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Abstract. The proton bifurcation for $T > 120$ K in the $HN_4IO_3 \cdot 2HIO_3$ crystal is considered as the origin of a phonon mixture. As a result, a supplementary term describing phonon fluctuations appears in the crystal Hamiltonian. This fluctuation correction forms the basis of a light absorption mechanism for mixed vibrational modes. An anomalous temperature behaviour of two modes that was previously found experimentally is explained in the framework of the present model.

1. Introduction

At the temperature $T_0 = 213$ K, the $NH_4IO_3 \cdot 2HIO_3$ crystal (AIH, that is ammonium triiodate hydrogen) undergoes a phase transition to a superionic state with a high protonic conductivity [1, 2]. However, the crystal manifests peculiarities even at lower temperature: the disorder of the proton subsystem precedes the superionic transition [3]; at $T_c = 120$ K a proton in an elementary cell becomes fuzzy between equilibrium positions of two possible H bonds (for $T < T_c$ each proton in the crystal is localized in only one of these two H bonds). The mechanism of the proton motion for $T > T_c$ is polaronic [4] and two vibrational modes are responsible for this motion: a polarized optical lattice mode (99 cm^{-1} mode) for $T_c < T < T_0$ and an intracellular mode (756 cm^{-1} mode) for $T > T_0$. These two modes are characterized by anomalous temperature behaviours: according to the IR spectrum, the first mode decreases markedly, and according to the Raman spectrum, the second one increases very markedly when the temperature changes from T_c to T_0 [4, 5].

The aim of the present paper is to explain the temperature behaviour of the above-mentioned lattice and intracellular modes. The proton bifurcation for $T > T_c$ is considered as the origin of phonon fluctuations in the AIH crystal. These fluctuations create a mixture of the lattice mode with the intracellular one. As a result, a new supplementary term appears in the crystal Hamiltonian. This fluctuation correction forms the basis of an anomalous light absorption mechanism for two particular modes.

2. Crystal polarization

In a polar crystal the operator of the field polarization has the form [6]

$$\hat{\boldsymbol{P}}(\boldsymbol{n}) = \frac{1}{\mathcal{V}} \sum_{\boldsymbol{q},j} \sqrt{\frac{\hbar}{2\gamma_j(\boldsymbol{q})\Omega_j(\boldsymbol{q})}} \, \frac{\boldsymbol{q}}{|\boldsymbol{q}|} \, e^{i\boldsymbol{q}\cdot\boldsymbol{n}}(\hat{b}_{j\boldsymbol{q}} + \hat{b}_{j-\boldsymbol{q}}^{\dagger}) \tag{1}$$

where $\mathcal{V}$ is the volume of a unit cell; $\hat{b}_{jq}^{\dagger}$ ($\hat{b}_{jq}$) is the Bose operator of creation (annihilation) of a phonon of the jth mode with the wave vector q and the cycle frequency $\Omega_j(q)$; n is the radius vector of a cell; and the polarization function is

$$\gamma_j(q) = \frac{4\pi}{\Omega_j^2(q)} \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right)^{-1}.$$

The operator of the interaction between the electromagnetic field $E(t) = E_0 e^{-i\omega t + \eta t}$ and the polar crystal has the form

$$\hat{H}_{int} = \hat{P} \cdot E(t) = \sum_{q,j} d_j(q) \cdot E_0 e^{iq \cdot n - i\omega t + \eta t} (\hat{b}_{jq} - \hat{b}_{jq}^{\dagger}) \tag{2}$$

where

$$d_j(q) = \sqrt{\frac{\hbar \Omega_j(q)}{8\pi(1/\varepsilon_\infty - 1/\varepsilon_0)\mathcal{V}}} \frac{q}{|q|}. \tag{3}$$

The polarization of the crystal in the field $E(t)$ is defined as

$$\langle P(n,t) \rangle = \text{Tr}\{\hat{\rho}_{int} \hat{P}(n,t)\} \tag{4}$$

where the addition to the statistical operator $\hat{\rho}_0$ is equal to

$$\hat{\rho}_{int} = \hat{\rho}_0 + \frac{1}{i\hbar} \int_{-\infty}^{t} [\hat{H}_{int}(\tau), \hat{\rho}_0] \, d\tau \tag{5}$$

$$\hat{\rho}_0 = e^{-\hat{H}_0/k_B T} / \text{Tr } e^{-\hat{H}_0/k_B T}. \tag{6}$$

Prior to the first phase transition ($T < T_c$), the Hamiltonian operator was

$$\hat{H}_0 = \sum_{j,q} \hbar \Omega_j(q) \left(\hat{b}_{jq}^{\dagger} \hat{b}_{jq} + \frac{1}{2} \right). \tag{7}$$

The crystal polarization $\langle P \rangle$ can be found using formula (4). After performing simple transformations and integration over τ, we obtain (for the Fourier component of polarization)

$$P_r(q, \omega) = \frac{-1 + \varepsilon_{rr'}(q, \omega)}{4\pi} E_{0r'} \tag{8}$$

where (only two modes are taken into account)

$$\varepsilon_{rr'}(q, \omega) = \varepsilon_{rr'}^{(0)} + \sum_{j=1}^{2} d_{jr}(q) d_{jr'}(q)$$

$$\times \left[\frac{2\omega(\omega^2 - \Omega_j^2(q))}{(\omega^2 - \Omega_j^2(q))^2 + 4\omega^2 \eta^2} + i\eta \frac{4\omega^2}{(\omega^2 - \Omega_j^2(q))^2 + 4\omega^2 \eta^2} \right]. \tag{9}$$

Here $\varepsilon_{rr'}(q, \omega)$ is the permittivity of a polar crystal.

Upon the first phase transition ($T > T_c$), when a proton in a unit cell is bifurcated, the proton deforms the lattice and interacts with crystal vibrations. The interaction leads to the rearrangement of the phonon spectrum. Corresponding transformations of the $\Omega_j(q)$-values can be obtained in the framework of the small-polaron model. For the AIH crystal, the $\Omega_{1,2}(q)$ change only by a few cm^{-1} when the temperature passes the point $T = T_c$ on the temperature scale [4, 5] and further on, for $T > T_c$, they remain constant ($\Omega_1 = 99$ cm^{-1} and $\Omega_2 = 756$ cm^{-1}). However, according to the experiment [4, 5], in the AIH crystal these two modes which provide the proton polaron motion have anomalous temperature behaviour, unlike all the other modes of the crystal. Consequently, in this case the proton should influence the intensity of atomic vibrations of the crystal.

3. The influence of fluctuations on $\varepsilon(q, \omega)$

The first phase transition leads to very interesting changes in the AIH lattice. For $T > T_c$, protons are bifurcated, i.e. each proton does not have a strictly fixed position but migrates ceaselessly between two H bonds. Protons in a polar crystal are strongly connected with the most polarizable longitudinal optic mode—that is, the 99 cm^{-1} mode in the AIH crystal. Hence, it is reasonable to assume that it is just by means of this mode that the proton bifurcation is activated most of all.

With two possible positions of the proton the neighbouring sites move in different potential wells. However, the frequency of proton jumps is very large, of the order of 10^{13}–10^{14} s^{-1}. Therefore the sites have not managed to occupy new equilibrium positions. So, the stationary state of the lattice is not fixed, but fluctuates uninterruptedly. A similar statement is true for IO$_3$ pyramids in the cell, whose collective behaviour is described by the 756 cm^{-1} mode. Thus, the proton bifurcation can be considered as a distinctive fluctuation source that induces an additional displacement δu_l of the cellular sites. The intensity I_1 of the source is directly connected with the lattice mode, 99 cm^{-1}; i.e. the real fluctuation displacement of the lth site should be described by the term $\delta u_l(I_1)$. This term can be presented in the form $\delta u_l = u_{2l}g_l(I_1)$ where $g_l(I_1)$ is a function of the intensity of the phonon field of the 99 cm^{-1} mode. Let us introduce the Hamiltonian function for a model cubic lattice:

$$\Delta \mathcal{H} = K + U. \tag{10}$$

Here the kinetic and potential energies are respectively

$$K = \frac{m}{2} \sum_l \delta \dot{u}_l^2 \qquad U = \frac{\gamma}{2} \sum_l (\delta u_l - \delta u_{l-a})^2. \tag{11}$$

In (11) m is the mass of the IO$_3$ pyramid; γ is the effective elasticity constant of the model lattice; and a is the lattice vector. The transition to new collective variations A_q which characterize a collective fluctuation motion of the IO$_3$ pyramids could be made by means of the canonical transformation (see, e.g., [7])

$$\delta u_l = \frac{1}{\sqrt{N}} \sum_q A_q \exp(i l \cdot q) \tag{12}$$

where $A_q = A_q^*$ and N is the quantity of the IO$_3$ pyramids in the lattice. In the new representation the kinetic and potential energies take the form

$$K = \frac{m}{2} \sum_q \dot{A}_q \dot{A}_{-q} \qquad U = \frac{m}{2} \sum_q \Delta \Omega^2(q) \, A_q A_{-q} \tag{13}$$

where

$$\Delta \Omega^2(q) = 4 \frac{\gamma}{m} \sin^2(a \cdot q/2). \tag{14}$$

Further we can write the Lagrange function as $L = K - U$ and find the generalized momentum $P_q = \partial L/\partial \dot{A}_q = m \dot{A}_{-q}$. The classical energy (10) as a function of the generalized variables A_q and P_q has the form

$$\Delta \mathcal{H} = \frac{1}{2} \sum_q \left[\frac{1}{m} P_q P_{-q} + m \, \Delta \Omega^2(q) \, A_q A_{-q} \right]. \tag{15}$$

A change of variables from A_q and P_q to operators $\hat{A}_q$ and $\hat{P}_q$ transforms the energy (15) to the energy operator $\Delta \mathcal{H}$.

In the usual case, the permutation relations

$$[\hat{A}_q, \hat{P}_{q'}]_- = i\delta_{qq'} \qquad [\hat{A}_q, \hat{A}_{q'}]_- = [\hat{P}_q, \hat{P}_{q'}]_- = 0 \tag{16}$$

hold. However, in our case the displacement δu_q is a compound value: $\delta u_l = u_{2l} g_l(I_1)$. Therefore the collective variables A_q should have the same structure; this can be presented as follows:

$$A_q = \mathcal{A}_{2q} e^{(\alpha/2)N_{1q}} \tag{17}$$

where $\mathcal{A}_{2q}$ is the generalized collective variable of the motion of IO_3 pyramids, N_{1q} is the quantity of phonons with the wave vector q of the 99 cm^{-1} mode and α is the coefficient which characterizes the degree of influence of this lattice mode on the intracellular mode, 99 cm^{-1}, i.e. α is the constant of coupling between the two kinds of phonon. Note that the function of the fluctuation intensity $g_q(I_1)$ written in the q-representation (see (17)) is obviously in complete agreement with the expression for I of a normal phonon mode. The expression for I is determined by thermodynamic averaging:

$$I = \prod_q e^{\langle \hat{b}_q^\dagger \hat{b}_q \rangle}$$

(see, e.g., [8]). By this means, in our case the transition from variables A_q and P_q to the corresponding operators may be performed in the following manner:

$$A_q \to \hat{A}_{2q} e^{(\alpha/2)\hat{N}_{1q}}$$
$$P_q \to m(\hat{A}_{2,-q} e^{(\alpha/2)\hat{N}_{1q}})^\cdot = \hat{P}_{2q} e^{(\alpha/2)\hat{N}_{1q}} + \frac{\alpha}{2} m \hat{A}_{2,-q} e^{(\alpha/2)\hat{N}_{1q}} \dot{\hat{N}}_{1q}. \tag{18}$$

Here one takes into account that the generalized variable $\mathcal{P}_{2q}$ corresponds to $m\dot{\mathcal{A}}_{2,-q}$; $\hat{N}_{1q}$ is the operator of the phonon quantity for the 99 cm^{-1} mode. Using relations (16) which should be valid for the operators $\hat{A}_{2q}$ and $\hat{P}_{2q}$ we obtain the permutation relations for compound operators (18):

$$[\hat{A}_q, \hat{P}]_- = i\hbar\delta_{qq'} e^{\alpha\hat{N}_{1q}} \qquad [\hat{A}_q, \hat{A}_{q'}]_- = [\hat{P}_q, \hat{P}_{q'}]_- = 0 \tag{19}$$

(here one sets $\dot{\hat{N}} = i\hbar[\hat{N}, \hat{H}_0]_- = 0$). Then one can pass from these operators $\hat{A}_q$ and $\hat{P}_q$ to the usual Bose operators for phonons $\hat{b}_{jq}^\dagger$ and $\hat{b}_{jq}$ ($j = 1, 2$) which satisfy standard permutation relations:

$$[\hat{b}_{jq}^\dagger, \hat{b}_{j'q'}]_- = \delta_{jj'}\delta_{qq'} \qquad [\hat{b}_{jq}, \hat{b}_{j'q'}]_- = 0. \tag{20}$$

The transition can be made via the following rules:

$$\hat{A}_q = \sqrt{\frac{\hbar}{2m\,\Delta\Omega(q)}}(\hat{b}_{2q} + \hat{b}_{2,-q}^\dagger)e^{(\alpha/2)\hat{b}_{1q}^\dagger \hat{b}_{1q}}$$
$$\hat{P}_q = i\sqrt{\frac{m\hbar\,\Delta\Omega(q)}{2}}(\hat{b}_{2q}^\dagger - \hat{b}_{2,-q})e^{(\alpha/2)\hat{b}_{1q}^\dagger \hat{b}_q}. \tag{21}$$

Substitution of the variables A_q and P_q in the right-hand side of (15) for the operators $\hat{A}_q$ and $\hat{P}_q$ from (21) converts (10) into the fluctuation Hamiltonian

$$\Delta\hat{\mathcal{H}} = \sum_q \hbar\,\Delta\Omega(q)\left[\hat{b}_{2q}^\dagger \hat{b}_{2q} e^{\alpha\hat{b}_{1q}^\dagger \hat{b}_{1q}} + \frac{1}{2}\right]. \tag{22}$$

Thus, the total Hamiltonian of the AIH crystal can be expressed as

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \Delta\hat{\mathcal{H}} \tag{23}$$

where the operators $\hat{\mathcal{H}}_0$ and $\Delta\hat{\mathcal{H}}$ are defined in (7) and (22) respectively.

3.1. Lattice mode absorption

Let us consider the electromagnetic field absorption by the lattice mode when the mode is perturbed by fluctuations. We suppose that the operator $\Delta\hat{\mathcal{H}}$ in (22) is a small perturbation, i.e. the fluctuation energy is smaller than the energy of regular vibrations. The absorption of the lattice mode has been derived from formulae (4) and (5) where the polarization operator $\mathcal{P}$ and the operator of the interaction $\hat{H}_{\text{int}}(\tau)$ are defined in the formulae (1) and (2) respectively, but the operator $\hat{\rho}_0$ should be transformed into

$$\widehat{\widetilde{\rho}}(\hat{\mathcal{H}}_0 + \Delta\hat{\mathcal{H}}) \simeq \hat{\rho}_0(\hat{\mathcal{H}}_0) - \hat{\rho}(\hat{\mathcal{H}}_0) \int_0^{1/k_B T} e^{\lambda\hat{\mathcal{H}}_0} \Delta\hat{\mathcal{H}} e^{-\lambda\hat{\mathcal{H}}_0} \, d\lambda. \tag{24}$$

Without going into technical detail of the calculations, we shall only note that the calculations of polarization and permittivity are reduced to finding and thermodynamically averaging the second term in (24):

$$\sum_q f_1(q, T) = -\left\langle \int_0^{1/k_B T} e^{\lambda\hat{\mathcal{H}}_0} \Delta\hat{\mathcal{H}} e^{-\lambda\hat{\mathcal{H}}_0} \, d\lambda \right\rangle$$

$$f_1(q, T) = -\hbar\,\Delta\Omega(q) \int_0^{1/k_B T} d\lambda \, \text{Tr}\left\{ \hat{\rho}_0 \exp\left(\lambda \sum_{j=1}^2 \hbar\Omega_j(q)\hat{b}_{jq}^\dagger \hat{b}_{jq} \right) \right.$$

$$\times \hat{b}_{2q}^\dagger \hat{b}_{2q} \exp(\alpha\hat{b}_{1q}^\dagger \hat{b}_{1q}) \exp\left(-\lambda \sum_{j=1}^2 \hbar\Omega_j(q)\hat{b}_{jq}^\dagger \hat{b}_{jq} \right) \right\} \tag{25}$$

$$= -\frac{\hbar\,\Delta\Omega(q)}{k_B T [\exp(\hbar\Omega_2(q)/k_B T) - 1]} \exp\left(\alpha \coth \frac{\hbar\Omega_1(q)}{2k_B T} \right).$$

So, the component of the dielectric function which represents the lattice mode (the term with $j = 1$ in (9)) should be supplemented with the factor $1 + f_1(q, T)$.

3.2. Intracellular mode absorption

The Hamiltonian of the interaction between the electromagnetic wave and the fluctuations of the intracellular mode in the crystal apparently has a form analogous to (2):

$$\hat{H}_{\text{int}}^{(\text{fl})}(t) = -\sum_q d^{(\text{fl})}(q) \cdot E_0(\hat{V}_q^\dagger - V_q)e^{i\omega t + \eta t}. \tag{26}$$

Here $\hat{V}_q^\dagger$ $(\hat{V}_q)$ is the effective operator for the creation (annihilation) of fluctuations of the intracellular mode:

$$\hat{V}_q = \hat{b}_{2q} e^{\alpha\hat{b}_{1q}\hat{b}_{1q}^\dagger}. \tag{27}$$

The operator of the fluctuation dipole moment (compare with [6]) is

$$\hat{P}_{\text{fl}}(n, t) = \sum_q d^{(\text{fl})}(q)e^{iq\cdot n}(\hat{V}_q^\dagger + \hat{V}_q). \tag{28}$$

In (26) and (28) $d^{(\text{fl})}(q)$ is the effective dipole moment of the fluctuations of the intracellular mode.

The polarization is defined as

$$\left\langle \hat{P}_{\text{fl}}(n, t) \right\rangle = \text{Tr}\{\hat{\rho}_{\text{fl}} \hat{P}_{\text{fl}}(n, t)\} \tag{29}$$

where the statistical operator

$$\widehat{\widetilde{\rho}}_{\text{fl}} = \widehat{\widetilde{\rho}}_0 + \frac{1}{i\hbar} \int_{-\infty}^t [\hat{H}_{\text{int}}^{(\text{fl})}(\tau), \widehat{\widetilde{\rho}}_0] \, d\tau. \tag{30}$$

Here $\widehat{\widetilde{\rho}}_0$ is given in (24). Furthermore we will discard secondary effects of an expansion of $\widehat{\widetilde{\rho}}_0(\hat{\mathcal{H}})$ in terms of $\Delta\hat{\mathcal{H}}$. Hence we assume that in (30) $\widehat{\widetilde{\rho}}_0 \simeq \hat{\rho}_0$. Then for the polarization of the intracellular mode we have

$$
\begin{aligned}
\langle P_{\mathrm{fl}}(n, t) \rangle &= \sum_{qq'} d^{(\mathrm{fl})}(q)(d^{(\mathrm{fl})}(q') \cdot E_0) \int_\infty^\tau \mathrm{d}\tau\ \mathrm{e}^{\mathrm{i}(\omega - \mathrm{i}\eta)\tau} \\
&\quad \times \{\hat{\rho}_0[(\hat{V}_q^\dagger + \hat{V}_q), (\hat{V}_{q'}^\dagger(\tau) - \hat{V}_{q'}(\tau))]\} \\
&= \sum_{qq'} d^{(\mathrm{fl})}(q)(d^{(\mathrm{fl})}(q') \cdot E_0) \exp[\alpha(2n_{1q} + 1)] \\
&\quad \times \int_{-\infty}^t \mathrm{d}\tau\ \{\exp[\mathrm{i}(\omega - \Omega_2(q) - \mathrm{i}\eta)\tau] + \exp[\mathrm{i}(\omega + \Omega_2(q) - \mathrm{i}\eta)\tau]\} \quad (31)
\end{aligned}
$$

where n_{1q} is the Planck function of lattice phonons. Upon calculation one finds that the dielectric function of the intracellular mode fluctuation obtained from (31) differs of the second term in (9) only by the factor

$$
f_2(q, T) = \frac{d_{2j}^{(\mathrm{fl})}(q)d_{2j'}^{(\mathrm{fl})}(q)}{d_{2j}(q)d_{2j'}(q)} \exp\left(\alpha \coth \frac{\hbar\Omega_1}{2k_{\mathrm{B}}T}\right). \quad (32)
$$

So, the component of dielectric function which represents the intracellular mode (the term with $j = 2$ in (9)) should be supplemented by the factor $1 + f_2(q, T)$.

The overall result for the imaginary part of the permittivity is

$$
\begin{aligned}
\mathrm{Im}\ \varepsilon(q, \omega, T) &= \frac{4\omega^2\eta}{(\omega^2 - \Omega_1(q)^2)^2 + 4\omega^2\eta^2} \\
&\quad \times [1 + f_1(q, T)] \frac{4\omega^2\eta}{(\omega^2 - \Omega_2(q)^2)^2 + 4\omega^2\eta^2}[1 + f_2(q, T)] \quad (33)
\end{aligned}
$$

where the functions f_1 and f_2 are defined in (25) and (32) respectively. We will analyse the expression (33) in the next section.

4. Discussion

The absorption of the 99 cm^{-1} and 756 cm^{-1} modes of the AIH crystal was investigated by Tarnavski *et al* [4, 5] from 80 to 300 K. They found that in the temperature interval between two phase transitions (from $T_c = 120$ K to $T_0 = 213$ K) the relative intensities of the absorption maximum (for the 99 cm^{-1} mode) and the scattering maximum (for the 756 cm^{-1} mode) have changed very markedly. The former decreases by approximately a factor of two at 213 K. The latter increases by approximately a factor of five at 213 K. Since the imaginary part of the permittivity defines the absorption (scattering) maximum, the expression obtained, equation (33), has to describe the real temperature behaviour of the two above-mentioned anomalous modes.

To carry out the qualitative analysis, let us write the function (32) in the form

$$
\mathrm{Im}\ \varepsilon_1 \propto \left\{1 - \sigma_1 \frac{\hbar\Omega_2}{k_{\mathrm{B}}T} \left[\exp\left(\frac{\hbar\Omega_2}{k_{\mathrm{B}}T}\right) - 1\right]^{-1} \exp\left(\alpha \coth \frac{\hbar\Omega_1}{2k_{\mathrm{B}}T}\right)\right\} \quad (34)
$$

for the lattice 99 cm^{-1} mode and

$$
\mathrm{Im}\ \varepsilon_2 \propto \left\{1 + \sigma_2 \exp\left(\frac{\hbar\Omega_1}{2k_{\mathrm{B}}T}\right)\right\} \quad (35)
$$

for the intracellular 756 cm^{-1} mode. There are three dimensionless parameters in relations (34) and (35): α is the constant of the phonon–phonon coupling; $\sigma_1 = \Delta\Omega/\Omega_2$ is the parameter which characterizes the fluctuation energy (see (25)) and $\sigma_2 = d_{2j}^{(fl)} d_{2j'}^{(fl)}/d_{2j} d_{2j'}$ is the relative change of the square of the dipole moment transition for the cellular mode.
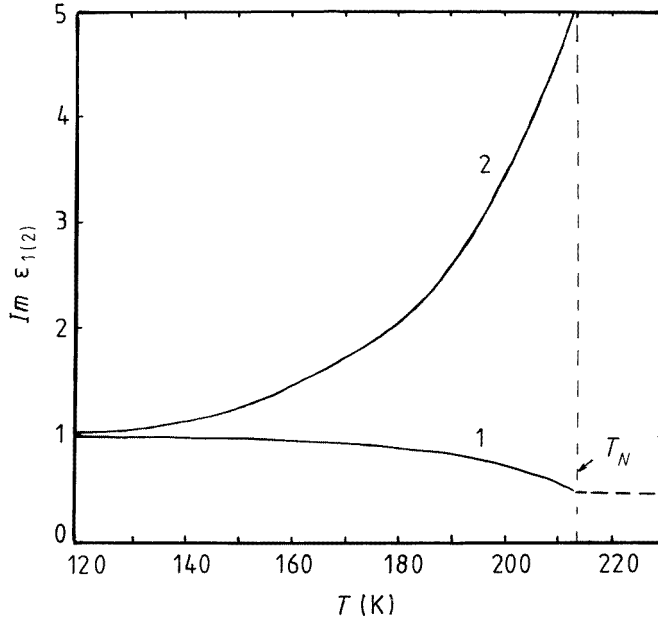
Figure 1. Im $\varepsilon_{1(2)}$ versus T for the two modes. The curves 1 and 2 are built up according to fomulae (34) and (35) respectively. $T_N = 213$ K is the normalized point.

The behaviour of Im $\varepsilon_{1(2)}$ as a function of T is shown in the figure 1. The curves are built up at the following magnitudes of parameters: $\alpha = 0.95$, $\sigma_1 = 2.56 \times 10^{-4}$, and $\sigma_2 = 7.77 \times 10^{-4}$. These two curves are quite consistent with the experimental data [4] on the intensity of the absorption of the 756 cm^{-1} mode: Im ε_1 decreases by a factor of two and Im ε_2 decreases by a factor of five when the temperture changes from 120 to 213 K.

Consequently, we can assert that the AIH crystal is characterized not only by a considerable phonon–phonon interaction, which leads merely to phonon anharmonicity. In this crystal the phonon–phonon coupling between the active lattice mode and the intracellular one is realized due to the proton bifurcation. The coupling allows us to introduce an additional term describing vibrational fluctuations into the basis Hamiltonian, formula (23). The anomalous temperature behaviour of the AIH crystal for $T > T_c$ is connected with those fluctuations. The availability of moderate phonon–phonon coupling ($\alpha = 0.95$) permits the intracellular mode, 756 cm^{-1}, to 'live' on the energy of phonons of the lattice mode, 99 cm^{-1}. Indeed, the average energy $\bar{E}$ of a vibration with the cycle frequency $\tilde{\omega}$ equals $\hbar\tilde{\omega}[\exp(\hbar\tilde{\omega}/k_B T) - 1]^{-1}$. Then, for the system under consideration one finds that $\bar{E}_2$ is several times smaller than $\bar{E}_1$. Hence, the lattice mode is more powerful than the intracellular one and, therefore, the latter has taken energy out of the former through the phonon–phonon coupling. So, at the second phase transition, i.e. at 213 K, the power of the lattice mode can no longer hold proton polarons very strongly and they become more mobile. Thus, the crystal goes into a superionic state in which the band polaron conductivity prevails [5].

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