spends in the "wrong" position with respect to the polarization. In Eq. (1), A is a constant of the order of unity,[3] whose uncertainty will not affect the conclusions.

In Fig. 2 the relaxation times T_1 for ^{35}Cl belonging to the DCl and HCl dipoles, at $T=55\pm0.1$ K, are reported. The ability to measure separately the relaxation times of the two species depends on the different resonance frequencies: 25 640 kHz for HCl and 27 493 kHz for DCl; this frequency shift is predominantly related to the different amplitudes of libration of the dipoles around the equilibrium positions,[3] as well as to the different values of the local order parameters $\langle s\rangle$.

III. THEORETICAL PICTURE AND ANALYSIS OF THE DATA

A. Static and dynamical properties of ferroelectric HCl-DCl mixed crystals

Following the approach already established,[3,6] a theoretical model for the effect of tunneling upon properties of the mixed ferroelectrics HCl-DCl will be presented in terms of a local order-disorder variable which assumes the value + 1 or − 1 according to the projection of the di-

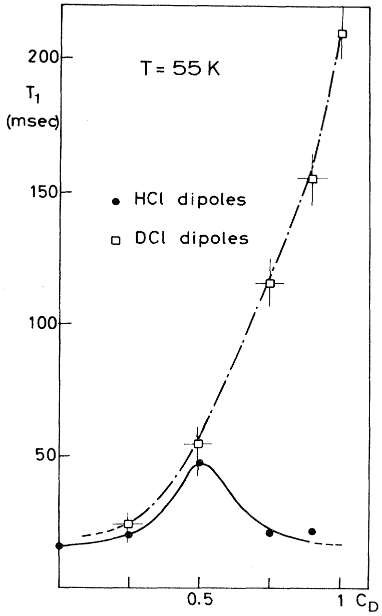

FIG. 2. NQR spin-lattice relaxation times for ^{35}Cl belonging to HCl dipoles (●) and to DCl dipoles (□) as a function of the DCl concentration c_D in the ferroelectric phase of HCl-DCl mixed crystals. Lines are only a guide for the eye.

pole moment on the polarization axis. To take into account the classical polarization fluctuations as well as the quantum tunneling of the dipoles, the model of an Ising spin in a transverse field[1] will be used. Then the Hamiltonian of the system can be written[3,6]

$$H=-\frac{1}{2}\sum_{i,j,\mathrm{H,D}} I_{ij}c_{\mathrm{H}}^{i}c_{\mathrm{D}}^{j}S_{z,i}^{\mathrm{H}}S_{z,j}^{\mathrm{D}} -\Omega_{\mathrm{H}}\sum_{i} c_{\mathrm{H}}^{i}S_{x,i}^{\mathrm{H}}-\Omega_{\mathrm{D}}\sum_{i} c_{i}^{\mathrm{D}}S_{x,i}^{\mathrm{D}} , \tag{2}$$

where c_{H}^{i} is 1 when a HCl dipole is at the ith position, and is zero otherwise (analogously for c_{D} in terms of the DCl dipoles). In Eq. (2) the interaction energy I_{ij} has been tentatively assumed particle independent, $\Omega_{\mathrm{H,D}}$ are the tunneling integrals between the two equilibrium positions of proton and deuteron, respectively, and $S_{\alpha}^{\mathrm{H,D}}$ are the usual Pauli spin matrices. With the possible exclusion of the dilute limits,[7] the virtual-crystal approximation (VCA), namely, the equivalent of the mean-field approximation for nonrandom systems, should provide a suitable physical picture. Therefore, by including in the expectation values of the pseudo-spin-operators a configurational average, from Eq. (2), the single-particle Hamiltonians become

$$\begin{aligned}\mathrm{H}_{\mathrm{HCl}}^{(i)}&=-\Omega_{\mathrm{H}}S_{x}^{\mathrm{H}}-h_{\mathrm{eff}}^{\mathrm{HCl}}S_{z}^{\mathrm{H}} ,\\ \mathrm{H}_{\mathrm{DCl}}^{(i)}&=-\Omega_{\mathrm{D}}S_{x}^{\mathrm{D}}-h_{\mathrm{eff}}^{\mathrm{DCl}}S_{z}^{\mathrm{D}} ,\end{aligned} \tag{3}$$

where

$$h_{z}=h_{\mathrm{eff}}^{\mathrm{DCl}}=h_{\mathrm{eff}}^{\mathrm{HCl}}=I_{0}(\langle S_{z}^{\mathrm{H}}\rangle c_{\mathrm{H}}+\langle S_{z}^{\mathrm{D}}\rangle c_{\mathrm{D}}) , \tag{4}$$

with $I_0=\sum_j I_{ij}$.

From the self-consistency equations for the expectation values in Eqs. (3), one obtains

$$\langle S_{z}^{\mathrm{H}}\rangle=\tfrac{1}{2}h_{z}\tanh(A_{\mathrm{H}}/2kT)A_{\mathrm{H}}^{-1} , \tag{5a}$$

$$\langle S_{z}^{\mathrm{D}}\rangle=\tfrac{1}{2}h_{z}\tanh(A_{\mathrm{D}}/2kT)A_{\mathrm{D}}^{-1} , \tag{5b}$$

where

$$A_{\mathrm{H,D}}=(\Omega_{\mathrm{H,D}}^{2}+h_{z}^{2})^{1/2} .$$

Moreover, by taking into account that $\Omega_{\mathrm{D}}\ll I_0$, the transition temperature T_c is given by the equation

$$\frac{c_{\mathrm{H}}}{2\Omega_{\mathrm{H}}}\tanh\frac{\Omega_{\mathrm{H}}}{2kT_c}=\frac{1}{I_0}+c_{\mathrm{D}}\frac{\Omega_{\mathrm{D}}^{2}-12k^{2}T_{c}^{2}}{48(kT_c)^{3}} . \tag{6}$$

It can be observed that for $c_{\mathrm{H}}=0$ and $\Omega_{\mathrm{D}}\ll I_0$, Eq. (6) yields the transition temperature $T_{c}^{\mathrm{class}}=I_0/4k$ expected for classical dipoles, namely with no tunneling fluctuations. A quantum parameter

$$q=2[(\Omega_{\mathrm{H}}-\Omega_{\mathrm{D}})c_{\mathrm{H}}+\Omega_{\mathrm{D}}]/I_0 \tag{7}$$

can be introduced to take into account the tunneling. While $q=0$ for classical dipoles, for $q=1$ quantum tunneling inhibits a ferroelectric transition at finite temperatures. Equation (6) predicts T_c monotonically decreasing when c_{H}, and therefore q, increases. It can be mentioned that through Eqs. (5) other static properties of the mixed crystals, as for instance the spontaneous polarization, could be derived in terms of q.

For the dynamical properties, it is well known[1] that a Hamiltonian of the form in Eq. (2) generates propagating waves of resonant character. This is not the case in HCl, since early dielectric dispersion measurements[8] indicate relaxational modes of diffusive type, thus implying strongly damped pseudo-spin-waves. Then the effective correlation time can be written $\tau=\gamma/\omega^2$, where γ is a damping factor and ω are the eigenfrequencies of the pseudo-spin-waves. In the framework of a standard random-phase linearization procedure, on the assumption $\Omega_{\mathrm{D}}\ll\Omega_{\mathrm{H}}\ll I_0$, the eigenfrequencies in the ferroelectric phase can be derived as[3]

$$\begin{aligned}\hbar^{2}\omega_{1}^{2}&\simeq I_{0}^{2}[c_{\mathrm{H}}(\langle S_{z}^{\mathrm{H}}\rangle-\langle S_{z}^{\mathrm{D}}\rangle)+\langle S_{z}^{\mathrm{D}}\rangle]^{2} ,\\ \hbar^{2}\omega_{2}^{2}&\simeq\omega_{1}^{2}\hbar^{2}+\Omega_{\mathrm{H}}^{2}-\Omega_{\mathrm{H}}I_{0}c_{\mathrm{H}}\langle S_{x}^{\mathrm{H}}\rangle .\end{aligned} \tag{8}$$

An inspection of Eqs. (5), taking into account Eq. (4) and the fact that I_0^2 is expected to be significantly greater than $\Omega_{\mathrm{H,D}}^{2}$, indicates that the local order parameter $\langle S_{z}^{\mathrm{H,D}}\rangle$ for the HCl and the DCl dipoles should not be much different (see later). Then Eqs. (8) show that the eigenfrequencies depend only slightly on the quantum parameter q. On the other hand, the experimental T_1 data reported in Fig. 2 prove that the effective reorientational time τ_{HCl} in pure HCl is more than an order of magnitude smaller than the corresponding τ_{DCl} in pure DCl. In consequence of the slight dependence of $\omega_{1,2}$ on q, the marked difference between τ_{HCl} and τ_{DCl} should therefore be ascribed to the damping factor γ, which, in turn, must be affected by the quantum tunneling. This qualitative conclusion is corroborated by a Green's-function description[9] of a damped transverse dynamical Ising model which indicates that for $T\rightarrow T_c$, $\gamma\propto T_c/\Omega^2$. For $T\ll T_c$,

γ is reduced, but is still expected to depend on Ω.

The above considerations suggest that a description for the HCl-DCl mixed crystals could be carried out in the framework of a dynamical Ising model of the Glauber type, earlier developed for magnetic systems[10] and successfully used to describe cooperative dipolar reorientations.[11] The different damping expected for the HCl and DCl dipoles can be taken into account by considering, in a heuristic way, two different single-particle relaxation times τ_H and τ_D. Such a description, although crude, is appealing for its inherent simplicity and the possibility of a better physical insight. In a first approximation τ_H and τ_D will be considered concentration independent. After a thorough discussion (see Sec. III B), the possible effect of localized modes in causing Ω_H to be a function of the concentration and to change significantly in the dilute limit will be taken into account.

Then the equations for the expectation values of the deviations from the VCA solutions, namely

$$\langle \delta S^{H,D}_{z,i}\rangle = \langle [S^{H,D}_{z,i}(t) - \langle S^{H,D}_z\rangle]\rangle = s^{H,D}_i(t) \ ,$$

after introducing the collective variable $s_{\vec{q}}$, will be written

$$\begin{aligned}\tau_H \frac{d}{dt} s^H_{\vec{q}}(t) &= -s^H_{\vec{q}}(t) + \frac{I(\vec{q})}{4kT}[c_H s^H_{\vec{q}}(t) + c_D s^D_{\vec{q}}(t)] \\ &\quad \times (1-\langle S^H_z\rangle^2) \ , \\ \tau_D \frac{d}{dt} s^D_{\vec{q}}(t) &= -s^D_{\vec{q}}(t) + \frac{I(\vec{q})}{4kT}[c_H s^H_{\vec{q}}(t) + c_D s^D_{\vec{q}}(t)] \\ &\quad \times (1-\langle S^D_z\rangle^2) \ ,\end{aligned} \tag{9}$$

where the Fourier transform of the VCA dynamical mean field is introduced. Far from the transition temperature a slight q dependence can be expected, and one can refer to the $q=0$ component in order to derive the behavior of the local order-disorder variable. Thus Eqs. (9) yield

$$\begin{aligned}\tau_H \frac{d}{dt} s_H &= -s_H + \alpha_H (c_H s_H + c_D s_D) \ , \\ \tau_D \frac{d}{dt} s_D &= -s_D + \alpha_D (c_H s_H + c_D s_D) \ ,\end{aligned} \tag{10}$$

where

$$\alpha_{H,D} = I_0 (1 - \langle S^{H,D}_z\rangle^2)/4kT \ , \tag{11}$$

with $\langle S^{H,D}\rangle$, the local order parameters, given by Eqs. (5). The solutions of Eqs. (10) are of the form

$$s_{H,D} = c_{1,2} e^{-t/\tau} \ , \tag{12}$$

and the eigenvalues are

$$\frac{1}{\tau_\pm} = \frac{1}{2} \left\{ \frac{1-\alpha_H c_H}{\tau_H} + \frac{1-\alpha_D c_D}{\tau_D} \pm \left[\left[\frac{1-\alpha_H c_H}{\tau_H} - \frac{1-\alpha_D c_D}{\tau_D} \right]^2 + 4\alpha_H \alpha_D c_H c_D \right]^{1/2} \right\} . \tag{13}$$

The general solutions are linear combinations of the eigenvectors

$$\begin{aligned} s_H(t) &= A c_1^+ e^{-t/\tau_+} + B c_1^- e^{-t/\tau_-} \ , \\ s_D(t) &= A c_2^+ e^{-t/\tau_+} + B c_2^- e^{-t/\tau_-} \ ,\end{aligned} \tag{14}$$

where A and B must be determined from the initial conditions. The relationship between the eigenvectors is easily obtained from Eq. (10) in the form

$$\frac{c_1^\pm}{c_2^\pm} = c_\pm = \frac{D_4 - D_1 \pm [(D_1 - D_4)^2 + 4D_2 D_3]^{1/2}}{2D_3} \ , \tag{15}$$

where

$$\begin{aligned} D_1 &= (1-\alpha_H c_H)/\tau_H \ , \\ D_2 &= \alpha_H c_D/\tau_H \ , \\ D_3 &= \alpha_D c_H/\tau_D \ , \\ D_4 &= (1-\alpha_D c_D)/\tau_D \ .\end{aligned} \tag{16}$$

From Eqs. (14) for $t=0$, A and B can be expressed in terms of $c_\pm$, and of $s_H(0)$ and $s_D(0)$. From this the correlation function for $s_{H,D}(t)$ can be derived.

The effective correlation times for the HCl and the DCl dipoles can be defined in terms of the normalized correlation functions[12]

$$\tau_e^{H,D} = \int_0^\infty \langle s_{H,D}(0) s_{H,D}(t)\rangle dt / \langle s_{H,D}(0)^2\rangle \ . \tag{17}$$

For the $t=0$ conditions, by assuming equally polarizable HCl and DCl sublattices, one can set $s_H(0)/s_D(0)=1$. The condition $s_H(0)/s_D(0)=-1$, corresponding to the "antiferroelectric" $t=0$ configuration, should be less favored and lead to negative values for $\tau_e^{H,D}$. Then, from Eq. (14) and (15), through Eq. (17) one obtains

$$\begin{aligned}\tau_e^H &= \frac{D_4 + D_2}{D_1 D_4 - D_2 D_3} \\ &= \frac{[1-\alpha_D(1-c_H)]\tau_H + \alpha_H(1-c_H)\tau_D}{1-\alpha_D + (\alpha_D - \alpha_H)c_H} \ , \\ \tau_e^D &= \frac{D_3 + D_1}{D_1 D_4 - D_2 D_3} = \frac{(1-\alpha_H c_H)\tau_D + \alpha_D c_H \tau_H}{1-\alpha_D + (\alpha_D - \alpha_H)c_H} \ .\end{aligned} \tag{18}$$

B. Analysis of the experimental results and discussion

Equation (6) gives the expected behavior of the transition temperature in the mixed crystals. The analysis of the experimental data (see Fig. 1) in light of Eq. (6) can be performed with the assumption $\Omega_D^2 \ll 12k^2T_c^2 \simeq I_0^2$. This inequality should hold in view of the strong mass dependence of the tunneling integral, for which $\Omega_D \ll \Omega_H$, and because Ω_H is expected to be smaller than I_0. The best fit of the data, under the above conditions, yields $I_0 = 420$ K and $\Omega_H = 82$ K. Therefore pure DCl can be considered a quasiclassical ferroelectric crystal for which $\Omega_D \simeq 0$, and the quantum parameter q in Eq. (7) becomes $q \simeq 0.39\ C_H$. In Fig. 3 the theoretical behavior for the transition tem-

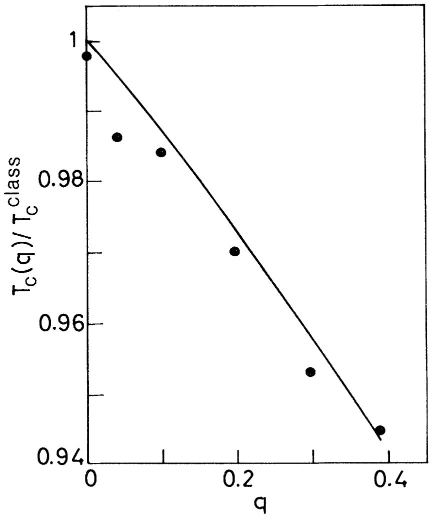

FIG. 3. Transition temperature as a function of the quantum parameter $q \simeq 0.39 c_H$, compared to $T_c^{\text{class}} = I_0/4k \simeq 105$ K for dipoles with no quantum tunneling contribution to the reorientations. Solid line is the theoretical behavior predicted by Eq. (6), with $I_0 = 420$ K and $\Omega_H = 82$ K, as explained in the text. Experimental data (●) are from Fig. 1.

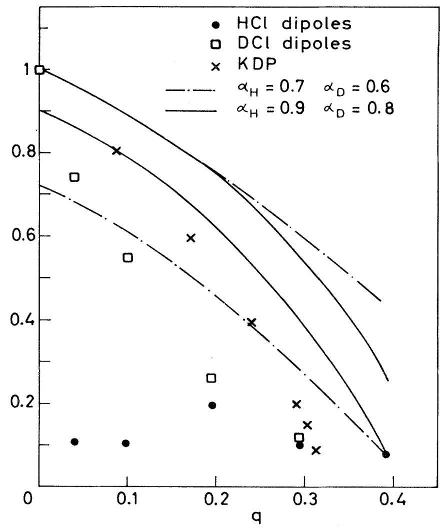

FIG. 4. Dependence of the ratio of the correlation times on the quantum parameter. Experimental values for the HCl and DCl dipoles are taken from the data in Fig. 2. For KDP, the data are from Ref. 14. Lines represent the theoretical behavior according to Eqs. (18) for two possible choices of the local order parameters, as explained in the text.

perature as a function of q is reported and compared with the experimental results, on the assumption $T_c^{\text{class}} = I_0/4 \simeq 105$ K. On the whole, Eq. (6) appears to describe satisfactorily the decrease of T_c due to quantum tunneling, and the estimates of I_0 and Ω_H appear corroborated.

With regard to the local order parameters $\langle S_z^H \rangle$ and $\langle S_z^D \rangle$ one can refer to Eqs. (5). Taking into account the estimates for I_0 and $\Omega_{H,D}$ one can observe that only in the case $\langle S_z^{H,D} \rangle \to 0$ could a sizable difference (around 30%) between $\langle S_z^H \rangle$ and $\langle S_z^D \rangle$ possibly occur. The first-order character of the transition rules out interest in this case. For nonvanishing order parameters, Eqs. (5) yield

$$\frac{\langle S_z^D \rangle}{\langle S_z^H \rangle} \simeq b \frac{\tanh a}{\tanh(ab)} , \tag{19}$$

with

$$a = h_z/2kT , \quad b = 1 + \Omega_H^2/2h_z^2 , \tag{20}$$

and h_z given by Eq. (4). Therefore for $I_0 = 420$ K and $\Omega_H = 82$ K, with $\langle S_z^H \rangle \sim \langle S_z^D \rangle \sim 0.8$, the difference between the local order parameters should be within a few percent and hardly detectable through static dielectric measurements (spontaneous polarization and/or static dielectric constant for pure HCl and pure DCl crystals).

For a discussion of the dynamical effects, let us refer to Eqs. (18). It should be remembered that, in view of Eq. (1) and the fact that $\langle s \rangle^2 = \langle S_z^{H,D} \rangle^2 \simeq 0.8 - 0.6$, which is practically the same for DCl and HCl dipoles, the T_1 values reported in Fig. 2 give the local correlation times directly. From Eq. (18), for pure crystals ($c_H = 0$ and $c_H = 1$), one has

$$\tau_e^{\text{HCl}} = \tau_H/(1-\alpha_H), \quad \tau_e^{\text{DCl}} = \tau_D/(1-\alpha_D) .$$

From Eqs. (11) and (19) $\alpha_H \simeq \alpha_D$, and therefore the ratio of the spin-lattice relaxation times for the pure crystals, namely 210 msec/16 msec = 13.1, can be attributed to a ratio of this order of magnitude between the single-particle relaxation times τ_H and τ_D for HCl and DCl dipoles [see Eq. (9)]. It should be mentioned that in the temperature range from 50 to about 70 K the ratio τ_D/τ_H appears temperature independent, within the experimental errors [for $T \geq 70$ K the relationship between T_1 and τ_e is no longer given by Eq. (1), because of the changeover to the fast-motion regime, and the evaluation of τ_e is more complicated and less reliable]. In the low-temperature region, where classical reorientations of the dipoles due to thermal motion should occur at a negligible rate, a flattening of the correlation time for HCl as a function of temperature can be expected.[13] However, it could be difficult to detect experimentally such a flattening, since dielectric dispersion measurements would have to be performed in a very low-frequency range, while the nuclear spin-lattice relaxation process could be dominated by competing mechanisms.

With regard to the ratio τ_D/τ_H discussed above, we would like to emphasize a remarkable coincidence with the case of KH_2PO_4 and KD_2PO_4, where the tunneling ions H and D are strongly coupled with the lattice. The correlation times for the effective relaxational modes have recently been evaluated by fitting the Brillouin spectrum on the basis of a model of polarization fluctuations coupled to acoustic phonons.[14] A value of 13 has been deduced for the ratio $\tau_{\mathrm{DKDP}}/\tau_{\mathrm{KDP}}$. The similarity of this value with the value for HCl-DCl is remarkable in view of the significant differences between the two systems. The similarity is most likely to be ascribed to the common origin of quantum tunneling effects.

With respect to the dependence of the relaxation times for the HCl and the DCl dipoles on deuteration, in Fig. 4 we compare the experimental data with the theoretical results derived in the framework of the model and the approximations described in Sec. III A. According to the previous conclusions, we have assumed that the effective relaxation time for pure DCl can be considered to be classical, i.e., due almost entirely to polarization fluctuations which result from thermal motion. In Fig. 4 we also report the values obtained for KDP-DKDP (potassium dideuterium phosphate) mixed crystals from the fitting of the Brillouin spectra[14]; in this case, for the evaluation of the quantum parameter q we have used for the interaction energy $I_0 \sim 545\ \mathrm{cm}^{-1}$ (an average between the values for pure KDP, $I \simeq 450\ \mathrm{cm}^{-1}$ and pure DKDP, $I \simeq 640\ \mathrm{cm}^{-1}$; it should be remembered that in KDP-type crystals, the interaction energy is mass dependent because of the coupling with the O-O lattice vibrations) and $\Omega_{\mathrm{H}} = 86\ \mathrm{cm}^{-1}$ (Ref. 15). It can be observed that the uncertainty in the above quantities affects only the scaling factor of q. Finally, it should be stressed that from the Brillouin scattering study only an "average" correlation time for the two types of dipoles is derived. In Fig. 4 the experimental results are compared with the theoretical expressions, as given by Eqs. (18). For α_{H} and α_{D}, according to Eqs. (11) and (19) we have chosen, for $T = 55$ K, values corresponding to about 80% and 83% of the spontaneous polarization ($\alpha_{\mathrm{H}} = 0.7$, $\alpha_{\mathrm{D}} = 0.6$) and to 73% and 75% ($\alpha_{\mathrm{H}} = 0.9$, $\alpha_{\mathrm{D}} = 0.8$). For $\alpha_{\mathrm{H}} = \alpha_{\mathrm{D}}$ a straight line would represent $\tau_e(q)$ vs c_{H} or q, as may be seen from Eqs. (18).

The general behavior of the correlation times τ_e^{D} for the DCl dipoles as a function of deuteration appears consistent with the theoretical model. In particular, it can be observed how the coupling with the fast-reorienting HCl dipoles leads also to short correlation times for the DCl dipoles. For example, in the $\mathrm{HCl}_{0.75}$-$\mathrm{DCl}_{0.25}$ crystal, $\tau_e^{\mathrm{H}} \simeq \tau_e^{\mathrm{D}}$, in satisfactory agreement with the results expected from the theoretical description. The agreement is also good for KDP if one assumes that in practice only the correlation time of the deuteron has been measured through the fitting of the Brillouin spectra.[14]

A discrepancy exists between the experimental data and the theoretical picture for the HCl dipoles in the dilute limit of $c_{\mathrm{H}} \rightarrow 0$. In fact, while for $c_{\mathrm{H}} \geq 0.5$ (see also Fig. 2) the correlation times of HCl dipoles increase for greater deuteration and are almost equal to those for the DCl dipoles; at lower c_{H} they exhibit reorientation fluctuations markedly faster than those for the DCl dipoles. This feature can be ascribed to a persistence of dynamical quantum effects in spite of the coupling with a matrix of classical dipoles. In the following section some suggestions on possible causes of such a phenomenon will be discussed.

C. Quantum tunneling in the dilute limit: Effects of localized phonons on the tunneling rate

A breakdown of a VCA approach can be somewhat expected in the dilute limits.[7] However, the short correlation times observed for the HCl dipoles in the mixed crystals when $c_{\mathrm{H}} \rightarrow 0$ cannot be considered a "trivial" breakdown of the dynamical VCA. In fact, besides the strength of the effect (the ratio $\tau_e^{\mathrm{D}}/\tau_e^{\mathrm{H}}$ is almost 10 for the $\mathrm{HCl}_{0.1}$-$\mathrm{DCl}_{0.9}$ crystal), the analogous feature is not observed in the opposite dilute limit ($c_{\mathrm{D}} \rightarrow 0$) where $\tau_e^{\mathrm{H}} \simeq \tau_e^{\mathrm{D}}$ as shown in Fig. 2.

In principle, the assumption of an Ising-type model for the local potential could be criticized. However, while one can expect that a more realistic potential leads to a better description, the persistence of tunneling-driven fluctuations still appears to require a different argument.

In view of the one-dimensional structure of the zigzag chain of the HCl or DCl dipoles one could speculate that the dipole reorientations are due to solitonlike domain-wall motions. This mechanism requires a quite different theoretical description. As a first impression, it seems hard to justify in any solitonlike picture the fact that in the dilute limit of $c_{\mathrm{H}} \rightarrow 0$, a soliton causes such a different rate of reorientation when an HCl dipole is met along a DCl chain.

A possible cause of the inadequacy of the model for small q could be a dependence of the tunneling integrals upon deuteration. The ordinary volume effect, namely a local compression of the HCl dipole in the DCl matrix, might be expected to cause a decrease of τ_e^{H}. In fact it seems reasonable to assume that a volume effect decreases Ω_{H}, thus increasing τ_e^{H}.[16]

Another possibility that should be taken into account is the coupling of the tunneling with the phonon oscillations within the wells. In the pseudospin picture of dipolar ferroelectrics this coupling is usually neglected,[1] thus pushing to infinite frequency the phonon peaks in the dielectric response. Though a significant effect of the phonon coupling is likely to occur, the above approximation might be accepted with some confidence when the lattice modes do not change much. However, for HCl dipoles in the dilute limit, where localized modes at higher frequencies can be expected, a possible changeover in Ω_{H} could occur. This effect might be considered as a particular form of breakdown of the dynamical VCA in the sense that a localized, site-dependent dynamics is generated. The usual approach for taking into account the effect of phonon modes on the tunneling rate is the truncation approximation.[17] This leads to a normalization of the tunneling amplitude by a factor related to the phonon frequencies. Recently, Sethna[18] pointed out that the truncation approximation is inadequate and suggested an instanton approach which avoids truncation. The same result has been achieved by Bocchieri,[19] by directly eliminating the degrees of freedom of the phonon field. In the following we will crudely apply the main conclusions of the aforementioned descriptions[18,19] to the HCl dipoles in the matrix of DCl by assuming, for simplicity, a coupling to a single phonon mode of frequency ω_{ph}. First, we write the tunneling matrix element explicitly as

$$\Omega=2\sqrt{3}\,\omega_{\mathrm{DW}}(\hbar S_{\mathrm{I}}/\pi)^{1/2}e^{-S_I/\hbar}\,, \tag{21}$$

where $\omega_{\mathrm{DW}}=4V_0^{1/2}/Q_0M^{1/2}$ is the double-well frequency given by the curvature of the local potential at the top of the barrier, and Q_0 is the distance between the two minima. Then we introduce in S_I, the action, the effective mass approximation

$$S_I=\int(2M^*V)^{1/2}dQ\,, \tag{22}$$

with

$$M^*=M+\lambda^2/m\omega_{\mathrm{ph}}^4\,, \tag{23}$$

where λ is a coupling parameter between the phonon and the tunneling coordinates and m is the mass of the phonon modes. On the assumption that λ is not strongly Q dependent, a crude estimate of $\int V^{1/2}dQ$ yields $S_I\sim M^{*1/2}Q_0V_0^{1/2}$, thus giving for Eq. (21)

$$\Omega\simeq8\sqrt{3/\pi}(\hbar/MQ_0)^{1/2}M^{*1/4}V_0^{3/4}e^{-M^{*1/2}V_0^{1/2}Q_0/\hbar}\,. \tag{24}$$

Although obtained through questionable approximations, this expression is in gratifying agreement with the tunneling transition probability W_T, for molecules in periodic barriers derived long ago by Das,[20] on the basis of a perturbation approach and the N-fold Mathieu equation. In fact, by considering only the ground torsional state and setting $N=4$, since the reorientation of the HCl dipole is about 90°, one can derive

$$\hbar W_T\simeq(\pi/\hbar)^{1/2}\frac{V_0^{3/4}}{I^{1/4}}e^{-(a/\hbar)I^{1/2}V_0^{1/2}}\,, \tag{25}$$

where I is the moment of inertia involved in the motion and a is a constant of the order of unity. If in Eq. (24) one sets $M^*\simeq M$ and defines an effective moment of inertia given by $I_{\mathrm{eff}}=MQ_0^2$, the equivalence with Eq. (25) is apparent. The important novelty in Eq. (24) is the presence of the mass M, "dressed" by the phonons, instead of the "bare" mass of the tunneling particle.

An estimate of λ can be obtained by considering that the dimensionless coupling $\lambda^2/m\omega_{\mathrm{ph}}^2M\omega_{\mathrm{DW}}^2$ is $\simeq1$ for the tunneling of the OH impurity in several alkali halides.[21] If one assumes that this approximately applies also to the 90° proton tunneling in the HCl chain, the dressed mass can be written $M^*\simeq M(1+\omega_{\mathrm{DW}}^2/\omega_{\mathrm{ph}}^2)$. From the apparent[13] activation energy $E_0=0.1$ eV, the double-well frequency in HCl should be $\omega_{\mathrm{DW}}\simeq8\times10^{13}$ rad sec^{-1}. Taking into account the various modes,[22] an effective frequency ω_{ph} can be estimated in the range $5\times10^{13}-10^{14}$ rad sec^{-1}. Thus in HCl one could have $M^*\simeq fM$, where f is a factor between 2 and 3. In partial support of this estimate one could observe that for bare masses, Eq. (24) yields the ratio of the tunneling integrals for the proton and deuteron $\Omega_{\mathrm{H}}/\Omega_{\mathrm{D}}\simeq40$ which seems too small. For $f_{\mathrm{H}}=f_{\mathrm{D}}=2.5$ one finds $\Omega_{\mathrm{H}}/\Omega_{\mathrm{D}}\simeq315$ which appears more realistic (in KDP the experimental findings are[16] $\Omega_{\mathrm{H}}\simeq86$ cm^{-1}, $\Omega_{\mathrm{D}}\leq0.4$ cm^{-1}).

If an effective mass does indeed determine the tunneling, the behavior of τ_e^{H} for $c_{\mathrm{H}}<0.5$ could be related to the progressive occurrence of localized modes for the proton, whose frequencies are higher than those for the DCl matrix. An increase of the frequencies by an amount of 20—30% increases the tunneling by a factor of 10. This increase would in turn decrease the damping and therefore the effective correlation times for the HCl dipoles in the $\mathrm{HCl}_{0.25}$-$\mathrm{DCl}_{0.75}$ and $\mathrm{HCl}_{0.1}$-$\mathrm{DCl}_{0.9}$ crystals, as shown in Fig. 4.

Although the above estimates should only be considered of a qualitative nature, one can conclude that, at present, the only hypothesis for the persistence of fast reorientation for the HCl dipoles in the DCl matrix when $c_{\mathrm{H}}\rightarrow0$ that can be accepted with some confidence is the hypothesis related to the effect of localized phonon modes on the tunneling rate. Quantitative corroboration through other complementary experimental measurements are highly desirable and could help in clarifying the controversial problem of the phonon-tunneling coupling in the dilute limit.

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[1] See, for instance, M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon, Oxford, 1977); R. Blinc and B. Zeks, in *Soft Modes in Ferroelectrics and Antiferroelectrics,* edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1974).

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[12] The definition of the correlation time through the area of the correlation function $g(t)$ has been used in order to take into account the effect of the coupling of one sublattice of the dipoles on the other sublattice. In fact, for $t \rightarrow 0$ the correlation functions for $s_{\mathrm{H}}(t)$ and $s_{\mathrm{D}}(t)$ decay with characteristic times given by $\tau_{\mathrm{H}}/(1-\alpha_{\mathrm{H}})$ and $\tau_{\mathrm{D}}/(1-\alpha_{\mathrm{D}})$, as in the pure HCl and DCl crystals, respectively. Therefore a definition of τ_e of the form $\tau_e^{-1} = -[dg(t)/dt]_{t=0}/g(0)$, as used for the ultraslow motion, would not take into account the details of the correlation functions. However, a definition of τ_e as in Eq. (17) could actually weight the long-time behavior of $g(t)$ more heavily.

[13] The problem of the temperature dependence of the effective correlation time $\tau=\gamma/\omega^2$, with γ and ω functions of Ω, is not straightforward. In fact, in addition to the fact that the relationship of γ with Ω can change with the temperature, Ω itself cannot be considered temperature independent, in view of the coupling with the phonons. Experimentally, one derives $\tau \propto T^{-n}$, with $n=1-5$ or more, according to the temperature range and/or the system [see S. Kapphan, J. Phys. Chem. Solids 35, 621 (1974) and H. B. Shore and L. M. Sander, Phys. Rev. B 12, 1546 (1975)]. In HCl, dielectric measurements (Ref. 8) and NQR T_1's (Refs. 4 and 3) phenomenologically suggest a temperature-activated correlation time, with activation energy $E_0 \simeq 0.1$ eV, in the temperature range $60 \leq T \leq 90$ K. Therefore the value for E_0 can be considered only a crude indication of the barrier in the local potential for the reorientation of the dipole.

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[16] Insights on the dependence of the tunneling on the local environments could be obtained through ^{35}Cl NQR T_1 measurements as a function of pressure in the ferroelectric phase. If the pressure dependence of Ω_{H} can be theoretically derived in a reliable way, these measurements in pure HCl could also permit a quantitative study of the dependence of the single-particle correlation time τ_{H} on the tunneling integral.

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