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Effect of strain on the protonic ordering in squaric acid

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Within a simple model it is shown how local strain fields impose an important symmetry-breaking constraint on protonic ordering in squaric acid ($C_4O_4H_2$), possibly implementing a first-order transition to the observed antiferroelectric state.

I. INTRODUCTION

The chemical constraints on a molecule of squaric acid ($C_4O_4H_2$) in the sense of Lewis[1] that all bonds are saturated can be satisfied, when only two of the four hydrogen atoms surrounding a given carbon-oxygen complex in the solid transfer charge to the molecule[2] (see Fig. 1). Classically speaking, the four energetically favorable protonic configurations are those in which hydroxyls are adjacently positioned about the cyclobutene ring. That in which the hydroxyls are diagonally positioned is energetically unfavorable, necessitating a double carbon bond across the diagonal for chemical stability in that case. It should be noted that the strong covalent double carbon bond on the side of the cyclobutene ring where the protons sit strongly distorts the squaric shape of the molecule into a trapezoidal form. In the solid state the molecules bind in planar layers[3-5] (see Fig. 2). Below a temperature $T_c \sim 97\,^\circ\mathrm{C}$, the protons order ferroelectrically within each plane, such that the chemical constraint on each molecule is satisfied. The protonic configuration in adjacent planes is antiferroelectric.

To a great extent the interest in squaric acid stems from the possibility that the protonic ordering is essentially a two-dimensional phenomenon, the substance then serving as a testing ground for renormalization-group theories, as well as for solutions to vertex or bond models.[6,7] Recent vertex model calculations[8,9] have predicted a second-order transition for the protonic ordering in squaric acid. Using a local normal coordinate scheme[10] for the protonic degrees of freedom, and a renormalization-group approach to eliminate certain irrelevant terms in the free energy, Feder[6,7] is lead to a three-dimensional x-y model for squaric acid that also exhibits a second-order transition. Recent experiments,[11,12] however, offer strong evidence that the transition in squaric acid is of the first order.

Basically, all current models for squaric acid suffer a common weakness: They neglect the distortive response of the cyclobutene ring to the protonic motion, and treat the squaric molecule as a *point*, assigning to this point some particular protonic configuration (vertex arrows or local normal coordinate). In view of the strong molecular distortions that are

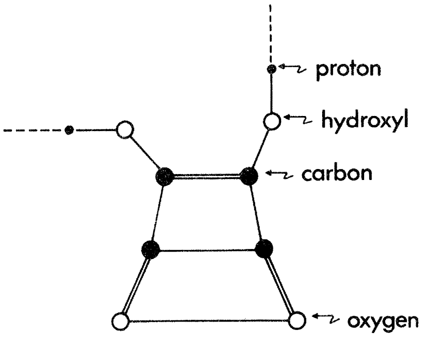

FIG. 1. Squaric acid molecule.

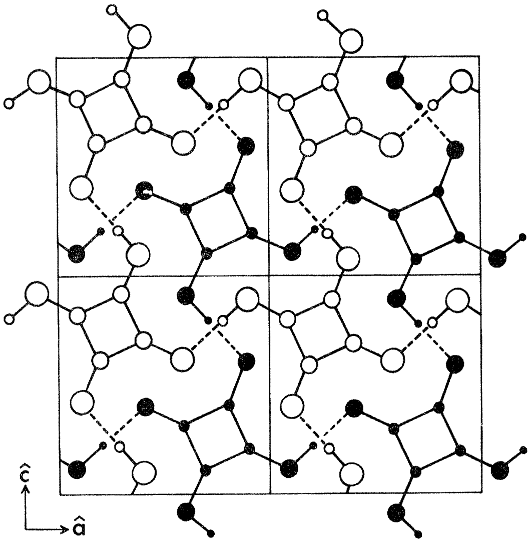

FIG. 2. Four unit cells of crystalline squaric acid. Black and white dots differentiate between neighboring squaric planes.

expected to be involved in protonic hopping, such approaches neglect an important aspect of the transition. In particular, these molecular deformations can lead to the formation of energetically unfavorable *local strains* within the squaric plane, implicating an effective driving force for the transition.

Another apparent weakness of the existing models is that they necessitate the *ad hoc* introduction of an antiferroelectric interplanar coupling, while at the same time admitting a ferroelectric coupling within the squaric plane. In the relatively successful Slater-Tagaki theory[13–15] of the protonic ordering in potassium dihydrogen phosphate (KDP) the ferroelectric state appears naturally as a result of crystal anisotropy. In squaric acid, however, the four chemically allowed configurations are crystallographically equivalent, and even when the ice constraints are imposed, without the *ad hoc* inclusion of appropriate order parameter couplings, *all* current models predict a paraelectric state for squaric acid.

In this paper it will be shown that *local* distortions of the lattice in response to protonic motion favor in a natural way the observed antiferroelectrically ordered state, and that a first-order transition to this state may occur as a result of the local strain effect.

II. FORMULATION

If it is assumed that the entropy of the system is primarily contained in the ferroelectric degrees of freedom, then the following separation of the Helmholtz free energy F is possible:

$$F = F_d + E_e + E_{de} \ , \tag{1}$$

where F_d contains solely protonic degress of freedom.

In a *uniformly* strained crystal the purely elastic energy E_e is given by[16]

$$E_e = \sum_{\Gamma} \sum_{j,j'} \tfrac{1}{2} c^{\Gamma}_{jj'} \sum_{i} \epsilon_i^{\Gamma j} \epsilon_i^{\Gamma j'} \ , \tag{2}$$

where Γ defines the irreducible representations of the crystal space group, i specifies the basis functions of the representation, and j and j' are used if more than one basis set carries the representation. The $\{c^{\Gamma}_{jj'}\}$ are phenomenological elastic constants, and the $\{\epsilon_i^{\Gamma j}\}$ are linear combinations of the Cartesian components of the uniform strain tensor, having the transformation properties of the $(\Gamma j i)$-basis functions.

The ferroelastic coupling term E_{de} which I assume to be of the *1-site* type, is given by[17–19]

$$E_{de} = -\sum_{f} \sum_{\Gamma} \sum_{j,j'} B^{\Gamma}_{jj'}(f) \sum_{i} \xi_i^{\Gamma j}(f)\, \eta_i^{\Gamma j'}(f) \ . \tag{3}$$

Here $f \equiv (n,s)$ labels the position of the sth *molecule* in the nth unit cell of the crystal. The 1-site coupling coefficients will be assumed to be site-independent. The ferroelectric degrees of freedom are summarized in the functions $\{\eta_i^{\Gamma j}\}$, which transform as do the $(\Gamma j i)$-basis functions. They are formed from bilinear combinations of the Cartesian components of a locally defined vector $\vec{\eta}(f)$ that specifies in a certain sense the electric polarization in a molecule.[6,7] The local strain functions $\{\xi_i^{\Gamma j}\}$ describe the molecular deformations, which, for reasons given in Sec. I, couple strongly to $\vec{\eta}(f)$ only at the site f.

If $\{\vec{R}_\delta\}_f$ are the position vectors of the atoms which neighbor the site at $\vec{R}_f$ in the *undeformed* crystal, then the 1-site local strain functions may be defined as[18,19]

$$\xi_i^{\Gamma j}(f) \equiv \sum_{\{\vec{R}_\delta\}_f} \xi_i^{\Gamma j}(f, f+\delta) \ , \tag{4}$$

where the *2-site* Cartesian components of the local strain tensor are given as

$$\xi_{xx}(f,g) = (X_f - X_g)(x_f - x_g) \ , \tag{5}$$

$$\xi_{xy}(f,g) = \tfrac{1}{2}[(X_f - X_g)(y_f - y_g) + (Y_f - Y_g)(x_f - x_g)] \ , \tag{6}$$

with similar expressions for the other components. Here $\vec{r}_f \equiv (x_f, y_f, z_f)$ is the displacement away from $\vec{R}_f \equiv (X_f, Y_f, Z_f)$ in the *deformed* crystal. It may be shown[18,19] that Eq. (3) reduces to the usual expression[17] for the ferroelectric free energy in the presence of a uniform strain, if one imposes the following condition:

$$b^{\Gamma}_{jj'} = 2a^2 B^{\Gamma}_{jj'} \tag{7}$$

in the case of a cubic crystal with lattice parameter a. Here the $b^{\Gamma}_{jj'}$ are the coupling coefficients for the uniform strain case.[17]

Assuming that the elastic degrees of freedom can *locally* follow the protonic motion,[20] the equilibrium atomic displacements can be calculated for a given configuration of the local normal protonic coordinates by minimizing F with respect to these displacements.

III. SYMMETRY CONSIDERATIONS

The free energy of the system must be invariant in form under the symmetry transformations of the high-temperature phase. The space group of this phase is tetragonal $I4/m$[5], which has two one-dimensional representations A and B, *each* with two inequivalent basis functions:

$$(x^2 + y^2 \ \text{and} \ z^2)_A \ ,$$

$$(x^2 - y^2 \ \text{and} \ xy)_B \ ,$$

as well as a two-dimensional representation E with basis functions $\{xz,yz\}_E$. Thus the irreducible strain functions may be written as

$$\begin{aligned} &\xi^{A1}=\xi_{xx}+\xi_{yy},\quad \xi^{A2}=\xi_{zz}\ ,\\ &\xi^{B1}=\xi_{xx}-\xi_{yy},\quad \xi^{B2}=\xi_{xy}\ ,\\ &\xi_1^E=\xi_{xz},\quad \xi_2^E=\xi_{yz}\ , \end{aligned} \tag{8}$$

whereas the irreducible protonic functions are given as

$$\begin{aligned} &\eta^{A1}=(\eta_x)^2+(\eta_y)^2,\quad \eta^{A2}=(\eta_z)^2\ ,\\ &\eta^{B1}=(\eta_x)^2-(\eta_y)^2,\quad \eta^{B2}=\eta_x\eta_y\ ,\\ &\eta_1^E=\eta_x\eta_z,\quad \eta_2^E=\eta_y\eta_z\ . \end{aligned} \tag{9}$$

The $I4/m$ symmetry demands that the 4th rank elastic tensors $(\tilde{C}_{ijkl})$ and $(\tilde{B}_{ijkl})$ be polar, each with 41 nonzero Cartesian elements, 21 of which are independent.[21] Using the usual index notation[22] to be assigned to the first or the last pair of Cartesian indices, the following relations between the irreducible and Cartesian components are obtained:

$$\begin{aligned} &C_{11}^A=\tfrac{1}{4}(C_{11}+C_{12}),\quad C_{11}^B=\tfrac{1}{4}(C_{11}-C_{12})\ ,\\ &C_{12}^A=\tfrac{1}{2}C_{13},\quad C_{12}^B=\tfrac{1}{2}C_{16}\ ,\\ &C_{22}^A=\tfrac{1}{2}C_{33},\quad C_{22}^B=\tfrac{1}{2}C_{66}\ ,\\ &C^E=\tfrac{1}{2}C_{44}\ , \end{aligned} \tag{10}$$

where symmetrization is implemented through the definition

$$C_{\alpha\beta}\equiv\tfrac{1}{2}(\tilde{C}_{\alpha\beta}+\tilde{C}_{\beta\alpha})\ . \tag{11}$$

Similar relations may be written down for the components of the ferroelastic tensor $\tilde{B}$, although in general, the symmetrization Eq. (11) cannot be employed, so that

$$B_{12}^A\equiv\tfrac{1}{2}\tilde{B}_{13}\neq B_{21}^A\equiv\tfrac{1}{2}\tilde{B}_{31}$$

and

$$B_{12}^B\equiv\tfrac{1}{2}\tilde{B}_{16}\neq B_{21}^B\equiv\tfrac{1}{2}\tilde{B}_{61}\ .$$

The quantity $\tilde{B}_{12}=\tilde{B}_{21}$ always by symmetry.[21]

IV. MODEL FOR SQUARIC ACID

As discussed in the Introduction it is the trapezoidal distortion of the carbon ring which couples strongly to the protonic motion. However, it is the motion of the oxygen atoms which leads to local straining over some small region of the crystal. Since the C-O and O-H . . . O bonding lengths and bonding angles are not expected to change much in the trapezoidally distorted molecule (see Fig. 1), we can consider the simplified model of Fig. 3. The C-O complex is replace by four "effective" atoms at the oxygen sites, interacting elastically as shown by wavy lines in the figure. Here the large black or white dots serve to distinguish between effective atoms on neighboring squaric planes, and the orientation of the protonic coordinates is represented by planar vectors.[6,7] In the absence of ferroelastic coupling (case shown in Fig. 3), the effective atoms lie in elastic equilibrium at the corners of a square, and the protonic state will be paraelectric "ice," if no dipolar couplings are added to the model.

It should be pointed out that there exists an important geometric constraint on the relative positions of molecules in neighboring squaric planes: The molecules of one plane are "nested" into the large empty spaces of the other, so that the apparently very open structure in a plane is strongly compensated in three dimensions. This leads to the fact that the perpendicularly oriented hydrogen bonds in nearest-neighbor planes are separated by only ~2.63 Å, as compared to ~4.4 Å between such bonds within a plane.[2] In fact Raman studies[23] indicate that the interplanar coupling is strongly localized in the crossed hydrogen bonds of Fig. 3. For this reason it is expected that the "perpendicular bisector" configuration of neighboring bonds along the crystal $\hat{b}$ *axis* will be strongly preserved in the strained crystal. This expectation is further reinforced by chemical shift measurements,[24] which indicate that the electronic environment of the protons in these bonds remains

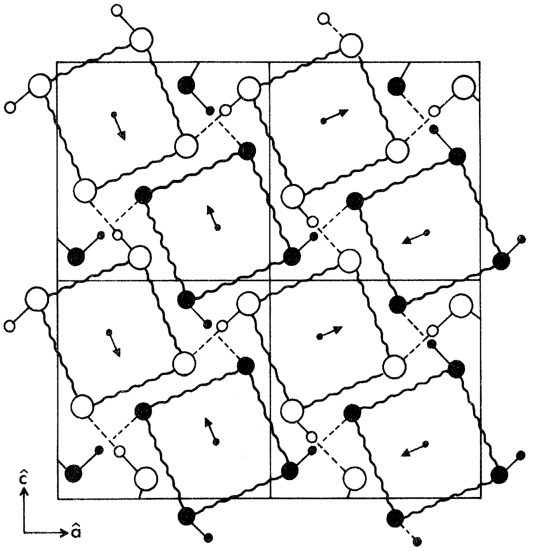

FIG. 3. Simplified model of squaric acid in which the C-O complex is replaced by four "effective" atoms at the oxygen sites which interact elastically (wavy lines). The protonic configuration is represented by the set of arrows.

unaltered as the crystal is cooled through the transition temperature T_c. Apparently the observed softening[25] of the quasilongitudinal and quasishear wave elastic modes, which propagate parallel to the crystallographic $\hat{a}$ and $\hat{c}$ axes shown in Fig. 3, is due primarily to a softening of the *intra*molecular force constants (wavy lines in Fig. 3), rather than to a softening of the hydrogen bonds which link the molecules.

Since this rigid bond picture for the crossed hydrogen bonds is also consistent with the molecular deformations discussed at length in connection with Fig. 3, a further simplification of the model is possible: The four effective atoms involved in the crossed bond configurations of Fig. 3 are considered to move as a single unit, and the rotational motion of this unit, which would involve a change in the hydrogen bonding angles relative to the squaric molecules, will be ignored. The imposition of these strong steric constraints on the atomic motion in neighboring planes leads to the strictly two-dimensional model shown in Fig. 4. Here the four atoms of a crossed hydrogen bond are represented by a single effetive atom at the sites where the bonds cross, depicted in the figure as a crossed dot. These atoms are then considered to be interacting through the elastic forces, represented by double wavy lines in the figure. In this "bedspring" model the information concerning the protonic configuration is fully contained in the sublattice of arrows on the sites, $\{f\}$; whereas the elastic configuration of the crystal is represented by the positions of the interaction centers (crossed dots), relative to the equilibrium sublattice of sites, $\{F\}$.

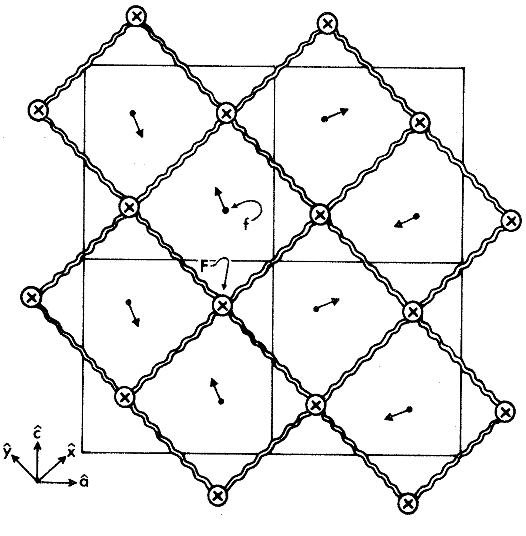

FIG. 4. Further simplified model in which the four atoms of a crossed hydrogen bond are represented as a single unit without internal degrees of freedom, denoted by a crossed dot. These units interact elastically (double wavy lines) and are in elastic equilibrium on the sublattice of points $\{F\}$. The protonic vectors lie on the interpenetrating sublattice $\{f\}$.

V. ELASTIC ENERGY IN THERMAL EQUILIBRIUM

The sites $\{f\}$, denoting the protonic configuration, will be designated by the integer pair, (α,β), whereas the sublattice of sites, $\{F\}$, denoting the positions of elastic equilibrium, are labeled by the pair (l,m). With this convention the irreducible strain functions are calculated to be

$$\xi^{A1}_{\alpha,\beta} = x_{l+1,m} - x_{l,m} + x_{l+1,m+1} - x_{l,m+1} + y_{l,m+1} - y_{l,m} + y_{l+1,m+1} - y_{l+1,m} \ , \tag{12}$$

$$\xi^{B1}_{\alpha,\beta} = x_{l+1,m} - x_{l,m} + x_{l+1,m+1} - x_{l,m+1} - y_{l,m+1} + y_{l,m} - y_{l+1,m+1} + y_{l+1,m} \ , \tag{13}$$

$$\xi^{B2}_{\alpha,\beta} = x_{l+1,m+1} - x_{l+1,m} + x_{l,m+1} - x_{l,m} + y_{l+1,m+1} - y_{l,m+1} + y_{l+1,m} - y_{l,m} \ . \tag{14}$$

Here the positive constant factors involving a, the unstrained distance between interaction centers, have been absorbed into the respective constants $\{B^{\Gamma}_{jj'}\}$ of Eq. (3).

For $T > T_c$ I consider a periodic fluctuation of the local protonic coordinate $\vec{\eta}_{\alpha,\beta} \equiv \vec{\eta}(\vec{R}_{\alpha,\beta})$ with wave vector $\vec{Q}$ in the model plane of Fig. 4:

$$\vec{n}_{\alpha,\beta} = \eta_0[\cos(\vec{Q}\cdot\vec{R}_{l,m}+\phi)\hat{x} + \sin(\vec{Q}\cdot\vec{R}_{l,m}+\phi)\hat{y}] \ , \tag{15}$$

where $\phi \equiv \theta + \vec{Q}\cdot\vec{d}$, θ being an arbitrary phase and $\vec{d} \equiv (\vec{R}_{\alpha,\beta} - \vec{R}_{l,m})$. Cyclic boundary conditions are assumed, and the phase of $\vec{\eta}$ is fixed, arbitrarily, by setting $\phi = 0$ in Eq. (15).

Defining the protonic *turn angle* as

$$\psi \equiv Q_x a = Q_y a \ , \tag{16}$$

where the second equality must hold by symmetry, the irreducible protonic functions may be written as

$$\eta^{A1}_{\alpha,\beta} = \eta_0^2 \ , \tag{17}$$

$$\eta^{B1}_{\alpha,\beta} = \eta_0^2 \cos[2\psi(l+m)] \ , \tag{18}$$

$$\eta^{B2}_{\alpha,\beta} = \eta_0^2 \sin[2\psi(l+m)] \ , \tag{19}$$

where a factor of $\frac{1}{2}$ in $\eta^{B2}_{\alpha,\beta}$ is absorbed into the respective coupling coefficients. Equation (17) shows that the fully symmetric terms in the elastic free energy are independent of the direction of $\vec{\eta}_{\alpha,\beta}$ in the model plane, so that only surface terms will survive the strong cancellation which occurs in the $A1$ terms of E_{de}. Since only bulk phenomena will be considered in this paper, the ferroelastic coupling energy may be written as follows:

$$E_{de} = -\sum_{l,m} (B^{B}_{11}\xi^{B1}_{l,m}\eta^{B1}_{l,m} + B^{B}_{12}\xi^{B1}_{l,m}\eta^{B2}_{l,m} + B^{B}_{21}\xi^{B2}_{l,m}\eta^{B1}_{l,m} + B^{B}_{22}\xi^{B2}_{l,m}\eta^{B2}_{l,m}) \ . \tag{20}$$

In view of Eqs. (12)–(19) the irreducible functions have been relabeled with the indices (l,m).

The purely elastic energy may be written as

$$E_e=\frac{1}{2}\sum_{l,m}\{\kappa_l[(x_{l+1,m}-x_{l,m})^2+(y_{l,m+1}-y_{l,m})^2]+\kappa_t[(x_{l,m+1}-x_{l,m})^2+(y_{l+1,m}-y_{l,m})^2]\}\ , \tag{21}$$

where κ_l and κ_t are longitudinal and transverse spring constants, respectively. When the strain is uniform this expression must reduce to Eq. (2), which suggests a method for expressing (κ_l, κ_t) in terms of the usual elastic constants. Here, however, κ_l and κ_t will be taken as the fundamental quantities.

Minimizing the elastic free energy with respect to a *particular* displacement $\vec{r}_{l,m}$ yields a set of $2NM$ coupled linear algebraic equations for the displacement components

$$\kappa_l(2x_{l,m}-x_{l+1,m}-x_{l-1,m})+\kappa_t(2x_{l,m}-x_{l,m+1}-x_{l,m-1})+\tfrac{1}{2}\eta_0^2[B_x(1-e^{4i\psi})e^{-2i\psi(l+m)}+B_x^*(1-e^{-4i\psi})e^{2i\psi(l+m)}]\equiv 0 \tag{22}$$

and

$$\kappa_l(2y_{l,m}-y_{l,m+1}-y_{l,m-1})+\kappa_t(2y_{l,m}-y_{l+1,m}-y_{l-1,m})+\tfrac{1}{2}\eta_0^2[B_y(1-e^{4i\psi})e^{-2i\psi(l+m)}+B_y^*(1-e^{-4i\psi})e^{2i\psi(l+m)}]\equiv 0\ , \tag{23}$$

where

$$\begin{aligned}B_x&\equiv(B_{11}^B+B_{21}^B)+i(B_{12}^B+B_{22}^B)\ ,\\ B_y&\equiv-(B_{11}^B-B_{21}^B)+i(B_{12}^B-B_{22}^B)\ ,\end{aligned} \tag{24}$$

and (N,M) is the range of (l,m).

Assuming solutions of the form

$$\begin{aligned}x_{l,m}&\equiv\int_{-\infty}^{\infty}A_x(\alpha)e^{i\alpha(l+m)}d\alpha\ ,\\ y_{l,m}&\equiv\int_{-\infty}^{\infty}A_y(\alpha)e^{i\alpha(l+m)}d\alpha\ ,\end{aligned} \tag{25}$$

Eq. (22) becomes

$$\int_{-\infty}^{\infty}A_x(\alpha)(1-\cos\alpha)e^{i\alpha(l+m)}d\alpha \equiv C_xe^{-2i\psi(l+m)}+C_x^*e^{2i\psi(l+m)}\ , \tag{26}$$

where

$$C_x\equiv\eta_0^2B_x[4(\kappa_l+\kappa_t)]^{-1}(e^{4i\psi}-1)\ , \tag{27}$$

with a similar equation for the y component.

By inspection, the solution of Eq. (26) is

$$A_x(\alpha)=(1-\cos\alpha)^{-1}[C_x\delta(\alpha+2\psi)+C_x^*\delta(\alpha-2\psi)]\ , \tag{28}$$

so that the displacements may be written as

$$\begin{aligned}x_{l,m}&=X_1\eta_{l,m}^{B1}+X_2\eta_{l,m}^{B2}\ ,\\ y_{l,m}&=Y_1\eta_{l,m}^{B1}+Y_2\eta_{l,m}^{B2}\ ,\end{aligned} \tag{29}$$

where

$$\begin{aligned}X_1&\equiv K_0[(B_{11}^B+B_{21}^B)\Omega_1+(B_{12}^B+B_{22}^B)\Omega_2]\ ,\\ X_2&\equiv K_0[(B_{12}^B+B_{22}^B)\Omega_1-(B_{11}^B+B_{21}^B)\Omega_2]\ ,\\ Y_1&\equiv K_0[-(B_{11}^B-B_{21}^B)\Omega_1-(B_{12}^B-B_{22}^B)\Omega_2]\ ,\\ Y_2&\equiv K_0[-(B_{12}^B-B_{22}^B)\Omega_1+(B_{11}^B-B_{21}^B)\Omega_2]\ ,\end{aligned} \tag{30}$$

with

$$\begin{aligned}K_0&\equiv[2(\kappa_l+\kappa_t)(\cos2\psi-1)]^{-1}\ ,\\ \Omega_1&\equiv(1-\cos4\psi)\ ,\\ \Omega_2&\equiv\sin4\psi\ .\end{aligned} \tag{31}$$

From Eqs. (29) one sees that the coefficients (X_1,X_2) and (Y_1,Y_2) weight the effect of the local protonic motions on the local lattice motions.

Using the fact that

$$\sum_{l,m}\eta_{l,m}^{B1}\eta_{l,m}^{B2}=0\ , \tag{32}$$

and that

$$\sum_{l=1}^{N}\sum_{m=1}^{M}(\eta_{l,m}^{B1,B2})^2\cong\frac{\eta_0^4NM}{2}\ , \tag{33}$$

when (N,M) are very large positive integers, the total ferroelastic energy *per molecule*, $E_T\equiv(E_e+E_{de})\times(NM)^{-1}$, is found to be

$$E_T=-\tfrac{1}{2}(\kappa_l+\kappa_t)(1-\cos2\psi)(X_1^2+X_2^2+Y_1^2+Y_2^2)\eta_0^4\ . \tag{34}$$

This is a *manifestly negative* fourth-order term in the Landau-Ginsburg free energy, which when dominant, will lead to a first-order transition.[26,27]

Substitution of Eqs. (30) into Eq. (34) yields the simple expression

$$E_T=-B_{de}\cos^2\psi\eta_0^4\ , \tag{35}$$

where

$$B_{de}\equiv2(\kappa_l+\kappa_t)^{-1}[(B_{11}^B)^2+(B_{12}^B)^2+(B_{21}^B)^2+(B_{22}^B)^2]\ . \tag{36}$$

Equation (35) shows that the total ferroelastic interaction energy favors either the purely ferroelectrically ordered state, $\psi = 0$ or equally well the *observed* ordered state, $\psi = \pi$. Equations (22) and (23) imply that for $\psi = 0$, π in a crystal with fixed center of mass the strain will be fully clamped in the bulk; whereas for other values of ψ the bulk strain is only partially clamped, leading to a higher net ferroelastic energy.

VI. SUMMARY

Within a simple model the ferroelastic instability of squaric acid is treated by imposing a spacially periodic fluctuation of the local normal protonic coordinate upon the paraelectric state of the lattice. It is shown that *local* strain fields define a symmetry-breaking axis in the squaric plane for the protonic order parameter. This may lead to a first-order transition to the experimentally observed ordered state. A more detailed analysis must await the determination of the ferroelastic constants,[28] as well as those appearing in the purely protonic terms of the Landau-Ginzburg free energy.[6,7]

In a future work a dynamic version of the local strain formalism will be used to describe the formation of clusters in connection with anomalous Brillouin scattering,[29] and chemical shifts,[12,30] observed recently in squaric acid.

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