

Influence of phase transitions on the ionic conductivity of protonic superconductors

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The temperature dependence of the proton conductivity in protonic superconductors $M\text{HAO}_4$ and $M_3\text{H}(\text{AO}_4)_2$ ($M=\text{K,Rb,Cs,NH}_4$; $A=\text{S,Se}$) is calculated for low-conducting phases near the phase-transition temperature. The observed deviations from the Arrhenius law in the temperature dependence of the conductivity below the phase-transition temperature can be explained by taking into account three facts: (1) the influence of the ferroelectric ordering, (2) the first-order character of the phase transition, and (3) the propagation of protonic defects. The study is based on using an exact solution of the equation of motion for the applied model.

Proton conducting solids are of potential interest for fuel cells, steam electrolysis, and as sensors. Proton conduction occurs in several types of materials including many hydrogen-bonded systems.¹⁻⁷ In some ferroelectric and ferroelastic hydrogen-bonded crystals the superionic conductivity was discovered: $M\text{HAO}_4$ and $M_3\text{H}(\text{AO}_4)_2$ ($M=\text{K,Rb,Cs,NH}_4$; $A=\text{S,Se}$) exhibit high proton conductivity in their high-temperature phases.³⁻⁷ However, below the phase-transition temperature the conductivity decreases with increasing temperature, and it cannot be explained by the conventional thermoactivation process.^{3,4} In the temperature range of about 30–60 deg in the vicinity of the phase transition, the observed temperature dependence may be approximated by the critical one; in the above-mentioned group of materials, the conductivity σ is proportional to $(T_0 - T)^{-\gamma}$, where T_0 is the stability limit of the paraelectric phase.^{3,4} Phase transitions in these materials are first-order ones characterized by temperature hysteresis.^{3,4} As is known,^{5,7} the superprotonic conductivity of disordered phases is a property of perfect lattice, while the protonic conductivity of ordered phases is due to proton defects. An additional peculiarity of the low-conducting phases should be ferroelectric order which can lead to asymmetry of the double-well potential for a proton. Thus, the main facts concerning the conductivity in the low-temperature, low-conductive phases of these materials are: (1) the conductivity in some temperature range below the phase transition is not caused by an activation process, and it is not described by the Arrhenius law; (2) the temperature dependence of the conductivity is fitted by a critical-temperature function; (3) the phase transition is of first order; (4) the ferroelectric order should influence the conduction mechanism leading to asymmetry in the double-well potential for a proton below the phase-transition temperature; (5) in ferroelectric phases the conductivity occurs by propagation of proton defects. In this paper I unify all five features within the framework of a simple model and make an attempt to explain the peculiarities of the conductivity below the phase transition.

I use the following Hamiltonian model^{8,9}:

$$H = \sum_i \left[\frac{m_i}{2} \left(\frac{du_i}{dt} \right)^2 + V(u_i) + \frac{K}{2} (u_{i+1} - u_i)^2 \right], \quad (1)$$

where t is time, u_i is the longitudinal displacement of the i th proton with mass m_i , and which moves in the asymmetric double-minimum potential:

$$V(u_i) = \frac{1}{2} A u_i^2 - \frac{1}{3} B u_i^3 + \frac{1}{4} C u_i^4, \quad (2)$$

where B and C are positive. The potential $V(u_i)$ is asymmetric even before the action of an external electric field E because of the ferroelectric order [the term $-eEu_i$ should be added to Eq. (2) for considering the conductivity process], e is the effective charge which depends on the proton-lattice interaction, and K is a positive constant of the interaction between protons. A is typically a linear function of temperature that may change its sign at the stability limit of the paraelectric phase T_0 , i.e., $A = \alpha(T - T_0)$.⁹⁻¹² This dependence yields a temperature-dependent barrier in the double-minimum crystalline potential $V(u_i)$. Equation (2) reflects the following facts: the phase transition is of first order and the asymmetric relief of the double-well potential for hydrogen bonds results from the ferroelectric ordering.

In the continuum approximation the equation of motion is

$$m' c_0^2 \left(1 - \frac{v^2}{c_0^2} \right) \frac{d^2 y}{ds^2} + m' \gamma v \frac{dy}{ds} - \frac{dV'}{dy} = 0, \quad (3)$$

where $s = x - vt$; $m c_0^2 = 2d^2 K$; d is the lattice parameter; $y = (C/B)u$; $m' = mC/B^2$; $V' = (a/2)y^3 - \frac{1}{3}y^2 + \frac{1}{4}y^4 - (\epsilon/27)y$; $a = AC/B^2$; $\epsilon = E/E_c$; $E_c = B^3/27eC^2$; γ is the damping coefficient.

One can obtain a particular solution of Eq. (3),¹⁰⁻¹⁴

$$y = y_2 + \frac{y_3 - y_2}{1 + \exp(s/\Delta)}, \quad (4)$$

$$y_1 = \frac{1}{3} \left[1 + 2(1 - 3a)^{1/2} \cos \frac{\phi}{3} \right], \quad (5)$$

$$y_{2,3} = \frac{1}{3} \left[1 - 2(1 - 3a)^{1/2} \cos \left(\frac{\pi \mp \phi}{3} \right) \right],$$

$$\phi = \arccos \left[\frac{(1 - 9a/2 + \epsilon/2)}{(1 - 3a)^{3/2}} \right], \quad (6)$$

where y_1 , y_2 , and y_3 are the roots of the equation $dV'/dy=0$. y_3 and y_2 correspond to minima of the potential V' ; the first root y_1 corresponds to the top of the potential barrier of the double-minimum potential. Solution (4) is a topological excitation being an asymmetric kink. It is obtained by treating the nonlinearity exactly, and not as a perturbation of a harmonic crystal. It corresponds to the transfer of a proton from one minimum of the asymmetric double-well potential to the other as s goes from $-\infty$ to $+\infty$. The kink motion is a consequence of the cooperative proton displacements. Equation (4) describes the transition region between protons being in one well, and protons being in the other one traveling along the chain under the influence of the external time-independent electric field E . Δ is the kink width showing that the transfer of a proton from the first site to the second one occurs step by step, with the step distance equal to

$$\Delta = \frac{c_0[2m'(1-v^2/c_0^2)]^{1/2}}{y_3 - y_2}. \quad (7)$$

The velocity v of the kink is given by

$$v = \frac{c_0}{\sqrt{1 + m' \gamma^2 / [2(1 - 3a) \cos^2[(\pi + \phi)/3]]}}. \quad (8)$$

These kinks describe defects in hydrogen-bonded chains like H_3O^+ or OH^- in ice.¹³⁻¹⁹ Such defects should be called ion states rather than ions because they do not move bodily in the chain. These ion states are generated by a translational motion of a proton along the hydrogen bond to a neighboring heavy ion. The ion states propagate along the hydrogen-bonded chain by proton jumps from one position in the hydrogen bond to another. Thus, the subsequent jumps of protons involve migration of charge along the hydrogen-bonded chain, and realize proton conductivity. Consequently, the velocity (8) is the velocity of the protonic defect. The kink of the same profile was obtained for the case which corresponds mathematically to the situation in which the coefficient $B=0$ in Eq. (2) (symmetric double-well potential before the external electric field action),^{13,14,17,18} but the expressions for the kink velocity v and the kink width Δ are essentially different. Kink solutions for nonlinear lattices including other asymmetric double-well and many-well potentials without an external electric field were obtained in Refs. 20 and 21.

The mobility of the proton defect can be found equating the power lost by protons due to damping, and the power which is the work (per unit time) done by electric force eE applied to protons. Then, after two integrations, I derive

$$\mu = \frac{9ec_0C^{3/2}}{(2m)^{1/2}\gamma B^2(1-3a)\cos^2(\phi/3-\pi/6)} = \frac{\mu_0}{(1+\sqrt{1-4a})^2}, \quad (9)$$

where ϕ is given by Eq. (6) for $\epsilon=0$ and μ_0 is given by

$$\mu_0 = \frac{48ec_0C^{3/2}}{(2m)^{1/2}\gamma B^2}. \quad (10)$$

If the electric conductivity is a protonic one and the protonic conduction is due to the transport of protonic defects, then the conductivity $\sigma = Ne\mu$, where N is the concentration

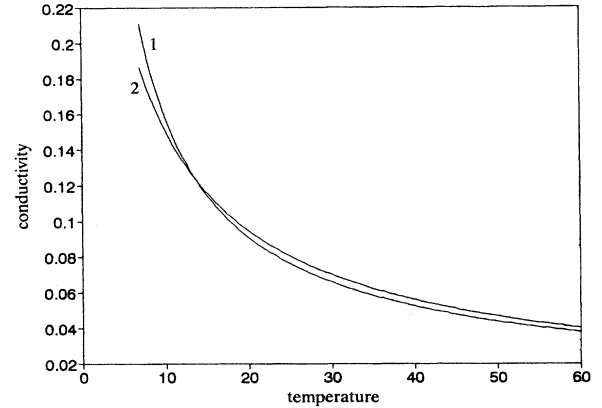


FIG. 1. The conductivity σ (in units of $Ne\mu_0$) as a function of temperature in degrees of K or C: curve 1 is an experimental result from Refs. 3 and 4 and curve 2 is calculated using Eq. (9).

of defects. This expression with Eq. (9) may be used for the description of the observed temperature dependence of the conductivity in proton superconductors.

The observed temperature dependence of the conductivity $\sigma(T)$ in RbHSeO_4 , CsHSO_4 , and CsHSeO_4 is not exponential but it is described by a power law $\sigma \propto (T_0 - T)^{-\gamma}$ in the temperature range $2^\circ \leq (T_0 - T) \leq 60^\circ$ or $5^\circ \leq (T_0 - T) \leq 35^\circ$ depending on the crystal, where the critical index changes with the crystal from 0.8 to 1.65.^{3,4} The maximal error in temperature measurements in Ref. 3 can be estimated as 5.7% from the definition of activation energies. Using (9) the experimental power law may also be presented as

$$\sigma \propto \frac{1}{\left\{ 1 + \left[1 + \frac{8}{9} \left(\frac{T_0 - T}{T_c - T_0} \right)^{1/2} \right]^2 \right\}}$$

in the temperature range $7^\circ \leq (T_0 - T) \leq 60^\circ$ within the 5.7% accuracy. T_c is the phase-transition temperature. The fitting is carried out in this range because in the immediate vicinity of T_0 [$\leq \Delta T$, where ΔT is the temperature hysteresis which is equal to $\sim 4^\circ - 7^\circ$ (Ref. 4)], the conductivity changes by two orders of magnitude, and due to a slow kinetics one cannot distinguish between the jump in the conductivity at T_0 and the critical change $\sigma(T_0 - T)$. For example, for $T_c - T_0 = 1.5^\circ$ (Ref. 3) $\gamma = 0.8$.⁴ For $B=0$, $\sigma \propto (T_0 - T)^{-\gamma}$ for $\gamma=1$ corresponding to one of the measured cases.⁴ In Fig. 1 the temperature dependence of the proton conductivity σ (in units of $Ne\mu_0$) is presented in MHAO_4 . The experimental curve 1 is obtained using the data of Refs. 3 and 4. The theoretical curve 2 is calculated with the help of Eq. (9). The fitting is carried out by the least-squares method. The temperature dependence found here reflects the experimental fact that conductivity in the low-temperature phase increases on approaching the phase transition temperature from below because the barrier of the crystalline potential V decreases. The finite value of the conductivity at T_c and its further growth are better described by this formula than by the critical temperature dependence,^{3,4} which indicates that the infinite value for the conductivity in T_0 or T_c is in disagreement

with the results of measurements,^{3,4} in which the conductivity does not exhibit a singularity at the phase-transition point.

To my knowledge, this calculation is the first attempt at the theoretical consideration of the phase transition influence on the conductivity in protonic superconductors. The model considers the influence of the ferroelectric ordering resulting in the asymmetry of the double-well potential on conductivity controlled by migration of proton defects. The cooperative effect leading to the asymmetry of the potential brings about the critical effect exhibited in the temperature dependence of the observed conductivity. The model shows the importance of both the collective ferroelectric effect and the first-order character of phase transitions in the consideration

of the conductivity in substances under study. Despite the simplicity of the model, it gives an exact analytical solution which is essentially different from the case of the symmetric double-well potential,^{13,14} and can be useful for the research of the protonic conductivity in proton superconductors. The great sensitivity of the hydrogen-bonded potential relief and the order of ferroelectric phase transitions to hydrostatic pressure⁶ makes such measurements a powerful tool for investigations of the conductivity in protonic superconductors.

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