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N. Pavlenko

PROTONIC CONDUCTIVITY AT THE SUPERIONIC PHASE TRANSITIONS

ЛЬВІВ

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Протонна провідність при суперіонних фазових переходах

Н. Павленко

Анотація. Побудована мікроскопічна модель для опису динаміки протонної підсистеми в суперіонних кристалах з водневими зв'язками, в якій описано механізм протонного транспорту, а також ефект зміщення сусідніх киснів при формуванні водневого зв'язка, що веде до сильної протон-фононної взаємодії та до утворення протонного полярону. На основі моделі, яка описує протонні впорядкування, враховано також віртуальний (в суперіонних фазах) або впорядкований характер системи водневих зв'язків. Протонна провідність обчислена в рамках терії Кубо (як приклад розглядались кристали класу $M_3H(XO_4)_2$). Проаналізовано температурні залежності провідності. Визначено ергії активації, а також вплив на їх значення внутрішніх далекодіючих полів, що виникають в результаті протонних впорядкувань.

Protonic Conductivity at the Superionic Phase Transitions

N. Pavlenko

Abstract. Microscopic model for the description of the proton subsystem dynamics in superionic crystals with hydrogen bonds is developed. Besides the including the proton transport mechanism, the effect of the nearest oxygens displacement at the hydrogen bond formation is accounted for. The latter fact is the reason for the strong proton-phonon coupling that leads to the polaronic effect. Using the occupation number formalism the virtual (in superionic phases) or ordered (in low-temperature phases) character of the hydrogen-bonded system is taken into account on the basis of the proton ordering model. The protonic conductivity studies are carried out in the frame of Kubo theory for the cases of superionic phases as well as at low-temperature phases with different types of proton ordering (as an example the $M_3H(XO_4)_2$ -class of crystals is considered). Temperature dependences of conductivity are analyzed. The activation energies for the static conductivity are determined; in this case the influence of internal field which appears as the result of the proton ordering is investigated.

1. Introduction

Hydrogen-bonded superionic crystals are well known for their proton orderings at low temperatures as well as for high protonic conductivity which increases significantly in the high-temperature superionic phases. In this case the conductivity phenomenon is connected with the dynamical disordering of the hydrogen-bond network resulting in the increase of the number of possible positions for protons. It is generally accepted from the results of the neutron scattering studies [1–3] that the proton transport proceeds in the frame of the two-stage Grotthuss mechanism. This process includes the transfer of the proton within the hydrogen bond (intrabond motion) and breaking of the hydrogen bond together with the reorientation of ionic group involved in the hydrogen bond formation (interbond transfer). Despite the detail experimental investigations of the proton migration process there still exist unresolved problems in the theoretical description of this phenomenon. It is caused by the complexity of the problem of proton transport in the two- or three-dimensional hydrogen-bond network.

In this work the crystals which belong to $M_3H(XO_4)_2$ (M=K, Rb, Cs, NH_4; X=Se, S) family are considered as the objects for the protonic conductivity investigations. In these compounds the conductivity is significantly higher in the conducting planes formed by the vertex O(2)-oxygens connected by the vitrual hydrogen bonds in superionic phases.

The crystals of this class are isomorphic that explains the similarity of phase sequences occurring in them. In most cases the superionic phase of trigonal symmetry transforms on cooling into ferroelastic phase of monoclinic or triclinic symmetry with the further ferroelectric ordering. The typical crystalline structure of the unit cell in the superionic phase with coordinate $\boldsymbol{R}_m = m_1\boldsymbol{a}_1 + m_2\boldsymbol{a}_2 + m_3\boldsymbol{a}_3$ in rhombohedral coordinate system with the lattice vectors

$$\boldsymbol{a}_1 = \left(-\frac{\sqrt{3}}{2}a_0, \frac{1}{2}a_0, \frac{1}{3}c\right) \quad \boldsymbol{a}_2 = \left(\frac{\sqrt{3}}{2}a_0, \frac{1}{2}a_0, \frac{1}{3}c\right) \quad \boldsymbol{a}_3 = \left(0, -a_0, \frac{1}{3}c\right)$$

is shown in Fig. 1. There are two XO_4 groups and three virtual hydrogen bonds $f = 1, 2, 3$ adjacent to the upper group XO_4'' in the elementary unit cell. Another three hydrogen bonds near the lower XO_4' group belong to the neighbouring unit cells with the vectors $\boldsymbol{R}_m - \boldsymbol{a}_f$.

In the low-temperature phase the frozen-in hydrogen bonds form well-defined sequences of dimers consisting of XO_4 tetrahedra connected by the $O(2)'$-H-$O(2)''$ hydrogen bridges. The two types of ordering with the different character of the dimer sequences can occur in this crystal class.

In the first case (phase III for $(NH_4)_3H(SeO_4)_2$ (TAHSe), phase III for $Rb_3H(SeO_4)_2$ (TRHSe)) the doubling of the unit cell along one of the translation vectors $\boldsymbol{a}_f$ corresponds to the star $\{\boldsymbol{k_4}\} = \{\frac{1}{2}\boldsymbol{b}_1, \frac{1}{2}\boldsymbol{b}_2, \frac{1}{2}\boldsymbol{b}_3\}$ in Kovalev notations [4]. In the case of $\boldsymbol{k}_4 = \frac{1}{2}\boldsymbol{b}_3$ the alternating dimer sequences along $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ directions are formed.

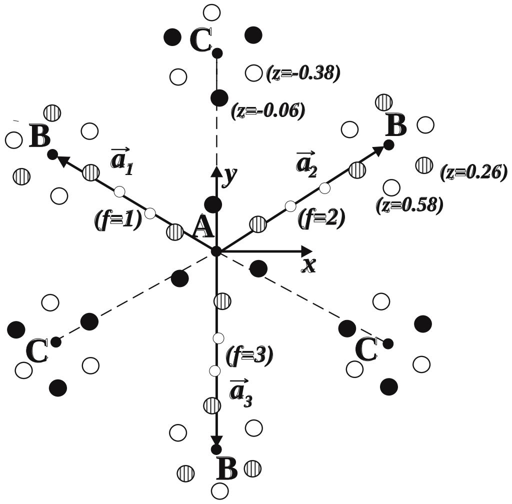


Figure 1. Projection of the rhombohedric primitive cell of TAHSe with lattice vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ on the (001) plane in the hexagonal coordinate system in phase II. The open, solid and hatched big circles correspond to the possible positions of O(2) oxygens with the different values of z; A ($z = 0$), B ($z = 1/3$) and C ($z = -1/3$) denote the positions of Se atoms in SeO_4' groups. The small circles indicate the proton positions within the hydrogen bond.

Another type of ordering (phase IV in TAHSe, phase II in $(NH_4)_3H(SO_4)_2$) is distinguished by the parallel sequences of dimers which include hydrogen bridges of the same index f. However, the hydrogen bonds are shifted alternatively by $\pm\delta$ ($\delta = 0.025b$ where b is the lattice parameter in phase IV) in the (x,y) plane. This corresponds to the ordering with the vector $\boldsymbol{k_8} = \frac{1}{2}(\boldsymbol{b_1} + \boldsymbol{b_2} + \boldsymbol{b_3})$.

The rearrangements of the hydrogen-bond network at the superionic phase transitions have been studied in the framework of the lattice-gastype model in [5]. In this case the Hamiltonian has the following form:

$$H = \frac{1}{2}\sum_{\substack{mm'\\ ff'}} \Phi_{ff'}(mm')n_{mf}n_{m'f'} - \mu\sum_{mf} n_{mf} \tag{1.1}$$

where $n_{mf} = \{0, 1\}$ is the proton occupation number for position f in the primitive unit cell at $\boldsymbol{R}_m$; $\Phi_{ff'}(mm')$ is the energy of the proton interactions, μ denotes the chemical potential which determines the average proton concentration.

The investigations of the thermodynamic properties of the proton subsystem have been carried out in [5,6] using the mean-field approximation as well as taking into account the short-range proton correlations and the gaussian fluctuations of the molecular field. The influence of the ionic group reorientations on the phase sequence has been also studied in [7]. It turned out that this effect is of the primary importance for the description of the phase sequence occurring in TAHSe with two superionic (I, II) and two ferroelastic III and IV phases.

This work uses the previous results concerning the proton orderings for the evaluation of the protonic conductivity. It is shown that the distinction of the different types the hydrogen bonding (virtual in the superionic phases and ordered at the low temperatures) leads to the temperature dependences of the protonic conductivity that is similar to the experimentally observed.

2. Polaronic effect and proton dynamics

It is well-known from [8–10] that the creation of the hydrogen bond induces the deformation of the XO_4 group involved in the bond formation. In particular, this process is accompanied by the shortening of the distance between the vertex oxygens $O(2)'$ and $O(2)''$ that leads to the localization of the proton between the oxygens (so-called polaronic effect) as well as to the increase of the activation energy for the bond breaking and hopping of the protonic polaron to another localized position in the lattice. To account this fact one should determine the normal vibration modes of the vertex oxygens in the conducting planes.

The potential energy of the oxygen subsystem in the harmonic approximation is given by:

$$\phi = \phi_0 + \sum_{mm'}\sum_{kk'}\sum_{\alpha\beta=1,3} \phi_{\alpha\beta}(mk;m'k')u_\alpha(mk)u_\beta(m'k'),$$

where $k = 1, 2$ is the sublattice number of the m-th unit cell and the force constants

$$\phi_{\alpha\beta}(mk;m'k') = \left.\frac{\partial^2\phi}{\partial u_\alpha(mk)\partial u_\beta(m'k')}\right|_0.$$

Taking into account the interaction between nearest neighbours in (x, y)-plane (the distances between upper and lower sublattice oxygens O(2) in cell which is about 7.3Å exceeds the separation between nearest oxygens in (x, y)-plane which amounts to 3.5 Å) the matrices $\phi(mk;m'k')$ can be represented in the following form:

$$\phi(m1;m+\boldsymbol{a}_1,2) = \begin{pmatrix} a & c \\ c & a+2/\sqrt{3}c \end{pmatrix},$$

$$\phi(m1;m+\boldsymbol{a}_2,2) = \begin{pmatrix} a & -c \\ -c & a+2/\sqrt{3}c \end{pmatrix},$$

$$\phi(m1;m+\boldsymbol{a}_3,2) = \begin{pmatrix} a+\sqrt{3}c & 0 \\ 0 & a-c/\sqrt{3} \end{pmatrix},$$

$$\phi(mk;mk) = \begin{pmatrix} h & 0 \\ 0 & h \end{pmatrix}.$$

Considering only displacements of the O(2) oxygens in (x, y)-plane, we have the following dynamical matrix:

$$D(\boldsymbol{k}) = \begin{bmatrix} D^{11} & D^{12} \\ D^{21} & D^{22} \end{bmatrix},$$

where

$$D^{12}(\boldsymbol{k}) = \begin{bmatrix} a(\mathrm{e}^{i\boldsymbol{k}\boldsymbol{a}_1} + \mathrm{e}^{i\boldsymbol{k}\boldsymbol{a}_2}) + (a+\sqrt{3}c)\mathrm{e}^{i\boldsymbol{k}\boldsymbol{a}_3} & c(\mathrm{e}^{i\boldsymbol{k}\boldsymbol{a}_1} - \mathrm{e}^{i\boldsymbol{k}\boldsymbol{a}_2}) \\ c(\mathrm{e}^{i\boldsymbol{k}\boldsymbol{a}_1} - \mathrm{e}^{i\boldsymbol{k}\boldsymbol{a}_2}) & (a+2\sqrt{3}c)(\mathrm{e}^{i\boldsymbol{k}\boldsymbol{a}_1} + \mathrm{e}^{i\boldsymbol{k}\boldsymbol{a}_2}) + (a-\sqrt{3}c)\mathrm{e}^{i\boldsymbol{k}\boldsymbol{a}_3} \end{bmatrix},$$

$$D^{11}(\boldsymbol{k}) = D^{22}(\boldsymbol{k}) = \begin{bmatrix} h & 0 \\ 0 & h \end{bmatrix}, \qquad D^{21}(\boldsymbol{k}) = D^{12}(-\boldsymbol{k}).$$

The problem of determination of the normal vibrational modes thus reduces to the evaluation of the eigenvalues (vibration frequencies) and polarization vectors of the matrix $D(\boldsymbol{k})$. In particular, for the case $\boldsymbol{k} = 0$ we have:

$$\omega_{1/3}(0) = h + (3a + \sqrt{3}c), \qquad \omega_{2/4}(0) = h - (3a + \sqrt{3}c), \tag{2.1}$$

$$\boldsymbol{u}_1 = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\0\\1\\0\end{pmatrix}, \qquad \boldsymbol{u}_2 = \frac{1}{\sqrt{2}}\begin{pmatrix}0\\-1\\0\\1\end{pmatrix}, \tag{2.2}$$

$$\boldsymbol{u}_3 = \frac{1}{\sqrt{2}}\begin{pmatrix}0\\1\\0\\1\end{pmatrix}, \qquad \boldsymbol{u}_4 = \frac{1}{\sqrt{2}}\begin{pmatrix}-1\\0\\1\\0\end{pmatrix},$$

that points on the existence of the two different types (in-phase and antiphase) of the oxygen vibrations with different frequencies. The similar situation is observed in other symmetric points of the Brillouin zone.

We should take into account the change of the proton potential on the hydrogen bond due to the antiphase vibrations of the oxygens that leads to the shortening of the bond length. Thus the modes $j = 2$ and $j = 4$ are considered with the coordinates of the polarization vectors $\boldsymbol{u}_2$ and $\boldsymbol{u}_4$ approximated by their values for $\boldsymbol{k} = 0$. After that the interaction of the protons with the oxygen vibrations can be represented in the second quantization form:

$$H_{pr-ph} = \sum_{mf}\sum_{\boldsymbol{k}j} \tau_{mf}(\boldsymbol{k}j)(b_{\boldsymbol{k}j} + b^{+}_{-\boldsymbol{k}j})n_{mf}, \tag{2.3}$$

where $b^{+}_{\boldsymbol{k}j}$, $b_{\boldsymbol{k}j}$ are the phonon creation and annihilation operators of j-th optical branch for the vector $\boldsymbol{k}$. The coefficients $\tau_{mf}(\boldsymbol{k}j)$ are given by:

$$\begin{aligned}
\tau_{m1}(\boldsymbol{k}j) = &-\sqrt{\frac{\hbar}{2NM\omega_j(\boldsymbol{k})}}\nabla V\left\{(u_{jx}(1) - 1/\sqrt{3}u_{jy}(1))\mathrm{e}^{i\boldsymbol{k}\boldsymbol{R}_m}\right.\\
&\left.-(u_{jx}(2) - 1/\sqrt{3}u_{jy}(2))\mathrm{e}^{i\boldsymbol{k}(\boldsymbol{R}_m+\boldsymbol{a}_1)}\right\},\\
\tau_{m2}(\boldsymbol{k}j) = &\sqrt{\frac{\hbar}{2NM\omega_j(\boldsymbol{k})}}\nabla V\left\{(u_{jx}(1) + 1/\sqrt{3}u_{jy}(1))\mathrm{e}^{i\boldsymbol{k}\boldsymbol{R}_m}\right.\\
&\left.-(u_{jx}(2) + 1/\sqrt{3}u_{jy}(2))\mathrm{e}^{i\boldsymbol{k}(\boldsymbol{R}_m+\boldsymbol{a}_2)}\right\},\\
\tau_{m3}(\boldsymbol{k}j) = &-\sqrt{\frac{\hbar}{2NM\omega_j(\boldsymbol{k})}}\nabla V\frac{2}{\sqrt{3}}\left\{u_{jy}(1)\mathrm{e}^{i\boldsymbol{k}\boldsymbol{R}_m} -\right.\\
&\left.u_{jy}(2)\mathrm{e}^{i\boldsymbol{k}(\boldsymbol{R}_m+\boldsymbol{a}_3)}\right\},
\end{aligned} \tag{2.4}$$

where $\nabla V = \frac{\partial V(\boldsymbol{r}_{mf}-\boldsymbol{R}^0_{m1})}{\partial u_x(m,1)}$, $\boldsymbol{r}_{mf}$ is the proton coordinate on the f-th bond of the m-th unit cell; $V(\boldsymbol{r}_{mf} - \boldsymbol{R}^0_{m1})$ is the interaction potential between the proton and the oxygen O(2) of the upper ionic group XO_4.

Besides that, the vibration energy of the oxygen subsystem in the harmonic approximation is given by:

$$H_{ph} = \sum_{\boldsymbol{k}j} \hbar\omega_j(\boldsymbol{k}) b^{+}_{\boldsymbol{k}j} b_{\boldsymbol{k}j}. \tag{2.5}$$

From the recent results of x-ray and neutron scattering studies [11] it is shown that the O(2)′-O(2)″ separation length can be reduced to 2.4 Å in the superionic phases that provides near barrierless proton transfer within the hydrogen bond [12]. Thus the description of the proton mobility can be based on the assumption of the one-minimum proton potential on the bond (in other words we neglect the intrabond proton transfer process). With this conjecture the proton transport process can be considered as the dynamical breaking and creation of the hydrogen bonds connected with the HXO_4 ionic group rotations:

$$H_t = \Omega_R \sum_{\substack{m\\ f\neq f'}} \left\{c^{+}_{mf}c_{mf'} + c^{+}_{m+\boldsymbol{a}_f-\boldsymbol{a}_{f'},f}c_{mf'} + H.c.\right\}. \tag{2.6}$$

Here c^{+}_{mf}, c_{mf} are the proton creation and annihilations operators. We represent the interbond proton hopping as the quantum tunneling with the corresponding transfer integral Ω_R.

Using the canonical Lang-Firsov transformation to the new equilibrium states of relaxed oxygens with the proton between them

$$\tilde{H} = \mathrm{e}^{iS}H\mathrm{e}^{-iS},$$

where

$$S = \sum_{mf} n_{mf}v_{mf}, \qquad v_{mf} = i\sum_{vekj}\frac{\tau_{mf}(\boldsymbol{k}j)}{\hbar\omega_j(\boldsymbol{k})}(b_{\boldsymbol{k}j} - b^{+}_{-\boldsymbol{k}j}). \tag{2.7}$$

we have the following Hamiltonian:

$$\begin{aligned}
\tilde{H} = \quad & -\tilde{\mu}\sum_{mf} n_{mf} + \frac{1}{2}\sum_{\substack{mm'\\ ff'}}\tilde{\Phi}_{ff'}(mm')n_{mf}n_{m'f'} + \\
& \sum_{\boldsymbol{k}j}\hbar\omega_j(\boldsymbol{k})b^{+}_{\boldsymbol{k}j}b_{\boldsymbol{k}j} + \tilde{H}_t,\\
\tilde{H}_t = \quad & \Omega_R\sum_{\substack{m\\ f\neq f'}}\left\{c^{+}_{mf}c_{mf'}X_{ff'}(mm) + \right.\\
& \left. c^{+}_{m+\boldsymbol{a}_f-\boldsymbol{a}_{f'},f}c_{mf'}X_{ff'}(m+\boldsymbol{a}_f-\boldsymbol{a}_{f'},m)\right\} + H.c.,
\end{aligned} \tag{2.8}$$

where the band narrowing factor

$$X_{ff'}(mm') = \mathrm{e}^{-\sum\limits_{\boldsymbol{k}j} \frac{\Delta\tau_{ff'}(mm'|\boldsymbol{k}j)}{\hbar\omega_j(\boldsymbol{k})}(b_{\boldsymbol{k}j} - b^{+}_{-\boldsymbol{k}j})},$$
$$\Delta\tau_{ff'}(mm'|\boldsymbol{k}j) = \tau_{mf}(\boldsymbol{k}j) - \tau_{m'f'}(\boldsymbol{k}j).$$

Here

$$\tilde{\mu} = \mu + \sum_{\boldsymbol{k}j} \frac{|\tau_{mf}(\boldsymbol{k}j)|^2}{\hbar\omega_j(\boldsymbol{k})},$$

$$\tilde{\Phi}_{ff'}(mm') = \Phi_{ff'}(mm') - 2\sum_{\boldsymbol{k}j} \frac{\tau_{mf}(\boldsymbol{k}j)\tau_{m'f'}(-\boldsymbol{k}j)}{\hbar\omega_j(\boldsymbol{k})}$$

are the proton chemical potential and the energy of interaction between protons which are renormalized due to the lattice polarization and formation of the protonic polaron as the result.

The description of the proton ordering using the Hamiltonian (2.8) without the directly included transfer term have been performed in [5]. It is shown that whereas MFA gives the qualitatively correct results concerning the phase transition sequence in $M_3H(XO_4)_2$ crystals, additional consideration of the gaussian fluctuations of the molecular field significantly decreases the transition temperature. It provides the possibility to compare quantitatively the results of the theoretical studies with the experimental data. Thus for the evaluation of the protonic conductivity we will use the temperature dependences of the thermodynamical functions, average proton occupancies $\bar{n}_{mf}$ and proton chemical potential obtained in gaussian approximation.

3. Protonic conductivity

The conductivity of protons can be found in the framework of the Kubo linear response theory [13,14]:

$$\sigma(\omega, T) = \frac{1}{V}\int_0^\infty dt \mathrm{e}^{i(\omega+i\varepsilon)t}\int_0^\beta d\lambda \langle J(t - i\hbar\lambda)J(0)\rangle, \qquad (3.1)$$

where the proton current is given by:

$$J = \frac{e}{i\hbar}[H, x] = \frac{e\Omega_R}{i\hbar}\sum_m \sum_{f\neq f'} \boldsymbol{R}_{ff'}[c^{+}_{mf}c_{mf'}X_{ff'}(mm)$$
$$+ c^{+}_{mf}c_{m+\boldsymbol{a}_f-\boldsymbol{a}_{f'},f'}X_{ff'}(m, m + \boldsymbol{a}_f - \boldsymbol{a}_{f'}) + H.c.], \qquad (3.2)$$

and $x = \sum_{mf} n_{mf}\boldsymbol{r}_{mf}$ is the proton polarization operator. Here the vectors connected the centers of the hydrogen bonds $\boldsymbol{R}_{ff'} = \boldsymbol{R}_{ff'}(mm) = \boldsymbol{r}_{mf} - \boldsymbol{r}_{mf'}$.

It is well-known that the proton current can be represented as a sum of two terms. The first part corresponds to the coherent motion with the bandwidth narrowed by the phonon average $\langle X_{ff'}(mm')\rangle$ that take into account the decrease of the proton transfer integral Ω_R due to the oxygens vibrations. The second part (polaronic current) describes the phonon-activated proton hopping between the localized sites in the lattice:

$$J_p = \frac{e}{i\hbar}[H, x] = \frac{e\Omega_R}{i\hbar}\sum_m \sum_{f\neq f'} \boldsymbol{R}_{ff'}[c^{+}_{mf}c_{mf'}\tilde{X}_{ff'}(mm)$$
$$+ c^{+}_{mf}c_{m+\boldsymbol{a}_f-\boldsymbol{a}_{f'},f'}\tilde{X}_{ff'}(m, m + \boldsymbol{a}_f - \boldsymbol{a}_{f'}) + H.c.], \qquad (3.3)$$

where the operators $\tilde{X}_{ff'}(mm') = X_{ff'}(mm') - \langle X_{ff'}(mm')\rangle$ characterize the phonon scattering processes which accompany the proton transfer. Further we will consider the polaronic transport which corresponds to the phonon activated hopping because of the dominant contribution of this part to the total protonic conductivity at the high temperatures. In this case the correlation function $\langle J(x)J(0)\rangle$ $(z = t - i\hbar\lambda)$ in (3.1) will be evaluated in the second order perturbation theory on the hopping term Ω_R at the strong proton-phonon coupling limit. This allows us to decouple the following averages

$$\langle c^{+}_{mf}(z)c_{m'f'}(z)\tilde{X}_{ff'}(mm')|_z c^{+}_{m_1f_1}c_{m'_1f'_1}\tilde{X}_{f_1f'_1}(m_1m'_1)\rangle \rightarrow$$
$$\langle c^{+}_{mf}(z)c_{m'f'}(z)c^{+}_{m_1f_1}c_{m'_1f'_1}\rangle\langle \tilde{X}_{ff'}(mm')|_z\tilde{X}_{f_1f'_1}(m_1m'_1)\rangle$$

to the proton and phonon parts which can be evaluated separately. The proton correlators can be obtained taking the proton part of the Hamiltonian (2.8) in the mean-field approximation:

$$\langle c^{+}_{mf}(z)c_{m'f'}(z)c^{+}_{m_1f_1}c_{m'_1f'_1}\rangle = \delta_{ff'_1}(m - m'_1)\delta_{f'f_1}(m' - m_1)$$
$$\bar{n}_{mf}(1 - \bar{n}_{m'f'})\mathrm{e}^{\frac{iz}{2\hbar}[\gamma_f(m) - \gamma_{f'}(m') + \tilde{\Phi}_{ff'}(mm')(\bar{n}_{mf} - \bar{n}_{m'f'})]}, \qquad (3.4)$$

where the internal field acting on the proton on the f-th bond of the m-th unit cell $\gamma_f(m) = \sum_{m'f'}\tilde{\Phi}_{ff'}(mm')\bar{n}_{m'f'}$.

Evaluation of the phonon correlation function yields:

$$\Psi_{ff'} = \langle \tilde{X}_{ff'}(mm')|_z\tilde{X}_{f'f}(m'm)\rangle = P^0_{ff'} \qquad (3.5)$$
$$\left(\exp\left[\sum_{\boldsymbol{k}j}\frac{|\Delta\tau_{ff'}(mm'|\boldsymbol{k}j)|^2}{(\hbar\omega_j(\boldsymbol{k}))^2}\frac{\cos\omega_j(\boldsymbol{k})(z + 1/2i\hbar\beta)}{\mathrm{sh}\frac{1}{2}\beta\hbar\omega_j(\boldsymbol{k})}\right] - 1\right)$$

Here

$$P^0_{ff'} = \langle\tilde{X}_{ff'}(mm')\rangle\langle\tilde{X}_{f'f}(m'm)\rangle = \tag{3.6}$$
$$\exp\left[-\sum_{\boldsymbol{k}j}\frac{|\Delta\tau_{ff'}(mm'|\boldsymbol{k}j)|^2}{(\hbar\omega_j(\boldsymbol{k}))^2}\mathrm{cth}\frac{1}{2}\beta\hbar\omega_j(\boldsymbol{k})\right].$$

The processes we are interested in going on in the temperature range near the superionic phase transition. This provides a possibility to assume

$$\sum_{\boldsymbol{k}j}\frac{|\Delta\tau_{ff'}(mm'|\boldsymbol{k}j)|^2}{(\hbar\omega_j(\boldsymbol{k}))^2\mathrm{sh}\frac{1}{2}\beta\hbar\omega_j(\boldsymbol{k})} >> 1,$$

that is valid at the high temperatures and in the strong proton-phonon coupling regime. In this case expansion of the exponent in (3.5) in the vicinity of $z = -\frac{1}{2}i\hbar\beta$ gives us:

$$\Psi_{ff'} = \mathrm{e}^{-\sum\limits_{\boldsymbol{k}j}\frac{|\Delta\tau_{ff'}(mm'|\boldsymbol{k}j)|^2}{(\hbar\omega_j(\boldsymbol{k}))^2}\mathrm{th}\frac{1}{4}\beta\hbar\omega_j(\boldsymbol{k})}\,\mathrm{e}^{-\frac{(z+1/2i\hbar\beta)^2}{4\tilde{\tau}^2}}, \tag{3.7}$$

where the parameter $\tilde{\tau}$ which characterizes the average hopping time length between two localized positions is given by:

$$\frac{1}{\tilde{\tau}^2} = 2\sum_{\boldsymbol{k}j}\frac{|\Delta\tau_{ff'}(mm'|\boldsymbol{k}j)|^2}{\hbar^2\mathrm{sh}\frac{1}{2}\beta\hbar\omega_j(\boldsymbol{k})}. \tag{3.8}$$

Taking the Einstein approximation for the optical phonon frequencies $\omega_2(\boldsymbol{k}) = \omega_4(\boldsymbol{k}) = \omega_0$, we have $\tilde{\tau}^2 = \frac{3}{20}\beta\frac{\hbar^2}{E_0}$ with the polaron binding energy $E_0 = \frac{\hbar^2(\nabla V)^2}{M(\hbar\omega_0)^2}$, M is the oxygen mass.

We use the procedure proposed in [15] with the deformation of integration contour in the complex plane for the integration of obtained expressions (3.5), (3.7) over t and λ. The resulting expression for the real part of the conductivity along the direction given by the vector $\boldsymbol{r}$ is the following:

$$\sigma(\omega)^{\boldsymbol{r}} = \frac{e^2\Omega_R^2}{\hbar^2}\frac{2\sqrt{\pi}}{v_c}\frac{\mathrm{sh}\beta\hbar\omega/2}{\hbar\omega/2}\mathrm{e}^{-5/12\beta E_0}\cdot\tilde{\tau}\times \tag{3.9}$$
$$\sum_{ff'}(\boldsymbol{R}^{\boldsymbol{r}}_{ff'})^2\bar{n}_f(1-\bar{n}_{f'})\mathrm{e}^{1/2\beta\hbar\alpha_{ff'}}\,\mathrm{e}^{-\tau^2(\omega+\alpha_{ff'})^2},$$

where v_c is the lattice volume, $\alpha_{ff'} = \Phi_0(1-\bar{n}_f+\bar{n}_{f'})/2\hbar$, $\Phi_0 = \Phi_{12}(m, m+\boldsymbol{a}_1-\boldsymbol{a}_2) = \Phi_{13}(m, m+\boldsymbol{a}_1-\boldsymbol{a}_3) = \Phi_{23}(m, m+\boldsymbol{a}_2-\boldsymbol{a}_3)$ is the interaction between the nearest neighbours. $\boldsymbol{R}^{\boldsymbol{r}}_{ff'}$ is the projection of $\boldsymbol{R}_{ff'}$ on $\boldsymbol{r}$.

4. Analysis of the transport coefficients

After consideration of (3.9) it becomes apparent that several different activation energies exist in the system:

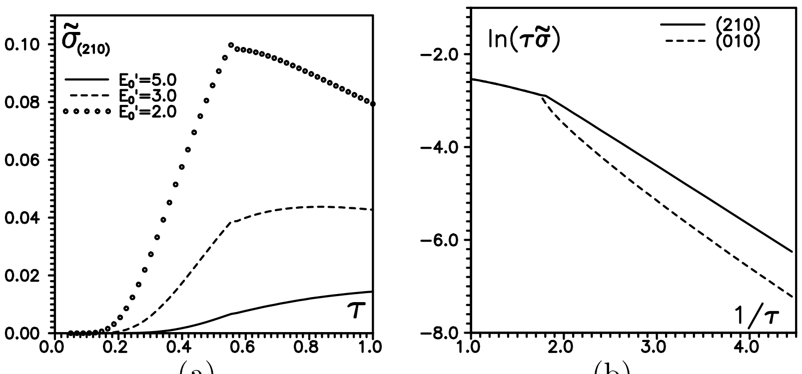
$$E_a^{ff'} = \frac{5}{12}E_0 - \frac{1}{4}\Phi_0(1-\bar{n}_f+\bar{n}_{f'}) + \frac{3}{80}\Phi_0^2(1-\bar{n}_f+\bar{n}_{f'})^2/E_0, \tag{4.1}$$

which correspond to the contribution of the different transfer processes (here we imply the transfer between the different sublattices) and appear in the expression for conductivity with different weights which change with temperature. It should be noted that the total activation energy (4.1) consists of the polaronic part (first term) and the part which appears in the result of the interproton interactions and proton orderings. The temperature dependence of the different phonon-activated transfer processes is determined by the redistribution of the average proton occupancies of three sublattice $f = 1, 2, 3$. In particular, in the superionic phase wheb the hydrogen-bond network is disordered, only one activation energy exists $E_a^0 = \frac{5}{12}E_0 - \frac{1}{4}\Phi_0 + \frac{3}{80}\Phi_0^2/E_0$.

In the low-temperature phase with the phase III (TAHSe)-type proton ordering ($\bar{n}_1 = 1$, $\bar{n}_2 = \bar{n}_3 = 0$ or $\bar{n}_2 = 1$, $\bar{n}_1 = \bar{n}_3 = 0$) in the saturation state $E_a^{23} = \frac{5}{12}E_0 - \frac{1}{4}\Phi_0 + \frac{3}{80}\Phi_0^2/E_0$ with zero weight and $E_a^{12} = E_a^{13} = \frac{5}{12}E_0 > E_a^0$ if $E_0 > \frac{3}{20}\Phi_0$, that holds in the case of the strong polaronic effect. In the phase with the ordering of phase IV (TAHSe)-type ($\bar{n}_3 = 1$, $\bar{n}_1 = \bar{n}_2 = 0$) the activation energy $E_a^{31} = E_a^{32} = \frac{5}{12}E_0$. Therefore the activation energy in the ordered phases is always higher than in the superionic phase that agrees with the experimental observations [16,17].

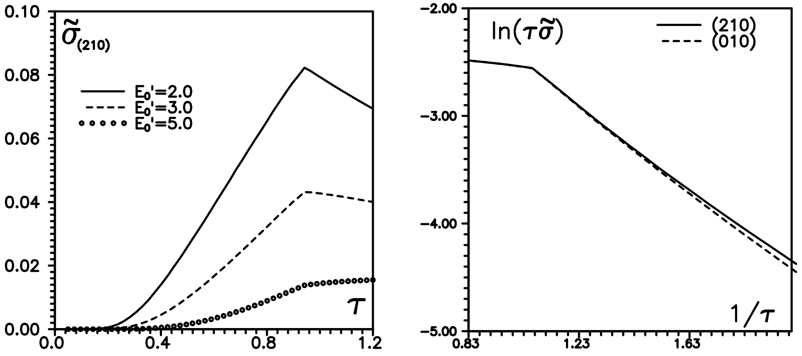
Temperature dependences of the conductivity evaluated using (3.9) along two different directions (210) and (010) in the (001) plane are shown in Figs. 2, 3 for the different values of the polaron binding energy E_0 and for the different types of the phase transitions. One can see that at $\tau \leq \tau_{si}$ (τ_{si} is the superionic phase transition temperature) the conductivity strongly increases that corresponds to the kink in the Arrhenius coordinates. Furthermore, the increase of the energy E_0 leads to the lower values of σ that is evident due to the stronger localization of the proton on the hydrogen bond.

evaluated from (4.1) are the following: in the superionic phase $E_a^0 = 0.18$ eV and in the saturation states of the ordered phases $E_a = 0.2$ eV, that is, this is lower than the experimentally obtained value ~ 0.3 eV at $\tau = \tau_{cr}$. To obtain the better fit to the experimental data is the low-temperature region it is necessary to take into account the additional short-range proton correlations which arise due to the polaronic effect



(a) (b)

Figure 2. Temperarure dependences of the protonic conductivity $\tilde\sigma = \sigma/c_0$, where $c_0 = 2e^2a_0^2\Omega_R^2\sqrt{\pi}/\hbar v_c|a|^2$ for $\tilde b = b/a = 1$, ($a = [\Phi_{11}(\boldsymbol{k} = 0) - \Phi_{12}(\boldsymbol{k} = 0)]/\sqrt{6}$, $b = [\Phi_{11}(\boldsymbol{k}_3) - \Phi_{12}(\boldsymbol{k}_3)]/\sqrt{2}$, the case of the phase transition II-IV is observed) $\Phi_0/|a| = 0.55$, $E_0' = E_0/|a|$; (b) the case of $E_0/|a| = 2$ in Arrhenius coordinates.



(a) (b)

Figure 3. Temperarure dependences of the protonic conductivity $\tilde\sigma$ for $\tilde b = 3$ (the case of the phase transition II-III is observed); (b) $E_0/|a| = 2$ in Arrhenius coordinates.

and lead to the larger values of the activation energy in the ordered phases. The relation $E_0 < 2\Omega_R$ follows immediately from the values of the parameters in Fig. 4 that is valid for the case of the strong proton-phonon coupling (small-polaron regime) [18].

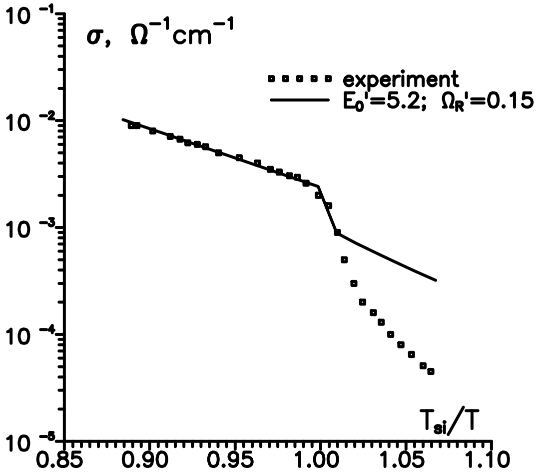


Figure 4. Comparison of the temperature dependences of the protonic conductivity, measured for the crystal TAHSe and calculated using (3.9), $\Omega_R' = \Omega_R/|a|$ (in this case $\Omega_R = 109$ cm^{-1}, $\hbar\omega_0 = 455$ cm^{-1}).

Fig. 4 shows the comparison of the obtained conductivity for TAHSe with the experimental measured values. The value of ∇V can be found from the evaluated in [12] dependence of the proton potential on the distance between oxygens, in this case $\nabla V = 2.4$ eV/Å. We can see that whereas in superionic phase both curves agree well, at the low temperatures the measured conductivity is lower. The observed drop od σ at the phase transition is steeper than calculated one. The values of the activation energy

Conclusions

In this work the protonic conductivity in superionic crystals has been analyzed in the frame of the proton ordering model with additional taking into account the reorientational proton transfer processes. The one-minimum approximation has been considered for the proton potential within the hydrogen bond. The expression for the conductivity is obtained using the Kubo theory for the regime of the strong coupling between protons and antiphase vibrational modes of the oxygens involved in the H-bond formation that leads to the shortening of this bond, localization of the proton and to the strong polaronic effect as the result. The following key points should be stressed. Firstly, we note that taking into account the rearrangement of protons at the superionic phase transition provide the possibility to obtain the temperature dependence of the protonic conductivity with the characteristic kink observed in experiments. Secondly, the evaluated activation energy in the superionic phase is lower than in the ordered phases due to the proton localization on the hydrogen bond as well as to the redistribution of the protons at the phase transition. The large polaron binding energy induces the significantly decrease of the conductivity value. And finally, to obtain the better fit of our results with experiment in the low-temperature phases, the short-range correlations between protons should be considered additionally.

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Наталя Іванівна Павленко

Протонна провідність при суперіонних фазових переходах

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