
A THREE-DIMENSIONAL MODEL OF H-BOND AND THE GEOMETRIC ISOTOPIC EFFECT

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The geometric isotopic effect in hydrogen-containing crystals of the KDP-type is investigated. A mechanism of changes of the hydrogen bonds lengths under the deuteron substitution is proposed. It is shown that (in the framework of the three-dimensional model for hydrogen bonds based on the Einstein approximation for anharmonic oscillators) the correspondence between experimental and theoretical data can be achieved if one takes into account the interactions between the neighboring chains of H-bonds in a crystal.

Introduction

It is known that KDP-type crystals with hydrogen bonds undergo structural ferroelectric or antiferroelectric phase transitions. The temperatures of these phase transitions essentially depend on the deuteron substitution. To explain the microscopic mechanism of the phase transitions in hydrogen-containing crystals, the quantum tunneling model was successfully applied [1]. This model, however, does not explain some experimental results connected with the isotopic proton substitution [2, 3]. In particular, this concerns the observed concentration dependences of the Curie temperature T_C for the phase transition of the order-disorder type. Later it was noticed [4 - 7] that the linear dependence of T_C as a function of the hydrogen bond length R (so-called geometric isotopic effect) can be explained in the same manner. To describe the isotopic changes in the structure and dynamics of hydrogen bonds, the problem of isotopic substitution was considered (see, for example, [8]) within the approach of the model crystal built from noninteracting infinite hydrogen-bonded chains. For the analysis of real crystal structures, however, it is necessary to take into account a three-dimensional structure of hydrogen bonds. In particular, in the case of real crystals, it is necessary to consider both stretching and bending vibrations of H-bonds as well the interactions between hydrogen-bonded chains.

The present paper aims at the elucidation of the isotopic changes of the hydrogen bond structure in the three-dimensional approximation in view of the interactions between chains of H-bonds in a crystal.

1. Three-dimensional Model for H-bonds

According to [9], the interaction energy between a proton (deuteron) and oxygen atoms can be approximated by the three-dimensional Morse potential

$$U(r) = D_0 \{ \exp(-2a(r-r_0)) - 2 \exp(-a(r-r_0)) \},$$

where $r = |\mathbf{r}|$ characterizes the proton (or deuteron) position with respect to an oxygen atom; D_0 , a , and r_0 are the parameters of the Morse potential. According to [10], the energy of the proton (deuteron), located on the symmetric H-bond, is described by the double-minimum Morse potential

$$\begin{aligned} V(r) &= U\left(x + \frac{R}{2}, y, z\right) + U\left(x - \frac{R}{2}, y, z\right) = \\ &= \frac{D_0}{4} \{ \exp(aR_0) [\exp(-2l_+) + \exp(-2l_-)] - \\ &- 4 \exp\frac{aR_0}{2} [\exp(-l_+) + \exp(-l_-)] \}, \end{aligned} \quad (1)$$

where

$$\begin{aligned} l_{\pm} &= \sqrt{a^2(y^2 + z^2) + a^2\left(x \pm \frac{R}{2}\right)^2}, \\ R_0 &= 2\left(r_0 + \frac{1}{a} \ln 2\right), \end{aligned}$$

and R is the distance between two neighboring oxygen atoms.

In Eq. (1), x , y , and z are the coordinates of the proton (or deuteron) with respect to the center of the

hydrogen bond. The shape of the double-minimum Morse potential (1) essentially depends on the H-bond length. The x_0 , y_0 , and z_0 are the coordinates of two positions for the proton (deuteron) in the double-minimum Morse potential. If $R > R_0$, then

$$x_0 = \pm \frac{1}{a} \cosh^{-1} \left(\exp \left(\frac{a}{2} (R - R_0) \right) \right), \quad y_0 = z_0 = 0.$$

One can see that the double-minimum proton potential transforms into the one-minimum potential ($x_0 = y_0 = z_0 = 0$) if $R \leq R_0$.

2. Free Energy of Hydrogen Bond Chains

Let us use the method developed in [8] for the quantum-statistical averaging of free energy F . According to this method, one should proceed from the dynamics of the isolated chains of H-bonds to the thermodynamics of a simple system of the interacting chains of H-bonds. In other words, according to this model, the crystal can be presented as a three-dimensional aggregate of the linear chains of hydrogen bonds. The well-known crystals CsH_2PO_4 and KH_2PO_4 [11], containing the infinite chains of H-bonds "attached" to PO_4 -groups, fully satisfy the requirements of this model. The interaction between the infinite chains of H-bonds can be introduced by the replacement l_{\pm} to L_{\pm} in Eq. (1):

$$L_{\pm} = \sqrt{a^2(x \pm R_2)^2 + b^2(y^2 + z^2)}.$$

The introduction of one additional parameter $b \neq a$, refers to the fact that the interaction between the chains of H-bonds changes the curvature of the proton potential curve (l) in the y - and z -directions.

Let us consider a crystal, which contains non-interacting protons (or deuterons) positioned in the double-minimum Morse potential. In this case, the system can be described by the Einstein model of an anharmonic oscillator with the energy $H = K + V + W$ (where K is the kinetic energy of the proton (or deuteron), V is the interaction energy determined by Eq. (1). Here, as follows from [8], W is the interaction energy between two oxygen atoms. This energy was chosen in the elementary form as

$$W = w_0 \{ \exp(-2a(R - R_m)) - 2 \exp(-a(R - R_m)) \},$$

where w_0 , R_m are the parameters of this potential. As follows from perturbation theory [6] for the free energy F , let us choose the Hamiltonian $H_0 = K + V_0 + W_0$ for harmonic oscillations of

protons (or deuterons) with ω_s and ω_b frequencies of stretching and bending vibrations of the proton on the H-bond. It should be note that, for the simplification of the following calculations, we use approximation in which $\omega_b = (1/2)(\omega'_b + \omega''_b)$, where ω'_b and ω''_b are the frequencies of the non-degenerate bending vibrations. We also choose the vibration energy for the oxygen atoms with the frequency ω . Then, according to [8, 11], the free energy F of the hydrogen-bonded chains standardized on the unit chain cell will be

$$F = F_0 + \langle H - H_0 \rangle \equiv F_0 + f,$$

where

$$F_0 = -kT \ln \left(\text{sp} \left\{ \exp \left(-\frac{H_0}{kT} \right) \right\} \right).$$

Here the averaging is performed for the Hamiltonian H_0 , as was done in [8]:

$$\langle \dots \rangle = \frac{\text{sp} \{ \exp(-H_0/kT) \}}{\text{sp} \{ \exp(-H_0/kT) \}},$$

where k is the Boltzmann constant. Therefore, we have

$$F_0 = +kT \ln \left(2 \sinh \frac{h \omega_s}{2kT} \right) + 2kT \ln \left(2 \sinh \frac{h \omega_b}{2kT} \right) + kT \ln \left(2 \sinh \frac{h \omega}{2kT} \right). \quad (2)$$

Here, ω is the vibrational frequency of oxygen atoms. The averaging action leads to the following equation for f :

$$f = \langle H - H_0 \rangle = \frac{D_0}{2} G_0 + w_0 B,$$

where

$$G_0 = \frac{\exp(-(\xi - \xi_0) + 2\lambda)}{(\xi + 4\mu)^2 - 4\chi^2} \{ (\xi^2 - 4\chi^2) \cosh 2\chi + 4\mu(\xi \cosh 2\chi - 2\chi \sinh 2\chi) \} - 4 \frac{\exp\left(-\frac{\xi - \xi_0}{2} + \frac{\lambda}{2}\right)}{(\xi + 2\mu)^2 - 4\chi^2} \{ (\xi^2 - 4\chi^2) \cosh \chi + 2\mu(\xi \cosh \chi - \chi \sinh \chi) \}, \quad (4)$$

$$B = \exp(-2(\xi - \xi_m) + 4\sigma_R) - 2 \exp(-(\xi - \xi_m) + \sigma_R). \quad (5)$$

Here, ξ , χ and ω_s , ω_b , and ω are the varying parameters of the free energy F

$$\xi = a \langle R \rangle, \quad \chi = a \langle x \rangle, \quad \text{and} \quad \xi_0 = aR_0, \quad \xi_m = aR_m.$$

In Eq. (4),

$$\lambda = \frac{a^2 h}{2 m \omega_s} \coth \frac{h \omega_s}{2 k T}, \quad \mu = \frac{b^2 h}{2 m \omega_b} \coth \frac{h \omega_b}{2 k T},$$

$$\sigma_R = \frac{a^2 h}{2 M \omega} \coth \frac{h \omega}{2 k T} \quad (6)$$

are the square-averaged values of thermal displacements for the hydrogen and oxygen atoms, $\sigma_R \ll \lambda, \mu$. The varying parameters ω_s , ω_b , ω of the free energy F can be found using the minimization procedure for the free energy F . By using this minimization action for the free energy F ($\partial F / \partial \omega_s = \partial F / \partial \omega_b = 0$) and Eqs. (2) and (6), one can obtain

$$\omega_s^2 = \frac{1}{2} \Omega_a^2 \frac{\partial G}{\partial \lambda}, \quad \text{where} \quad \Omega_a^2 = \frac{2 a^2 D_0}{m},$$

$$\omega_b^2 = \frac{1}{4} \Omega_b^2 \frac{\partial G}{\partial \mu}, \quad \text{where} \quad \Omega_b^2 = \frac{2 b^2 D_0}{m}. \quad (7)$$

Ω_a, Ω_b depend on the parameters of the double-minimum proton potential only. In Eq. (7), m is the mass of the proton (or deuteron). The obtained Eqs. (7) determine the dependences of the frequencies of stretching and bending vibrations of the protons (or deuterons) as the functions of the H-bond length.

3. Equations for Temperature Averaged Varying Parameters

Because the ratio μ/ξ and χ in Eq. (4) are small, the free energy f has the following form:

$$f = \frac{D_0}{2} G + w_0 \{ \exp(-2\sigma_R) \} (\xi - \bar{\xi})^2. \quad (8)$$

Here,

$$\bar{\xi} = \xi_m + 3\sigma_R,$$

$$G = [A^{-2}(\xi) \cosh 2\chi - 4A^{-1}(\xi) \cosh \chi] \exp(-\lambda),$$

$$A(\xi) = \exp \frac{1}{2} \left(\xi - a(2r_0 + \frac{\ln 4}{a} + 3\lambda - \frac{4\mu}{\xi}) \right),$$

where critical length

$$\xi_c^* = a(2r_0 + \frac{1}{a} \ln 4) + 3\lambda - \frac{4\mu}{\xi_c}$$

$$\xi_c = a(2r_0 + \frac{1}{a} \ln 4) + 3\lambda. \quad (9)$$

Considering the free energy minimum condition, a new equilibrium position for the proton (or deuteron) is

$$\chi(\xi) = \cosh^{-1} A(\xi), \quad \xi > \xi_c^*,$$

$$\chi(\xi) = 0, \quad \xi \leq \xi_c^*.$$

We note that, according to Eq. (9), the H-bond critical length ξ_c , determined in [8] at $\chi = 0$, decreases. It is clear that, due to the transversal degree of freedom for the H-bond, the double-minimum character of potential (1) remains unchanged at smaller values of the H-bond length. The equations for $\omega_s(\xi)$ and $\omega_b(\xi)$ are as follows if $\xi > \xi_c^*$:

$$\omega_s^2 = \Omega_a^2 \exp(-\lambda) (1 - A^{-2}(\xi)),$$

$$\omega_b^2 = \frac{2 \Omega_b^2}{\xi} \exp(-\lambda) A^{-2}(\xi),$$

and, when $\xi \leq \xi_c^*$,

$$\omega_s^2 = \Omega_a^2 \exp(-\lambda) \{ A^{-2}(\xi) - A^{-1}(\xi) \},$$

$$\omega_b^2 = \frac{2 \Omega_b^2}{\xi} \exp(-\lambda) \{ 2A^{-1}(\xi) - A^{-2}(\xi) \}.$$

The free energy minimum condition as a function of ξ , can be written as $\partial(\delta F) / \partial \xi = 0$. This new expression for the minimum condition leads to two equations for the equilibrium length $\xi_{H,D}$ of the H-bond. This length depends on the proton (or deuteron) position on the H-bond:

$$\xi_{H,D} = \bar{\xi} - \gamma \frac{\partial G(H,D)}{\partial \xi} \Big|_{\xi = \xi_{H,D}}. \quad (10)$$

Here, the non-dimensional parameter

$$\gamma = \frac{D_0}{2 w_0} \exp(2\sigma_R),$$

determined as the ratio of the energies for H⁺O and O...O interactions, gives a contribution into the magnitude of the thermodynamically equilibrium H-bond length. The expressions for $G(H,D)$, taken from Eq. (8), determine the functional dependence of the equilibrium length $\xi_{H,D}$.

From system (10), we can obtain the value $\Delta \equiv \xi_D - \xi_H$ using the following transcendental equations:

$$\Delta = \gamma \exp(-\lambda_H) \exp(-(\xi - \xi_{c,H}^*)) \times \left(1 - \exp\left(-2\lambda_H^* - \Delta + \frac{4\mu_H^*}{\xi_{c,H}^*}\right) \right), \quad \text{for } \xi > \xi_{c,H}^* \quad (11)$$

and

$$\Delta = -\gamma \exp(-\lambda_H) \left\{ \exp(-\xi(-\xi_{c,H}^*)) \times \left(1 - \exp\left(2\lambda_H^* + \frac{4\mu_H^*}{\xi_{c,H}^*}\right) \right) - 2 \exp\left(-\frac{(\xi - \xi_{c,H}^*)}{2}\right) \times \left(1 - \exp\left(\frac{\lambda_H^*}{2} - \frac{\Delta}{2} + \frac{2\mu_H^*}{\xi_{c,H}^*}\right) \right) \right\} \quad \text{for } \xi \leq \xi_{c,H}^* \quad (12)$$

$$\lambda_H^* = \lambda_H \frac{\sqrt{2}-1}{\sqrt{2}}, \quad \mu_H^* = \mu_H \frac{\sqrt{2}-1}{\sqrt{2}}.$$

The values of λ_H and μ_H are determined by Eq. (6) if m is the mass of the proton.

The dimensional value $\Delta/a \equiv \langle R_D - R_H \rangle_0$ as a function of the H-bond length $\langle R \rangle_0$ is presented in Fig. 1. There is a satisfactory agreement between the experimental results [4] and our theoretical data. One should note that, in the range $R < R_c$, the theoretical curve (solid line in Fig. 1) lies below zero, as the experimental data do. Taking into account that the experimental points presented for the range $R > R_c$ are characterized by a significant dispersion and inaccuracy, one could make a conclusion about a fair agreement between the experimental and theoretical data. The best agreement is achieved if the coefficient γ in Eqs. (11) and (12) is equal to ≈ 1 . The other parameters were taken as follows: $R_0 = 0.95 \text{ \AA}$, $a = 3 \text{ \AA}^{-1}$, $b = 3.9 \text{ \AA}^{-1}$, $D_0 = 272 \text{ kJ/mol}$. The dependences $\lambda(R)$ and $\mu(R)$ are shown in Fig. 2. The presented dependence $\lambda(R)$ agrees with the same dependence $\lambda(R)$ in [6]. To the best of our knowledge, the dependence $\mu(R)$ was not previously published jet. This dependence takes into account the three-dimensional model for H-bonds and the interaction between the infinite chains of H-bonds in a crystal.

Conclusions

In this work, we have proposed the approach, based on the three-dimensional model of hydrogen bond, to explain the geometric isotopic effect. The free energy for some model crystal composed from interacting

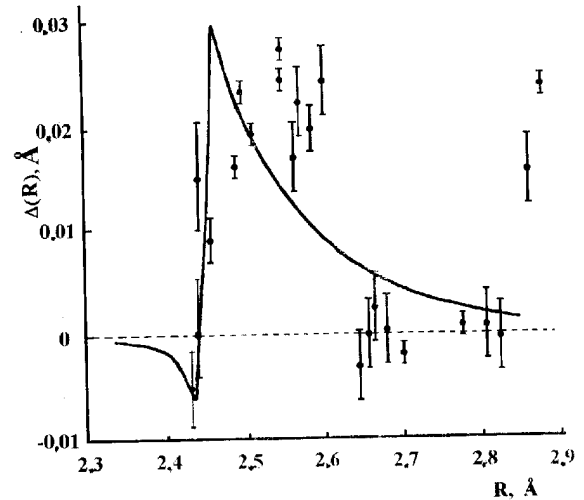


Fig. 1. Dependence $\Delta(R) \equiv R_{\text{ODO}} - R_{\text{OHO}}$. The solid line presents the results of our theoretical calculations. The experimental data were taken from [5]

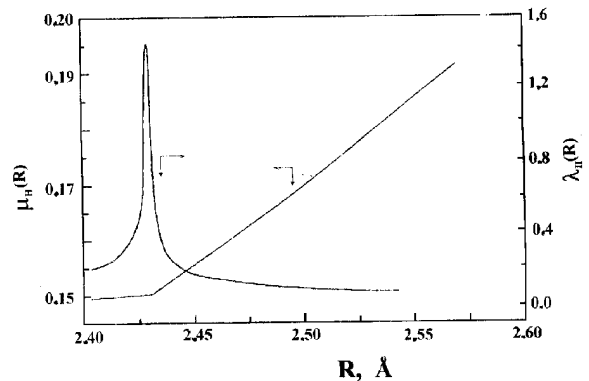


Fig. 2. Dependences $\lambda_H(R)$ and $\mu_H(R)$ obtained from Eqs. (10) and (11)

infinite hydrogen-bonded chains is obtained in the Einstein anharmonic oscillator approximation. It is shown that the critical length of the H-bond (the length at which the hydrogen bond is characterized by the one-minimum potential for a proton) is determined by the contribution of longitudinal and transversal fluctuations of the protons (or the deuterons), and the contribution from transversal fluctuations is negative. The obtained curve $\Delta(R)$ (solid line in Fig. 1) lies below zero in the range $R < R_c$ and has a minimum.

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