Regular article

Effects of diagonal strains in antiferroelectric squaric acid crystals

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The proton ordering model aimed at description of the phase transition and physical properties of antiferroelectric crystals of squaric acid is modified by taking into account the influence of diagonal lattice strains and of the local geometry of hydrogen bonds, namely of the distance $\delta$ between the H-sites on a bond. Thermal expansion, the spontaneous strain $\varepsilon_1 - \varepsilon_3$, and specific heat of squaric acid are well described by the proposed model. However, a consistent description of hydrostatic pressure influence on the transition temperature is possible only with further modifications of the model.

Key words: antiferroelectricity, hydrogen bond, phase transition, thermal expansion, hydrostatic pressure

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1. Introduction

The crystals of squaric acid, $\text{H}_2\text{C}_4\text{O}_4$ (3,4-dihydroxy-3-cyclobutene-1,2-dione) are an epitome of two-dimensional hydrogen bonded antiferroelectrics. The hydrogen bonded $\text{C}_4\text{O}_4$ groups form parallel to $ac$ planes, stacked along the $b$-axis. Spontaneous polarization in the planes arises below the transition, with the neighbouring planes polarized in the opposite directions. Below the transition point at 373 K, the crystal symmetry changes from centrosymmetric tetragonal, $I4/m$, to monoclinic, $P2_1/m$. On this spontaneous symmetry-changing strains $\varepsilon_1 - \varepsilon_3$ (orthorhombic) and $\varepsilon_5$ (monoclinic), both of $B_g$ symmetry, arise [1–3]. Hydrostatic pressure rapidly decreases the transition temperature with the slope of about 11 K/kbar [4–6].

Elastic and thermoelastic properties of squaric acid are remarkably anisotropic. Compressibility and thermal expansion [7] are much higher in a direction perpendicular to the planes of hydrogen bonds than within the planes. The symmetry-changing strains $\varepsilon_1 - \varepsilon_3$ and $\varepsilon_5$ are confined to the $ac$ plane. Caused by electrostriction anomalous parts of the diagonal strains $\varepsilon_1$, $\varepsilon_3$ and $\varepsilon_2$ have different signs [2].

There is also experimental evidence for non-equivalence of hydrogen bonds going along two perpendicular directions (e.g. [1, 8]). Difference between degrees of proton ordering on these bonds is about 2% at $T_N - 13$ K and $T_N - 21$ K [1]. The O-H and H-site distances are also found to be slightly different for the perpendicular bonds.

Theoretical description of the phase transition in squaric acid is usually based on some versions of the proton ordering model, either two-dimensional, invoking four-particle correlations between protons within the planes [9–12], or one-dimensional, where either non-interacting [13] or coupled [14], perpendicular pseudospin chains are considered. The four-particle model can be reduced to the model of interacting one-dimensional chains by the proper choice of the model parameters [13]. The four-particle Hamiltonians are basically identical to those of $\text{NH}_4\text{H}_2\text{PO}_4$, antiferroelectrics of the $\text{KH}_2\text{PO}_4$ family.

Deformational effects in squaric acid were first addressed in [9–11], where the coupling between spins and spontaneous lattice distortion was included into the model. In Ref. [12] the proton-phonon coupling was added, and hydrostatic pressure effects on the phase transition temperature and dielectric
permittivity of pure and deuterated squaric acid crystals were described by assuming the model parameters to be pressure dependent and by performing a new fitting procedure for each considered value of pressure.

Since the phase transition in squaric acid is usually attributed to proton ordering, which triggers displacements of heavy ions and rearrangement of electronic density, then it is expected that just like in the KH2PO4 family crystals, here the pressure-induced changes in the geometry of the hydrogen bonds should play an important role in the pressure effects on the phase transition and physical properties of the crystal. The most crucial parameter here has been found [15, 16] to be the distance δ between the two equilibrium positions of a proton on a hydrogen bond.

None of the mentioned above earlier theories for the squaric acid crystals explicitly considers the role of the geometrical parameters of hydrogen bonds in the pressure effects on the phase transition in squaric acid. None of them include the thermal expansion of the crystal into consideration either.

So, similarly as it has been done for Rochelle salt [17], we intend to develop a unified deformable model for squaric acid that can describe the effects associated with the diagonal lattice strains: thermal expansion and influence of external hydrostatic pressure. We shall also include dependence of the interaction constants on the H-site distance δ into the model.

2. The Model

There are two formula units in the low-temperature phase unit cell of squaric acid. In our model the unit cell consists of two C4O4 groups and four hydrogen atoms (f = 1, 2, 3, 4, see fig. 1) attached to one of them (the A type group). All hydrogens around the B type groups are considered to belong to the A type groups, with which the B groups are hydrogen bonded. Note that the two C4O4 groups of each unit cell belong to different neighboring layers. The center of each hydrogen bond lies exactly above (and below) the centers of the hydrogen bonds in the layers above and below it (as seen along the b axis). The bonds around each A type group are numbered counterclockwise.

As usually in the proton ordering models, we consider interactions between protons, leading to ordering in their system. Motion of protons in double-well potentials is described by pseudospins, whose two eigenvalues σ = ±1 are assigned to two equilibrium positions of the proton. We take into account the presence of the diagonal components of the lattice strain tensor ε11, ε22, and ε33 that are induced via thermal expansion or by application of external hydrostatic pressure.

The system Hamiltonian in the case of squaric acid

\[ H = U_{seed} + H_{long}^{\text{intra}} + H_{long}^{\text{inter}} + H_{short} \]  (1)

includes intralayer long-range interactions \( H_{long}^{\text{intra}} \), ensuring ferroelectric ordering within each separate layer, interlayer \( H_{long}^{\text{inter}} \) responsible for antiferroelectric stacking of polarized layers, the short-range configurational interactions between protons \( H_{short} \), and the so-called “seed” energy

\[ U_{seed} = v N \left[ \frac{1}{2} \sum_{ij=1}^{3} c_{ij}^{(0)} \varepsilon_i \varepsilon_j - \sum_{i=1}^{3} c_{i}^{(0)} \alpha_i^{(0)} (T - T_i^0) \varepsilon_i \right], \]  (2)

containing elastic and thermal expansion contributions associated with uniform lattice strains; \( c_{ij}^{(0)} \) are the corresponding “seed” elastic constants, whereas \( \alpha_i^{(0)} \) are the “seed” thermal expansion coefficients.

\( T_i^0 \) determine the reference point of the thermal expansion of the crystal, which can be chosen arbitrarily. \( v \) is the unit cell volume, and \( N \) is the number of the unit cells in the crystal.

The mean field approximation is employed for the long-range intralayer

\[ H_{long}^{\text{intra}} = -\frac{1}{2} \sum_{y=1}^{N_y} \sum_{qf}^{qf'} j_{yf'}^{\text{intra}} (qq') \frac{\sigma_{yqf}^{qf'}}{2} \frac{\sigma_{yqf'}^{qf'}}{2} \approx -2 \sum_{yqf} j_{yqf}^{\text{intra}} (\sigma_{yqf}) \frac{\sigma_{yqf}}{2} + \frac{1}{2} \sum_{yqf} j_{yqf}^{\text{intra}} (\sigma_{yqf}) \frac{\sigma_{yqf}}{2}, \]  (3)
Figure 1. Crystal structure of squaric acid as viewed along the $b$ axis. Figure is taken from [18, 19]. Two adjacent layers are shown, with black and open circles each. The A and B type C$_4$O$_4$ groups are indicated (see text for explanation), and the hydrogen bonds are numbered.

\[ F_{\text{long}}^{\text{inter}} = -\frac{1}{2} \sum_y \sum_{y'} \sum_{qq'} J_{ff'}^{\text{inter}} (yy'; qq') \frac{\sigma_{yyf} \sigma_{y'q'f'}}{2} \approx -2 \sum_{yyf} F_{yyf}^{\text{inter}} \frac{\sigma_{yyf}}{2} + \sum_{yyf} F_{yyf} \langle \sigma_{yyf} \rangle . \quad (4) \]

interactions. Here $y$ stands for the layer index, $N_y$ is the total number of the layers, $q$ is the index of the A type C$_4$O$_4$ group, and $f$ is the bond index. The internal mean fields are

\[ F_{yyf}^{\text{intra}} = \frac{1}{4} \sum_{q'f'} J_{ff'}^{\text{intra}} (qq'), \quad F_{yyf}^{\text{inter}} = \frac{1}{4} \sum_{y'q'f'} J_{ff'}^{\text{inter}} (yy'; qq') \]

The following symmetry of the pseudospin mean values is assumed for the antiferroelectrically ordered two-sublattice model in absence of external electric field

\[ \langle \sigma_{yyf} \rangle = \exp[\mathbf{k}_2 \mathbf{R}_y] \eta_f, \quad (6) \]

Here $\mathbf{k}_2 = (0, b_2, 0)$; $b_2$ is the basic vector of the reciprocal lattice; the factor $\exp[\mathbf{k}_2 \mathbf{R}_y] = \pm 1$ denotes two sublattices of an antiferroelectric, $\mathbf{R}_y$ is the position vector of the $y$-th layer, and

\[ \eta_1 = -\eta_3, \quad \eta_2 = -\eta_4, \quad \eta_1 \approx \eta_2. \quad (7) \]

The last relation reflects the mentioned in Introduction slight non-equivalence of hydrogen bonds, linking C$_4$O$_4$ groups along the $a$ and $c$ axes.
Even though each particular interaction parameter $J^{\text{intra}}_{ff'}(qq')$ and $J^{\text{inter}}_{ff'}(yy'; qq')$ is obviously changed by the strains $\varepsilon_1$ and $\varepsilon_3$, the symmetry of the long-range interaction matrices Fourier transforms

$$
J^{\text{intra}}_{ff'}(0) = \sum_{q'q''} J^{\text{intra}}_{ff'}(qq'') \quad \text{and} \quad J^{\text{inter}}_{ff'}(k_2) = \sum_{q-q''} \sum_{y-y''} J^{\text{inter}}_{ff'}(yy'; qq'') \exp[i k_2 (R_y - R_{y''})]
$$

over the bond indices $f$ and $f'$ nonetheless remains unchanged in presence of the orthorhombic strain $\varepsilon_1 = \varepsilon_3$:

$$
J_{11} = J_{22} = J_{33} = J_{44}, \quad J_{12} = J_{23} = J_{34} = J_{41}, \quad J_{13} = J_{24} \tag{8}
$$

both for $J^{\text{intra}}_{ff'}$ and $J^{\text{inter}}_{ff'}(k_2)$. Taking into account Eqs. (6)-(8), we can write the Hamiltonians of the long-range interactions as

$$
H_{\text{long}} = H^{\text{intra}}_{\text{long}} + H^{\text{inter}}_{\text{long}} = Nv [\eta_1^2 + \eta_2^2] - 2v \sum_{yy} \exp[i k_2 R_y] \left[ \eta_1 \frac{\sigma_{yy1} - \sigma_{yy3}}{2} + \eta_2 \frac{\sigma_{yy2} - \sigma_{yy4}}{2} \right], \tag{9}
$$

where

$$
v = v^{\text{intra}}(0) + v^{\text{inter}}(k_2) = \frac{J^{\text{intra}}_{11}(0) - J^{\text{intra}}_{13}(0)}{4} + \frac{J^{\text{inter}}_{11}(k_2) - J^{\text{inter}}_{13}(k_2)}{4} \tag{10}
$$

We also took into account the fact that $N_y N_q A = N$.

For the sake of simplicity, we shall hereafter ignore the weak non-equivalence of the perpendicular chains of hydrogen bonds and use a single order parameter

$$
\eta \equiv \eta_1 = \eta_2 = -\eta_3 = -\eta_4 \tag{11}
$$

instead of Eq. (7).

The short-range Hamiltonian should include the four-particle correlations between protons sitting around each C$_2$O$_4$ group, of both A and B types. It can be shown, as it has been done for the KH$_2$PO$_4$ ferroelectrics, that the contributions of the correlations from the A and B type groups to the total thermodynamic potential are equal. The Hamiltonian of the short-range interactions in this case can be written as

$$
H_{\text{short}} \rightarrow 2 \sum_{yy} H^A_{yy} \tag{12}
$$

where the expression for $H^A_{yy}$ has been derived in Appendix

$$
H^A_{yy} = V \left[ \frac{\sigma_{yy1} \sigma_{yy2}}{2} + \frac{\sigma_{yy2} \sigma_{yy3}}{2} + \frac{\sigma_{yy3} \sigma_{yy4}}{2} + \frac{\sigma_{yy4} \sigma_{yy1}}{2} \right] + U \left[ \frac{\sigma_{yy1} \sigma_{yy3}}{2} + \frac{\sigma_{yy2} \sigma_{yy4}}{2} \right] + \Phi \frac{\sigma_{yy1} \sigma_{yy2} \sigma_{yy3} \sigma_{yy4}}{2}, \tag{13}
$$

the interaction constants are linear functions of the Slater-Takagi energies

$$
V = -\frac{\varepsilon - w_1}{2}, \quad U = \frac{\varepsilon + w_1}{2}, \quad \Phi = 2\varepsilon - 8w + 2w_1. \tag{14}
$$

The four-particle cluster approximation will be used for the short-range interactions, described by the Hamiltonian $H_{4f}$. With the long-range interactions taken into account in the mean field approximation, the thermodynamic potential of the system should be written as

$$
G = -e N \sum_{i=1}^{3} \sigma_i \varepsilon_i + NU_{\text{seed}} - \frac{1}{\beta} \sum_{yy} \left[ 2 \ln \text{Sp} \exp(-\beta H^A_{yy}) - \frac{4}{f} \ln \text{Sp} \exp(-\beta H^d_{YY}) \right] \\
+ \sum_{yaf} \left( F^{\text{intra}}_{yyaf} + F^{\text{inter}}_{yyaf} \right) \frac{\langle \sigma_{yyf} \rangle}{2}. \tag{15}
$$
Here \( \sigma_1 = \sigma_2 = \sigma_3 = -p \), and

\[
F_{\text{intra}}^\text{yq} + F_{\text{inter}}^\text{yq, yq} = \hat{E}_{\text{intra}}^\text{yq} + F_{\text{inter}}^\text{yq} = F_{\text{intra}}^\text{yq, yq} = F_{\text{intra}}^\text{yq} - F_{\text{inter}}^\text{yq} = F_{\text{inter}}^\text{yq} = \exp[i k_2 R_g] v \eta. \tag{15}
\]

The four-particle cluster Hamiltonian is

\[
H_{\text{qf}}(4) = H_{\text{qf}}^A - \sum_{f=1}^{4} z_{\text{qf}} \frac{\sigma_{\text{qf}}}{\beta}, \tag{16}
\]

where

\[
z_{\text{qf}} = \beta [\Lambda_{\text{qf}} + 2 F_{\text{intra}}^\text{yq} + 2 F_{\text{inter}}^\text{yq}].
\]

\( (\beta = [k_B T]^{-1}) \). The fields \( \Lambda_{\text{qf}} \) are the effective cluster fields that describe short-range interactions of the spin \( \sigma_{\text{qf}} \) with the particles from outside the cluster \( q \). They are determined from the self-consistency condition that pseudospin mean values calculated with the four-particle \( (16) \) and with the one-particle Hamiltonians must coincide. We get

\[
z_{\text{yq1}} = \frac{z_{\text{yq2}} = -z_{\text{yq3}} = -z_{\text{yq4}} = \exp[i k_2 R_g] z,}{\frac{z}{2} \ln \frac{1 + \eta}{1 - \eta} + \beta \nu \eta}. \tag{17}
\]

Taking into account Eqs. \((9), (11), (16), (17)\), the thermodynamic potential per one unit cell is obtained in the following form

\[
g = U_{\text{seed}} - \frac{4}{\beta} [\ln D + \ln(1 - \eta^2)] + 2 \nu \eta^2 - v \sum_{i=1}^{3} \sigma_i \epsilon_i, \tag{18}
\]

where

\[
D = a + \cosh 2z + 4b \cos z + 1, \quad a = \exp(-\beta \epsilon), \quad b = \exp(-\beta w).
\]

In the earlier theories \([16, 20]\) the short-range Slater-Takagi energies in the \( KH_2PO_4 \) family crystals were considered as quadratic functions of the distance \( \delta \). For the squaric acid we shall employ the same scheme. Using the term of the relative deviation of \( \delta \) from its value \( \delta_0 \) at ambient pressure (we shall call it a displacement \( \mu' \))

\[
\mu' = \frac{\delta - \delta_0}{\delta_0}, \tag{19}
\]

we take that

\[
\epsilon = \epsilon_0 (1 + \mu')^2, \quad w = w_0 (1 + \mu')^2. \tag{20}
\]

Here the quadratic in \( \mu' \) terms, omitted in \([16]\), now are included into consideration.

For the parameter of the long-range (dipole-dipole) interactions \( \nu \) both the dependence of the dipole moments on \( \delta \) and the changes in the interaction parameter due to the overall crystal deformation \([16]\) and associated with changes in the equilibrium distances between protons (dipoles) are taken into account

\[
\nu = \nu_0 (1 + \mu')^2 + \sum_{i=1}^{3} \psi_i \epsilon_i. \tag{21}
\]

It should be underlined that none of the earlier theories \([16, 20]\) described the thermal expansion of the crystals; therefore, the deformational effects there were only those caused by external pressures. On the contrast, in the present model the strains \( \epsilon_i \) are induced both by temperature changes and by external pressures. In the mean field approximation the expansion \([21]\) gives rise to the terms of the electrostriction type in the Hamiltonian, linear in the strains and quadratic in the sublattice polarization (order parameter \( \eta \)).
In [16, 20] the distance \( \delta \) was treated as a pressure dependent and temperature independent model parameter, with the linear pressure dependence chosen either from available experimental data or by fitting the theory to experiment for the transition temperatures. In the present work we shall use the similar approach and take \( \delta \) to vary according to its experimentally observed above the transition linear temperature \([1]\) and external hydrostatic pressure \( p \) \([15]\) dependences

\[
\delta = \delta_0[1 + \delta_p p + \delta_T (T - T_{N0})],
\]

(22)

where \( T_{N0} \) is the transition temperature at ambient pressure. It means that the anomalous temperature behavior of \( \delta \) below the transition point and its jump at \( T_N \) are ignored.

Minimization of the thermodynamic potential \( \{18\} \) with respect to the order parameter \( \eta \) and strains \( \varepsilon_i \)

\[
\frac{\partial g}{\partial \eta} = 0, \quad \frac{\partial g}{\partial \varepsilon_i} = 0
\]

yields the following equations

\[
\eta = \frac{\sinh 2z + 2b \sinh z}{D}, \quad \sigma_i = \sum_{j=1}^{3} c_{ij}^{(0)} \varepsilon_j - \sum_{j=1}^{3} c_{ij}^{(0)} \alpha_j^{(0)} (T - T_j^0) + \frac{2\psi_i \eta}{\nu} \left( \eta - \frac{2 \sinh 2z + 2b \sinh z}{D} \right).
\]

From above it follows that in equilibrium

\[
\varepsilon_k = \alpha_k^{(0)} (T - T_k^0) + \sum_{i=1}^{3} \sigma_i \delta_{ki}^{(0)} - \frac{2\eta^2}{\nu} \sum_{i=1}^{3} \psi_i \delta_{ki}^{(0)},
\]

(23)

where \( \delta_{ki}^{(0)} \) is the matrix of “seed” elastic compliances, inverse to \( c_{ij}^{(0)} \). One can see, that at zero pressure in the paraelectric phase (\( \eta = 0 \)) the microscopic contributions to the strains vanish, whereas in the ordered phase they are proportional to \( \eta^2 \), indicating the electrostriction type contributions, and are governed by the parameters \( \psi_i \).

The molar entropy of the proton system is

\[
\Delta S = -\frac{1}{2} \left( \frac{\partial g}{\partial T} \right)_p = k_B \ln[(1 - \eta^2)D] - \frac{1}{DT} [ae + 4bw \cosh z] - \frac{2\nu \eta^2}{T}.
\]

(24)

3. Calculations

In the calculations, the thermodynamic potential is minimized numerically with respect to the order parameter \( \eta \). Simultaneously, the strains \( \varepsilon_i \) are determined.

The quantities that have to be described include:

- the temperature curves at ambient pressure of
  - sublattice polarization (order) parameter,
  - macroscopic lattice strains \( \varepsilon_i \),
  - thermal expansion coefficients and specific heat
- the pressure curves of
  - transition temperature \( T_N \),
  - lattice strains \( \varepsilon_i \).
Since we do not want to overcomplicate the fitting procedure by adopting different values of the model parameters for the paraelectric and antiferroelectric phase, the chosen matrix quantities \( c_{ij}^{(0)} \), \( \alpha_i^{(0)} \), \( T_i^{(0)} \) should obey the tetragonal symmetry of the paraelectric phase, namely \( c_{11}^{(0)} = c_{33}^{(0)} = c_{12}^{(0)} \), \( \alpha_1^{(0)} = \alpha_3^{(0)} \), \( T_1^{(0)} = T_3^{(0)} \).

The “seed” elastic constants \( c_{ij}^{(0)} \) are associated with macroscopic strains \( \varepsilon_i \). There are four of them: \( c_{11}^{(0)} \), \( c_{22}^{(0)} \), \( c_{12}^{(0)} \), and \( c_{13}^{(0)} \). We take \( c_{11}^{(0)} \) to be equal to the experimental value of \( c_{11}^{[21]} \) above the transition point. Experimental elastic constant \( c_{22}^{(0)} \) was found to slightly decrease with increasing temperature \( [21, 22] \). The “seed” \( c_{22}^{(0)} \) is chosen accordingly, coinciding with the data of \([23]\). Finally, \( c_{12}^{(0)} \) and \( c_{13}^{(0)} \), for which no convincing experimental data is available, were chosen to provide a correct fit to the experimental \([23]\) pressure dependence of the lattice constants.

The parameters of the short-range correlations \( \epsilon_0 \) and \( \omega_0 \) govern the temperature behavior of the order parameter \( \eta \) (in particular, the magnitude of its jump at the transition \( \Delta \eta_c \), and steepness of its rise to saturation) and the value of the transition temperature at ambient pressure \( T_{N0} \). The latter is also extremely sensitive to the value of the long-range interaction parameter \( \epsilon_0 \). Hence, the set of \( \epsilon_0 \), \( \omega_0 \), and \( \nu_0 \) is chosen to yield \( T_{N0} = 373.5 \) K, \( \Delta \eta_c \approx 0.57 \), as well as correct rise \( \eta \) between the transition and saturation. Contributions of the double-ionized configurations are neglected by putting \( \psi_1 \rightarrow \infty \).

The “seed” thermal expansion coefficients \( \alpha_i^{(0)} \) as well as the parameters \( \psi_i \) are determined by fitting the theoretical temperature dependences of diagonal lattice strains to experimental data \([7, 24]\). In fact, \( \alpha_i^{(0)} \) must be simply equal to the corresponding paraelectric experimental values, as is seen directly in Eq. \([23]\). The parameters \( \psi_i \), on the other hand, are unambiguously determined by fitting the calculated anomalous parts of the strains to the experiment below the transition temperature, using Eq. \([23]\). As \( \psi_i \) are relevant for the ordered phase only, they do not have to adhere to the symmetry of the paraelectric phase; hence we can take \( \psi_1 \neq \psi_3 \), as is indeed required by the just described fitting.

As we have already mentioned, the temperatures \( T_i^{(0)} \) determine the reference point of the thermal expansion of the crystal, which can be set arbitrarily. Thus \( T_i^{(0)} \) are not fitting parameters of the model and, therefore, also can be chosen arbitrarily. In our calculations we chose them to yield zero values of the lattice strains \( \varepsilon_i \) just above the transition temperature at ambient pressure. In fact, \( T_1^{(0)} = T_2^{(0)} = T_{N0} = 373.5 \) K, as seen from Eq. \([23]\).

As already described, we take \( \delta \) to vary according to its experimentally observed linear temperature and external hydrostatic pressure \([22]\). The coefficients \( \delta_T \) and \( \delta_p \) are deduced from the data of \([15]\) and \([15]\).

**Table 1.** The adopted values of the model parameters.

| \( \epsilon_0/k_B \) | \( \omega_0/k_B \) | \( \nu_0/k_B \) | \( \psi_1/k_B \) | \( \psi_2/k_B \) | \( \psi_3/k_B \) | \( \alpha_1^{(0)} \) (10^{-5} K^{-1}) | \( \alpha_2^{(0)} \) (10^{-4} K^{-1}) | \( \delta_T \) (kbar^{-1}) | \( \delta_p \) (kbar^{-1}) |
|---|---|---|---|---|---|---|---|---|---|
| 395 | 1100 | 79.8 | -518 | 445 | 1096 | 1.2 | 13.0 | 2 | -0.014 |

In figure 2 we show the calculated temperature dependence of the order parameter \( \eta \) and the spontaneous strain \( \varepsilon_1 - \varepsilon_3 \) at ambient pressure. Experimental points for \( \eta \) were obtained from the \(^{13}\)C NMR measurements. A clear first order phase transition is observed, with the jump of the order parameter \( \Delta \eta \approx 0.57 \). The spontaneous strain \( \varepsilon_1 - \varepsilon_3 \) is negative below the transition and, as follows from Eq. \([23]\), is proportional to the square of the order parameter \( \eta^2 \).

The temperature dependences of the diagonal lattice strains \( \varepsilon_i \) and the corresponding thermal expansion coefficients are shown in fig. 3. The coefficients were calculated by numerical differentiation of the strains with respect to temperature.
A clear anisotropy of the thermoelastic properties of squaric acid within the ac plane and in the perpendicular direction is seen. The strain $\varepsilon_2$ has a downward jump at the transition and a negative anomalous part in the ordered phase. The strains $\varepsilon_1$ and $\varepsilon_3$, on the other hand, have upward jumps and positive anomalous parts. As is shown above (see Eq. (23)), the anomalous contributions to the macroscopic strains are strictly proportional to the square of the order parameter $\eta^2$. The thermal expansion coefficients $\alpha_1 = \alpha_3$ in the paraelectric phase are by one order of magnitude smaller than $\alpha_2$; their anomalies at the transition point are of different signs.

The specific heat of the proton subsystem is calculated by numerical differentiation of the entropy

$$\Delta C_p = -\frac{T}{M} \left( \frac{\partial \Delta S}{\partial T} \right)_P,$$

where $M = 114.06 \, \text{g/mol}$ is the molar mass of squaric acid. The corresponding temperature curve is given in fig. 4. The experimental points for the anomalous part of the specific heat are obtained by subtracting the regular part, best described as a slightly non-linear curve $C_{\text{reg}} = -0.48803 + 0.00738T - 7.3 \cdot 10^{-6}T^2 \,(\text{J/g K})$, from the total specific heat as it was measured in [26]. One can see that a satisfactory agreement with experiment is obtained, even though the specific heat was not directly involved in the described above fitting procedure.

The calculated hydrostatic pressure dependences of the paraelectric lattice constants are shown in...
Figure 4. Temperature dependence of the specific heat of squaric acid. Line: the theory; symbols are experimental points derived from the data of [26] as described in text.

The lattice constants were determined as $a = a_0[1 + \epsilon(1)]$, $b = b_0[1 + \epsilon(2)]$, where $a_0 = 6.137$ Å, $b_0 = 5.327$ Å are the values of the lattice constants just above the transition point at ambient pressure [7]. A good agreement with experiment is obtained.

Figure 5. Lattice constants at 292 K as functions of hydrostatic pressure. Lines: the theory; symbols are experimental points taken from [23].

In figure 6 we plot the hydrostatic pressure dependence of the phase transition temperature in squaric acid. As expected, the calculated transition temperature decreases with pressure (the dashed line). Quantitatively, however, completely non-satisfactory results are obtained. With the pressure variation of $\mu'$ as observed experimentally [15] and the parameters $\psi_i$ determined by fitting to the lattice strains below transition at ambient pressure, the rate, with which the calculated transition temperature decreases with hydrostatic pressure, $\partial T_c / \partial p = -19.5$ K/kbar, is nearly twice as large as the experimental one. The observed disagreement means, foremost, that Eq. (21) yields a too fast decrease of the long-range interaction parameter $\nu$, to which the theoretical values of the transition temperature are most sensitive. The pressure variation of the Slater-Takagi energies is less important here.

Below we discuss a possible origin of the model inconsistency and ways to solve this problem. To this end, let us look closely at the obtained pressure dependence of $\nu$.

It is expected that the term $\sum_i \psi_i \epsilon_i$ in presence of high hydrostatic pressure would be positive, thereby leading to an increase of the long-range interaction parameter $\nu$ due to the reduction of the average interparticle distances in the compressed crystal. However, when the values of the parameters $\psi_i$ are chosen to fit to the experimental data [7] for the anomalous spontaneous temperature behavior of the strains $\epsilon_i$ below the transition at ambient pressure, the sum $\sum_i \psi_i \epsilon_i$ in presence of high pressure becomes negative, not slowing, as expected, but enhancing the decrease of $\nu$ caused by the decrease of the H-site distance $\delta$.

An obvious workaround but rather clumsy way to obtain the necessary pressure dependence of $\nu$ is to assume that there are some other high-pressure factors, not included into (21) and (20), and to include...
them empirically via the terms $k_p p$, namely

$$\varepsilon = \varepsilon_0 \left[ (1 + \mu')^2 + k_{p1} p \right], \quad w = w_0 \left[ (1 + \mu')^2 + k_{p1} p \right],$$

(25)

and

$$\nu = \nu_0 \left[ (1 + \mu')^2 + k_{p2} p \right] + \sum_{i=1}^{3} \psi_i \varepsilon_i.$$

(26)

We can speculate, for instance, that external pressure causes a redistribution of electron density, thereby changing the effective charges of the ions and, as a result, the interactions between them. Introduction of two extra fitting parameters $k_{p1}$ and $k_{p2}$ indeed allows us to describe the pressure variation of the transition temperature (see fig. 5, the solid line). At $k_{p1} = k_{p2} = 0.0151$ kbar$^{-1}$ we obtain $\partial T_c / \partial p = -10.7$ K/kbar, in total agreement with experiment. Other combinations of $k_{p1}$ and $k_{p2}$ values can be found, also yielding the desired fit for the $T_c$ vs $p$ dependence. On this the already obtained good agreement with experiment for the system behavior at ambient pressure is not affected.

A less speculative approach to the problem is, however, to recall that the essential non-linear temperature variation of the distance $\delta$ below the phase transition [1] is ignored in the present model. If we expand it by considering $\delta$ as an independent thermodynamic variable, not as a preset model parameter, then not only the theory will be more consistent and adequate, but also the discussed above problem with the pressure variation of the long-range interaction parameter may be solved. Preliminary calculations show, however, that it does not suffice to simply determine $\delta$ (or, rather its displacement $\mu'$) by minimization of the thermodynamic potential, but the system Hamiltonian has to be changed too. In particular, the terms like $c_\mu(\mu')^2$ and $\mu' \sum_i c_{i\mu} \varepsilon_i$ has to be included into $U_{seed}$ (here $c_\mu$ and $c_{i\mu}$ are components of the force-constant and internal-displacement tensors [27]). The term $c_\mu(\mu')^2$ alone does not solve the problem, and the mixed terms $\mu' \sum_i c_{i\mu} \varepsilon_i$ are required. This modification of the model is currently in progress and will be subject of a separate paper.

4. Conclusions

We present a modification to the proton ordering model, aimed to describe the effects associated with diagonal lattice strains in H-bonded antiferroelectric crystals of squaric acid. These effects include thermal expansion of the crystals, appearance of spontaneous strain $\varepsilon_1 - \varepsilon_3$ below the phase transition, and the shift of the transition temperature with hydrostatic pressure. On this, both the macroscopic lattice strains and the changes in the local geometry of hydrogen bonds are found to be essential. As usually, the quadratic dependence of the parameters of short-range and long-range interactions between protons on the H-site distance $\delta$ is assumed.

The deformational phenomena at ambient pressure are well described by the developed theory. On the other hand, the experimental dependence of the transition temperature on hydrostatic pressure can
be described only, if we assume that there are additional mechanisms to the pressure dependence of the interaction constants of the model, other than via the electrostriction interactions with the diagonal macroscopic strains and via shortening of $\delta$, or if we suggest further modification of the model, in which $\delta$ would be considered as an independent thermodynamic variable.

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Appendix

Similarly to as it is done for NH$_4$H$_2$PO$_4$, the antiferroelectrics of the KH$_2$PO$_4$ type family, it is assumed that the energy of four lateral configurations $\varepsilon_a$, where two protons are in positions close to the adjacent oxygens of the C$_4$O$_4$ group, whereas two other protons are closer to the neighboring C$_4$O$_4$ groups, is the lowest of all. The next level is two diagonal configurations with the energy $\varepsilon_s$, where the
protons are close to the opposite oxygens. Then there are eight single-ionized configurations with three or only one close protons, having the energy $\varepsilon_1$, and two double-ionized configurations ($\varepsilon_0$) with four or no protons at all close to the given C₄O₄ group. It is believed that $\varepsilon_a < \varepsilon_s \ll \varepsilon_1 \ll \varepsilon_0$.

The above scheme is developed for strictly square-shaped C₄O₄ groups (point group C₄h). That is the statistically average symmetry of the paraelectric phase, where the hydrogens are placed, also statistically, in the middle of the hydrogen bonds. In fact, when two protons are in the most energetically favorable lateral configurations, C₄O₄ groups are isosceles trapezoids (point group C₁h). It is believed that the local distortion is caused by two single and two double covalent bonds, connecting the four oxygens to the carbons, and formation of the double C–C bond within the C₄O₄ skeleton, as shown in Fig. 7. Double bonds are shorter than single between analogous atoms. Since the origin of the skeleton distortion is chemical bonding with the local proton configuration, and not the macroscopic uniform lattice strains, all four lateral configurations still have the same energy of the short-range interactions, no matter what their orientation with respect to the crystallographic axes is (see Table 2). The same holds for the diagonal (point group C₂h), single-ionized (point group C₁), and double-ionized groups (point group D₂h). It means that no splitting of the short-range energy levels by the macroscopic spontaneous strain takes place, in contrast to what was assumed in earlier theories for squaric acid [9] or for KH₂PO₄ type crystals [28, 29].

\[ H_{yq}^A = \sum_{i=1}^{16} N_i(yq) E_i, \quad \hat{N}_i(yq) = \prod_{j=1}^{4} \left(1 + s_f \sigma_{yqf} \right) \] 

where $N_i(yq)$ is the operator of the four-particle configuration $i$; $s_f = \pm 1$ is the sign of the eigenvalue of the $\sigma_{yqf}$ operator in this particular configuration; $E_i$ is the energy of the configuration. It is assumed that $s_f = +1$ if a proton at the $j$th bond is localized at the H-site proximal to the given A type C₄O₄ group, and $s_f = -1$ if the proton is localized at the other (distal) H-site of the same bond. Using Eq. (27), we arrive at the following expression for the Hamiltonian

\[ H_{yq}^A = V \left[ \frac{\sigma_{yq1} \sigma_{yq2}}{2} + \frac{\sigma_{yq2} \sigma_{yq3}}{2} + \frac{\sigma_{yq3} \sigma_{yq4}}{2} + \frac{\sigma_{yq4} \sigma_{yq1}}{2} \right] + U \left[ \frac{\sigma_{yq1} \sigma_{yq3}}{2} + \frac{\sigma_{yq2} \sigma_{yq4}}{2} \right] + \Phi \left[ \frac{\sigma_{yq1} \sigma_{yq3}}{2} \sigma_{yq4} \right] \]

(28)

Here

\[ V = -\frac{\varepsilon - w_1}{2}, \quad U = \frac{\varepsilon + w_1}{2}, \quad \Phi = 2\varepsilon - 8w + 2w_1, \]

(29)

and

\[ \varepsilon = \varepsilon_s - \varepsilon_a, \quad w = \varepsilon_1 - \varepsilon_a, \quad w_1 = \varepsilon_0 - \varepsilon_a \]

are the Slater-Takagi type energy parameters. Note that the model of non-interacting perpendicular one-dimensional chains is obtained from Eq. (16) at $\Phi = V = 0$, i.e. at $\varepsilon = w_1 = 2w$, where the following order of the configuration energies should be assumed [13] $\varepsilon_a < \varepsilon_1 < \varepsilon_s = \varepsilon_0$. 

Figure 7. Lateral, diagonal, single and double ionized proton configurations around an A type C₄O₄ group in squaric acid. The hydrogen bonds $f = 1, 2, 3, 4$ are numbered. Two equilibrium positions of each proton are shown, and the signs $s_f = \pm 1$ of the eigenvalues of the $\sigma_{yqf}$ operators are indicated.
Table 2. Proton configurations and their energies

| l | s₁ s₂ s₃ s₄ | Eₗ |
|---|-------------|----|
| 1 | ++ −−       | E₁₂ |
| 2 | − + ++      |    |
| 3 | − − ++      |    |
| 4 | + − − +     |    |
| 5 | − + − +     | Eₓ |
| 6 | + − − +     |    |
| 7 | + − − −     | E₁ |
| 8 | − + − −     |    |
| 9 | − − + +     |    |
| 10| − − − +     |    |
| 11| − + − −     |    |
| 12| + − − +     |    |
| 13| + + − +     |    |
| 14| + + − −     |    |
| 15| − − − −     | E₀ |
| 16| + + + +     |    |