

NMR study of proton dynamics in ferroelectric $\text{KIO}_3 \cdot 2\text{HIO}_3$ crystal

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The temperature dependence of the proton spin-lattice relaxation time T_1 has been studied in ferroelectric $\text{KIO}_3 \cdot 2\text{HIO}_3$ crystal. It is shown that the proton jumping along $\text{O}-\text{H}\cdots\text{O}$ contact has been shown to be the main relaxation mechanism. At temperatures exceeding the phase transition one, $T > T_c$, the proton relaxation is caused by the motion thereof in symmetric two-well potential of the hydrogen bond with activation energy $E_a = 3.4$ kcal/mol. At $T < T_c$, the proton ordering in asymmetric two-well potential occurs with activation energies $E_{a1} = 4.1$ kcal/mol and $E_{a2} = 2.5$ kcal/mol. Evaluation of equilibrium constant value $a = p_1/p_2$, where p_1 and p_2 are the probabilities of proton being in position "1" or "2" of double-well potential near T_c gives the value $a \approx 40$, but yet at $T_c - T = 50$ K, $a \approx 150$, thus evidencing a high proton ordering degree on H-bond below the phase transition.

Исследована температурная зависимость времени протонной спин-решеточной релаксации в сегнетоэлектрическом кристалле $\text{KIO}_3 \cdot 2\text{HIO}_3$. Показано, что основным механизмом релаксации являются перескоки протонов вдоль водородного контакта $\text{O}-\text{H}\cdots\text{O}$. Выше температуры фазового перехода T_c релаксация обусловлена движением протонов в симметричном двухъямном потенциале водородной связи с энергией активации $E_a = 3,46$ ккал/моль. При $T < T_c$ происходит упорядочение протонов в асимметричном двухъямном потенциале с энергиями $E_{a1} = 4,1$ ккал/моль и $E_{a2} = 2,5$ ккал/моль. Оценка константы равновесия $a = p_1/p_2$, где p_1 и p_2 — вероятности нахождения протона в положении "1" или "2" двухъямного потенциала, вблизи T_c дает значение $a \approx 40$, но уже при $T_c - T = 50$ К $a \approx 150$, что свидетельствует о высокой степени упорядочения протона на водородной связи ниже фазового перехода.

The crystal of potassium triiodate $\text{KIO}_3 \cdot 2\text{HIO}_3$ possesses triclinic symmetry at room temperatures (P1, $z = 2$) [1–3]. At $T = 213$ K, a second order structural phase transition is observed. It is assumed [4] that at the temperatures $T < T_c$, takes place the ordering of protons in asymmetric two-well potential, above the phase transition temperature the protons forming the hydrogen contacts $\text{O}-\text{H}\cdots\text{O}$ localized near the crystal symmetry centers.

NMR studies of this crystal have shown that its proton spectrum consists of a single narrow line that indicates to a relatively rapid motion of protons along hydrogen

bonds. The same is confirmed by a high conductivity in this crystal ($\sim 10^{-6}$ $\Omega\text{-cm}$) [2] that may be explained by exceeding of protons localization positions over their amount. NQR studies of the potassium triiodate have shown that at $T < T_c$ there are 6 lines [4] in the NQR spectrum, thus evidencing, that all six IO_3 groups occupy non-equivalent positions at these temperatures. Above the phase transition temperature T_c , the ^{127}I NQR spectrum is not observed [4] that seems to be due to high proton conductivity, that averages the electric field gradient and resulting in a considerable broaden-

ing of resonance line and, as a consequence, in its disappearance.

To elucidate the nuclear magnetic relaxation mechanisms and to determine the crystal dynamic characteristics and phase transition peculiarities in this crystal, the temperature dependence of the proton spin-lattice relaxation time (SLR) T_1 in polycrystalline $\text{KlO}_3 \cdot 2\text{HlO}_3$ have been measured in the temperature range 77–300 K. The temperature was stabilized to within ± 0.1 K. The SLR time T_1 measurements were made using the Larmor frequency 19.2 MHz, an ISP 2-13 HF-spectrometer and pulse sequence $90^\circ-t-90^\circ$. The SLR time as a function of temperature is presented in Figure.

According to the classic theory of spin relaxation caused by dipole-dipole resonance interaction, the SRL rate T_1^{-1} is defined by the following expression [5]:

$$T_1^{-1} = C \frac{\gamma^4 \hbar^2}{r^6} \left(\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right), \quad (1)$$

where C is a constant depending on the crystal structure; t_c , the correlation time that characterizes the rate of the local field fluctuations and shows Arrhenius temperature behavior:

$$\tau_c = \tau_0 \exp(-E_a/RT).$$

The plot of T_1 temperature dependence according to this expression has a V-like shape with a minimum T_1 value at the coincidence of experimental Larmor frequency ω_0 and frequencies of proton jumping τ_c^{-1} ($\omega_0 \tau_c = 0.62$). Since $T_1 \sim \tau_c$, the slope of $\log T_1$ dependence vs inverse temperature enables to determine the potential barrier value for proton reorientation or jumping. When the proton jumps occur in symmetric two-well potential, the barrier values both in a high temperature (where $\omega_0 \tau_c \ll 1$) and in a low temperature (where $\omega_0 \tau_c \gg 1$) regions must coincide, if the predominant relaxation mechanism is the same. In our case, there are two features of temperature dependence of the SLR time. First, the values of activation energy in the high temperature region ($E_1 = 0.86$ kcal/mol) and in the low temperature one ($E_2 = 1.24$ kcal/mol) are different. Second, the obtained barrier values are extremely low.

The asymmetry in the temperature dependence of the SLR time can arise up at including of new relaxation mechanisms at the transition to higher temperatures. How-

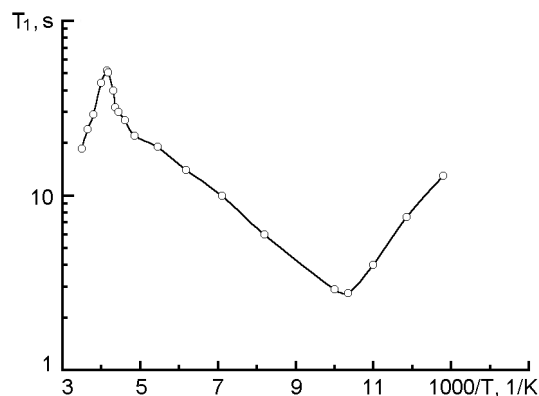


Fig. Temperature dependence of the proton spin-lattice relaxation time T_1 .

ever, in this case, the appearance probability of mechanisms with more higher barrier rises with temperature elevation. This will be reflected in the larger activation energy value calculated from the SLR measurements; but in our case, the value of activation energy in a high temperature region decreases. Such situation arises only when proton moves in asymmetric two well potential, i.e. between two non-equivalent positions with the energy difference ΔH [6].

Thus, taking into account the indicated feature of temperature SLR dependence, we, following [6], have assumed that such behavior of relaxation time T_1 is caused by the proton motion in asymmetric two-well potential of the hydrogen bond $\text{O}-\text{H}\cdots\text{O}$. Then, for correlation time of proton jumping, it may be written:

$$\tau_c^{-1} = \nu_{1-2} + \nu_{2-1}, \quad (2)$$

where ν_{1-2} and ν_{2-1} are frequencies of jumps from "deep" well 1 to "shallow" well 2 and backwards, which are determined as:

$$\begin{aligned} \nu_{1-2} &= \nu_0 \exp[-(H + \Delta H)/RT]; \\ \nu_{2-1} &= \nu_0 \exp(-H/RT), \end{aligned} \quad (3)$$

where H — energy barrier for jumps from "shallow" well to "deep" one.

As follows from (2) and (3), under condition $\Delta H \gg RT$, the correlation time τ_c is defined mainly by the proton jumps from "shallow" to "deep" well:

$$t_c = t_0 \exp(H/RT). \quad (4)$$

In this case, expression for proton SLR rate, which caused by jumping motion of spin in asymmetric potential is [7]:

$$T_1^{-1} \approx \frac{a}{(a+1)^2} \left(\frac{\tau_s}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_s}{1 + 4\omega_0^2 \tau_c^2} \right),$$

where $a = v_{1.2}/v_{2.1} = \exp(\Delta H/RT)$ — equilibrium constant.

If $\Delta H \gg RT$, the expression for relaxation time becomes simplified:

$T_1 \sim \exp[-(H-\Delta H)/RT]$, for a high temperature range, where $\omega t_c \ll 1$

$T_1 \sim \exp(H + \Delta H)/RT$ for a low temperature range, where $\omega t_c \gg 1$.

Thus, the slopes of $\log T_1$ vs. T^{-1} at temperatures above and below minimum T_1 will differ. That was demonstrated by the obtained values of E_1 and E_2 which allows to determine asymmetric potential parameters:

$$E_1 = H - \Delta H = 0.86 \text{ kcal/mol and}$$

$$E_2 = H + \Delta H = 1.24 \text{ kcal/mol.}$$

This makes it possible to find the shallow potential well depth H and difference between two wells ΔH : $H = 1.05$ kcal/mol and $\Delta H = 0.86$ kcal/mol. It is obvious that in the investigated temperatures range, the condition $\Delta H \gg RT$ is not fulfilled, which is in contradiction to the above-mentioned phase transition model. If the obtained H values will be used to calculate the proton jump correlation time along hydrogen bond, another contradiction appears. The value of correlation time t_c determined from the condition $\omega_0 t_c = 0.616$ at minimum of time T_1 temperature dependence gives the value $t_c = 5.1 \cdot 10^{-9}$ s. Then, the correlation time constant $t_0 = 2.2 \cdot 10^{-11}$ s. At the same time, to can be determined as inverse frequency of proton longitudinal oscillation along O—H bond. It is just the frequency $\nu_{\text{O—H}}$ equal to 2300 cm^{-1} [8] corresponding to the value $t_0 = 1.4 \cdot 10^{-14}$ s that is consistent with the length of $R(\text{O} \cdots \text{O})$ hydrogen contact [1].

Such contradiction can be explained by rising proton tunneling probability at low temperatures that results in weakening of SLR time T_1 temperature dependence and consequently to the underestimated value of E_2 and two-well potential parameters H and ΔH in the low temperature region.

To determine the true values of H and ΔH , we use the value $t_0 = 1.4 \cdot 10^{-14}$ s which

gives the correlation time $t_c = 5.1 \cdot 10^{-9}$ s at the temperature of minimum time T_1 . Taking this into account, we have get such values for the two-well potential: $H = 2.46$ kcal/mol and $\Delta H = 1.6$ kcal/mol. In this case, correlation time of proton jumps along the hydrogen bond meets the law $t_c = 1.4 \cdot 10^{-14} \exp(2.46/RT)$. It is important to note that $\Delta H \gg RT$ for the whole temperature region below the phase transition temperature T_c , that is in accordance with the proton ordering model at phase transition.

Evaluation of equilibrium constant value $\alpha = p_1/p_2$, where p_1 and p_2 are the probabilities of proton being in position "1" (deep well) or "2" (shallow well) of the two-well potential, respectively, gives near T_c the value $\alpha \approx 40$, but yet at $T_c - T = 50$ K, $\alpha \approx 150$, thus evidencing a high proton ordering degree on H bond at temperatures below the phase transition.

Thus, the predominant mechanism of proton spin-lattice relaxation in the crystal under study at the temperature $T > 100$ K is the proton motion in asymmetric two-well potential of hydrogen bond $\text{O—H} \cdots \text{O}$. The contribution of proton tunneling into relaxation becomes noticeable at low temperatures ($T < 100$ K). The change of the spin relaxation activation barrier at the phase transition temperature T_c is caused by a transition from symmetric two-well potential with $E_a = 3.46$ kcal/mol to asymmetric one with $H = 2.46$ kcal/mole and $\Delta H = 1.6$ kcal/mole, that confirms the offered model of the order-disorder phase transition.

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ЯМР дослідження динаміки протонів у сегнетоелектричному кристалі $\text{KIO}_3 \cdot 2\text{HIO}_3$

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Досліджено температурну залежність часу протонної спин-граткової релаксації у сегнетоелектричному кристалі $\text{KIO}_3 \cdot 2\text{HIO}_3$. Показано, що основним механізмом релаксації є стрибки протонів вздовж водневого контакту $\text{O}-\text{H}\cdots\text{O}$. Вище температури фазового переходу T_c релаксація обумовлена рухом протонів у симетричному двоємному потенціалі водневого зв'язку з енергією $E_a = 3,46$ ккал/моль. При $T < T_c$ має місце упорядкування протонів у асиметричному двоємному потенціалі з енергіями $E_{a1} = 4,1$ ккал/моль і $E_{a2} = 2,5$ ккал/моль. Оцінка константи рівноваги $a = p_1/p_2$, де p_1 та p_2 — вірогідності знаходження протона у положенні "1" або "2" двоємного потенціалу, дає значення $a \approx 40$, але вже при $T_c - T = 50$ К $a \approx 150$, що вказує на високий ступінь упорядкування протона на водневому зв'язку нижче фазового переходу.