Quantum Paraelectricity and Subsequent Disappearance of Bond Alternation of Molecule Caused by Proton Dynamics in Squaric Acid Crystal

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The temperature-pressure phase diagram was determined for a crystal of squaric acid which consists of molecular sheets of $[C_4O_4]^{2-}$ skeletons and intervening protons. Under hydrostatic pressures, the paraelectric phase composed of the polar (C_{1h}-distorted) molecules is realized even near 0 K due to a joint quantum motion of the protons and deforming molecular skeletons. Further application of pressure causes a disappearance of the π-bond alternation of the constituent molecule at all temperatures caused by enhanced motion of the protons.

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The dynamics of strongly correlated protons in ionic or molecular crystals with hydrogen bonds causes, in general, a variety of phase transitions and accompanying lattice structural changes [1]. In those solids, the behavior of protons is critically affected by the distance [2] between the two oxygen sites sandwiching the protons: With a sufficiently close O-O distance the proton shows a back-and-forth (tunneling and/or thermal) motion between the minima of the double-well-type potential and with an even shorter distance below some critical value ($\sim$2.45 Å) the proton essentially locates at the central position between the two oxygens. Therefore, application of pressure, which reduces the O-O distance [3], significantly affects the dynamical behavior of protons and hence physical properties of hydrogen-bonded crystals. For example, hydrostatic pressure decreases the critical temperature (T_c) for the dielectric phase transition in many hydrogen-bonded (anti)ferroelectrics, such as the families of potassium dihydrogen phosphate (KDP) [4]. In an extreme case, the dielectric phase transition was observed to vanish (down to 0 K) under high pressure [5,6].

In this Letter, we present the temperature-pressure (T-P) phase diagram for one of the most prototypical molecular dielectrics with networks of hydrogen bonds: a crystal of squaric acid ($H_2C_4O_4$, abbreviated as H_2SQ) (see Fig. 1 for the molecular structure). We have found that there are two boundaries in the T-P phase diagram for the H_2SQ crystal at all temperatures below 375 K: One is for the ordinary dielectric phase transition associated with the order-disorder transition of proton sites and the other is for disappearance of the bond alternation of the constituent molecule caused by enhanced proton motion under high pressures. The paraelectric phase near the former phase boundary was proved to be still composed of the polar H_2SQ molecules even at low temperatures, which may be interpreted in terms of quantum paraelectricity.

Molecules of H_2SQ form two-dimensional (2D) networks of hydrogen bonds in the crystal [7]. The hydrogen bonds align polar (with C_{1h} symmetry) molecules along the same direction within each molecular sheet, as schematically shown in Fig. 1(a). These polar-molecular sheets stack along the b axis (normal to the molecular sheet) in an antiferroelectric manner, alternating sheet polarizations. An antiferroelectric (AFE) to paraelectric (PE) phase transition occurs associated with the order-

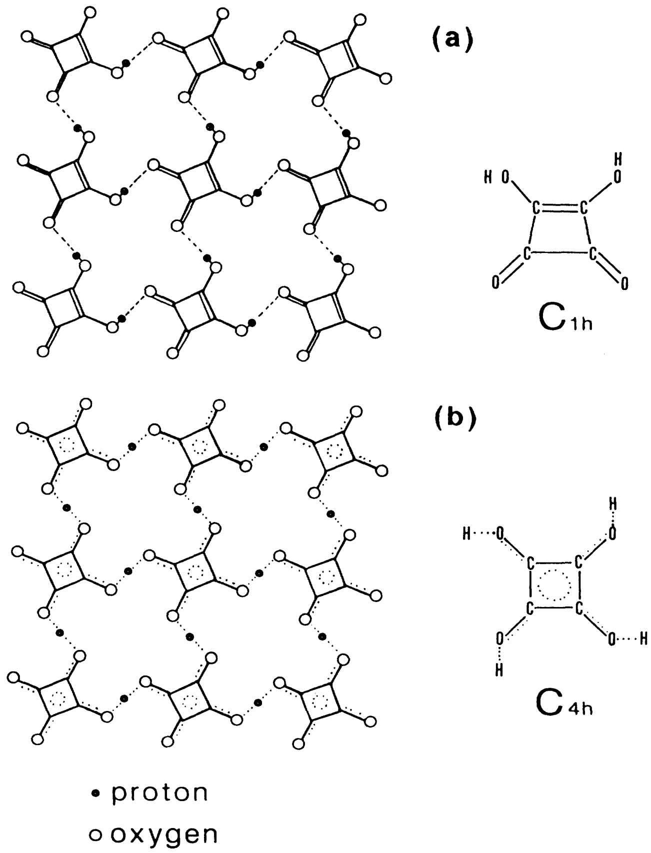

FIG. 1. Schematic structure of molecular sheet and a constituent molecular unit in H_2SQ crystal: (a) at ambient pressure and (b) at high pressures (> 3 GPa).

disorder transition of proton sites (i.e., melting of the proton lattice) at 375 K [8-11] at ambient pressure. A very similar dielectric phase transition is observed also by applying a pressure of 0.7 GPa [9-11] at 300 K. Upon the dielectric phase transition, the crystal structure changes from the monoclinic (AFE phase; $P2_1/m$, $Z=2$) to the tetragonal form (PE phase; $I4/m$, $Z=1$) [12,13]. In the high-temperature PE phase, however, each squaric molecule still sustains the asymmetric (C_{1h} distorted) shape [8,9] due to the chemical bonding with the neighboring two protons among the surrounding four protons [see Fig. 1(a)]. In other words, the local structure around each SQ^{2-} skeleton is essentially the same as that in the AFE (low-temperature) phase [14,15] apart from the absence of the long-range ordering of proton sites and molecular polarities.

With increasing pressure beyond the critical pressure P_c for the dielectric phase transition, the H_2SQ crystal (and its deuterated analog D_2SQ) was found to undergo another structural change at least around room temperature [8,9]; that is, a disappearance of the C_{1h}-type distortion of SQ^{2-} skeletons at approximately 3 GPa for H_2SQ and approximately 7 GPa for D_2SQ at 300 K. As probed by Raman spectroscopy, the SQ^{2-} skeleton in the crystal appears to be transformed from the asymmetric [C_{1h}, Fig. 1(a)] to the centrosymmetric [C_{4h}, Fig. 1(b)] form under high pressures. The proposed schematic model for the structure of the molecular sheet under high pressures is shown in Fig. 1(b). In this study, we pay special attention to the quantum nature of the structural changes at low temperatures and high pressures.

The two structural changes, i.e., the order-disorder transition of proton sites and the symmetry change of the constituent molecule, were detected by measurements of the dielectric constant and Raman spectra, respectively. The temperature dependence of the dielectric constant under high pressures was measured with an *LCR* meter operated at 1 kHz and a specially designed cubic-anvil-type pressure cell, details of which were described elsewhere [16]. An *a*-plate (or *c*-plate) sample, 0.15 mm in thickness and 1.2×0.5 mm^2 in area, was cut from a crystal ingot and the surfaces were painted with silver paste to act as electrodes. An electric field was applied parallel to the molecular sheets. Raman spectra under high pressures were measured on a cleaved *ac* face of the single crystal using a conventional diamond-anvil cell [8] with liquid paraffin as a pressure-transmitting medium. Pressure-induced changes of the dielectric constant and Raman spectra showed good reversibility for a pressure cycle. We observed no indication of inhomogeneity of pressure within the cell, for example, in spectral profiles of some sharp Raman bands whose frequencies are pressure sensitive.

First, we present results for the pressure dependence of the critical temperature (T_c) for the dielectric phase transition in the H_2SQ crystal. Figure 2 shows the temperature dependence of the dielectric constant (in-plane component) for the H_2SQ crystal under various hydrostatic pressures. The critical temperature T_c, indicated by an arrow in Fig. 2, was determined by the inflection point in the $\varepsilon(T)$ curve. At ambient pressure, the dielectric constant critically increases approaching T_c ($=375$ K) from below and remains almost constant (~ 400) above T_c [17], which is typical of the AFE phase transition. With increasing pressure, T_c rapidly decreases probably due to a reduction of the O-O distance [18] and a resultant activation of the proton motion. As T_c decreases with pressure, the critical behavior of the dielectric constant becomes less obvious: For example, at 2.9 GPa the dielectric constant shows a broad maximum reminiscent of a phase transition around 40 K (see the inset of Fig. 2). At 3.1 GPa, however, there is no trace of a phase transition and the dielectric constant monotonously increases with decreasing temperature. Notably, the dielectric constant at 3.1 GPa is still large (230-240) even near 0 K.

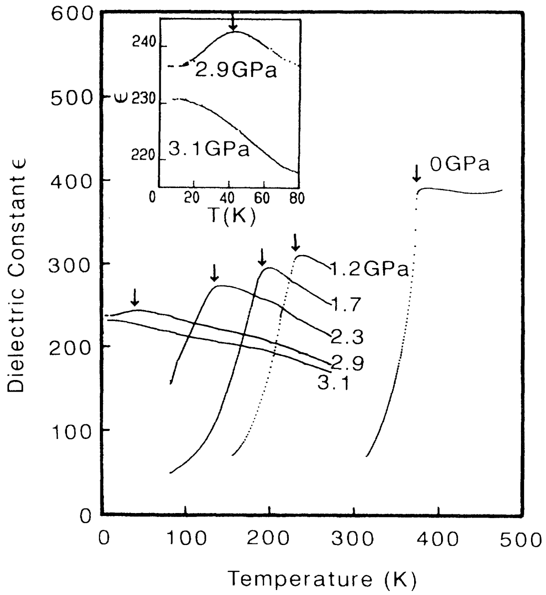

FIG. 2. Temperature dependence of the dielectric constant in H_2SQ crystal at various hydrostatic pressures. Arrows indicate the critical temperatures. Inset: Magnification of the data at low temperatures and high pressures.

The critical temperatures thus obtained are plotted with open circles in Fig. 3 against the values of hydrostatic pressure. Except for the low-temperature (<100 K) region, the phase boundary is approximately represented by a straight line with a slope of -106 K/GPa, which is in agreement with the value previously reported for data [10,11] taken above 270 K. On approaching zero temperature, the slope becomes steeper and finally the phase transition vanishes around 3.0 GPa. In other words, the protons and polar-molecular skeletons cannot show long-range ordering under pressures above 3.0 GPa even near 0 K. However, the large dielectric constant observed (see

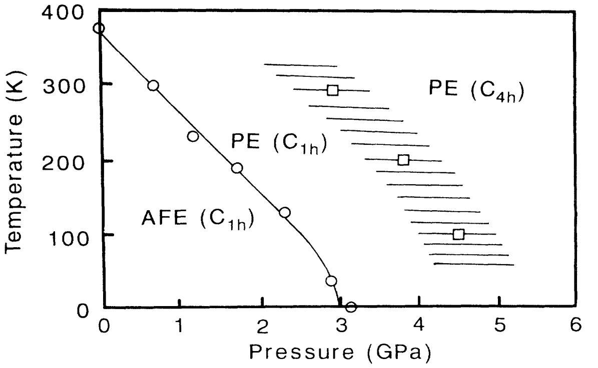

FIG. 3. Temperature-pressure phase diagram for H₂SQ crystal. AFE (C_{1h}) and PE (C_{1h}) stand for the antiferroelectric and the paraelectric phase consisting of the C_{1h}-distorted molecules, respectively, and PE (C_{4h}) stands for the PE phase consisting of the molecules with C_{4h} symmetry. The solid line for the AFE-PE phase boundary is merely a guide to the eye. The hatching represents the C_{1h}-C_{4h} boundary including a typical error bar.

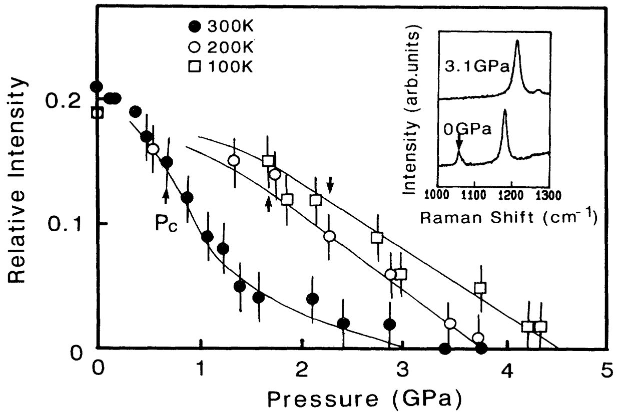

FIG. 4. Pressure dependence of relative intensity of the pseudo-E_u to pseudo-B_g intramolecular C-C stretching mode at 100 K (squares), 200 K (open circles), and 300 K (solid circles). The solid lines are merely a guide to the eye. Arrows indicate the critical pressures (P_c) for the dielectric phase transition at each temperature. Inset: Raman spectra for the C-C stretching modes at ambient pressure (lower) and 3.1 GPa (upper) at 300 K.

the inset of Fig. 2) implies residual short-range ordering, which should produce spatially and temporally fluctuating polar domains in the molecular sheets. Such a possible quantum nature of the low-temperature PE phase could be confirmed in this study by spectroscopically probing the polar distortion of the constituent molecules (*vide infra*).

As mentioned above, the H_2SQ crystal shows another structural change under high pressures; that is the symmetry change (C_{1h} to C_{4h}) of the constituent molecules (see Fig. 1). This indicates that the π-bond alternation within the H_2SQ molecule disappears due to the effectively weakened chemical bonds between the SQ^{2-} skeleton and the outer protons. Here, we have investigated such a symmetry change with varying temperature by high-pressure Raman spectroscopy. The critical pressure for the symmetry change, which will be hereafter referred to as P_s to be distinguished from the critical pressure P_c for the dielectric phase transition, was also found to be temperature dependent, and increases with decreasing temperature, as shown in the following.

The inset of Fig. 4 shows Raman spectra for H_2SQ at ambient pressure (lower) and 3.1 GPa (upper) at 300 K. The lower- and higher-lying modes are due to the intramolecular C-C stretching modes, which would be assigned to the E_u and B_g modes [8], respectively, in the hypothetically centrosymmetric (C_{4h}) molecular symmetry. The lower-lying mode (pseudo-E_u mode) indicated by an arrow completely disappears at 3.1 GPa (upper spectra), while the higher-lying mode (pseudo-B_g mode) remains essentially unchanged except for a slight increase of its mode frequency. Such a selective deactivation can be interpreted in terms of the above-mentioned C_{1h}-C_{4h} symmetry change of the constituent molecules [7,8]. The pseudo-E_u mode remains sharp above P_c, but shows a critical reduction of its intensity with pressure. Therefore, we can utilize this pseudo-E_u mode as a sensitive probe for the C_{1h}-type distortion (or π-bond alternation) of the individual H_2SQ molecules and to estimate the critical pressure P_s for the symmetry change.

The intensity ratio of the lower-lying pseudo-E_u mode to the higher-lying pseudo-B_g one is plotted against the hydrostatic pressure at various temperatures in Fig. 4. The intensity ratio, which represents the relative magnitude of the C_{1h}-type distortion of the constituent molecule, decreases continuously with pressure and eventually goes to zero. However, there is no distinct change in the intensity ratio at P_c (indicated by an arrow in Fig. 4) for each pressure run at the respective temperature. This indicates that the dielectric phase transition under high pressure can be characterized, even at low temperatures, by the order-disorder transition of proton sites or equivalently of the directions of the polar (C_{1h}-distorted) molecules. Looking at Fig. 4, one may notice that the C_{1h}-type distortion remains up to a higher pressure with lowering temperature. Such a temperature-dependent behavior cannot be ascribed to an inhomogeneity of pressure, for example, due to solidification of the pressure-transmitting medium at low temperatures, because no saturation in intensity reduction was observed (see Fig. 4) and the Raman profile of both modes which show pressure-induced frequency shifts remained sharp even at high pressures.

The critical pressure P_s for the symmetry change was approximately estimated by extrapolation, as shown by the eye-guiding lines in Fig. 4. The estimated values of P_s are plotted in Fig. 3 with open squares; they have rather long error bars due to the difficulty in determining precisely the vanishing point of the Raman band. The phase diagram shown in Fig. 3 indicates that two successive structural transitions occur at any temperature below 375 K in the H_2SQ crystal with increasing pressure: (1) the ordinary dielectric phase transition and (2) the C_{1h}-C_{4h} symmetry change of the constituent molecules. Both of the phase boundaries shift toward the higher-pressure side with decreasing temperature.

As evidenced by a large isotope effect on P_s (approximately 3 GPa for H_2SQ and approximately 7 GPa for D_2SQ at 300 K) [9] as well as the strong temperature dependence of P_s as observed, proton dynamics undoubtedly plays an important role in this symmetry change. With increasing pressure the effective potential barrier for protons becomes lower, which allows enhanced back-and-forth motion of protons. In contrast to such a proton motion, the deforming motion of SQ^{2-} skeletons, that is, a rearrangement of the chemical bonding with surrounding protons, may take a longer time since it involves displacements of the heavier constituent C and O atoms. Therefore, the symmetry change may be viewed as a sort of *motional narrowing effect*: The deforming motion of the skeleton cannot follow the rapid proton motion when the crystal is positioned beyond the C_{1h}-C_{4h} boundary of the T-P phase diagram shown in Fig. 3. In the region near P_s (the hatched region in Fig. 3) the quantum motion of protons (or the so-called proton tunneling) should contribute dominantly to this symmetry change of the molecule. Nevertheless, some thermally assisted process for this effect appears not to be negligible, which may be the origin of the observed temperature dependence of P_s.

It should be stressed that even at low temperatures near 0 K the C_{1h}-type distortion remains in the pressure region between 3.0 and 4.5 GPa, where the dielectric phase transition already vanishes. In other words, the joint quantum motion of the protons and deforming SQ^{2-} skeletons disturbs long-range ordering of protons in such a T-P region. From a viewpoint of dielectrics, the C_{1h}-distorted H_2SQ molecule produces a large polarizability, but cannot show long-range ordering due to the quantum fluctuation of the proton-skeleton coupled motion. Therefore, the presently observed phenomenon may be interpreted in terms of the concept of quantum paraelectricity, which was originally introduced to interpret the anomalous dielectric properties for $SrTiO_3$ and $KTaO_3$ [19,20] near 0 K. A similar proton-skeleton coupled motion may also play some role in the T-P phase diagrams for the hydrogen-bonded ionic crystals of KDP families [5,6], in which the $PO_4{}^{3-}$ tetrahedrons show temperature-dependent C_2-type distortions [21], and large dielectric constants near 0 K in their pressure-induced PE phase [5].

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