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MODEL FOR PARAMAGNETIC PROBE IN HYDROGEN BONDED FERROELECTRIC

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Dedicated to Professor Boran Leontić on the occasion of his 70$^{\text{th}}$ birthday

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The modified strong dipole-proton coupling model and Monte Carlo calculation are employed to describe paramagnetic defect in hydrogen bonded ferroelectric. In this model, probe is treated as "soft" dipole impurity in the system with $N = 108$ dipoles. The effective double-well type potential of the probe is obtained and its temperature dependence in the paraelectric phase is studied. It is shown that the experimentally detected activation energy of the polarization fluctuation of the SeO_4^{3-} probe can be related to the effective activation energy. The model is compared with the earlier proposed local "pseudo freeze-out" model which exhibits larger deviation from the experimental results than the suggested modified strong dipole-proton coupling model.

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1. *Introduction*

The paramagnetic centers (AsO_4^{4-}, SeO_4^{3-} or CrO_4^{4-}) have been employed as probes to study slow lattice dynamics and low-frequency ($10^7 - 10^{10}$ Hz) polarization fluctuations of the KH_2PO_4, KDP-, type hydrogen bonded ferroelectrics in the vicinity of the paraelectric-ferroelectric, PE-FE, phase transition temperature, T_c [1,2]. Although several attempts have been made to describe dynamics behaviour of paramagnetic probes, detailed theoretical description is still rather scarce. In the early studies [3–5] it was noted that paramagnetic probes exhibit a local mode at EPR time scale. A local behaviour of the probe has been attributed to transformation from the high to the low symmetry EPR spectra at temperature T^* well above

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T_c. By employing modified Bloch equations, such phenomenon was frequently used for obtaining the low-frequency molecular motion in the KDP-type of lattices in the temperature region around T^*. The obtained motional dynamics was described by a simple Arrhenius-type correlation time $\tau = \tau_0 \exp(\Delta E/kT)$ in some reports [6,7] or non-Arrhenius behaviour in other studies [8,9]. The microscopic origin of the Arrhenius-type of τ was not discussed in detail. On the other hand, a deviation from the Arrhenius law is interpreted by employing theoretical models, which predict a local motional freezing, LMF, of spin probe in the PE phase [10,11]. According to the LMF model [10] ΔE of the probe should increase as temperature approach to T_c in the PE phase. It was shown recently that some of non-Arrhenius behaviour can be ascribed to the omission of at least two processes: a) line broadening which depends exponentially on temperature [12,13] and b) inhomogeneous broadening due to the proton spin flip transition [14]. By employing EPR technique [13] this was indeed found to be the case for KDP:SeO_4^{3-} system where ΔE is essentially the temperature independent down to $T_c = 120$ K.

Since the temperature dependence of ΔE obtained by the LMF model [10] was not supported by recent experimental results [12–15], an important question about the microscopic origin of ΔE still remains open. One of experimental observations which can help in the description of the microscopic origin of ΔE is the fact that τ, obtained in deuterated ferroelectric (^{1}H is replaced by ^{2}H), exhibits the same Arrhenius behaviour with larger ΔE and smaller τ_0 values than in nondeuterated lattices [12-14]. Indeed, by employing recently suggested model of strong dipole-proton coupling (SDPC) for description of the phase transition in KDP lattice [16,17], the values of the barrier height of the double-well type dipole potential and values of τ_0 are calculated for KDP and KD_2PO_4, DKDP, lattices [18]. The results show that large barrier height and smaller τ_0 are present in the DKDP than in the KDP lattice. Therefore, the barrier height of double-well potential can be roughly approximated with the measured ΔE parameter. However, there is an additional uncertainty regarding the above approximation. It is expected that the double-well potential exhibits temperature dependence in a temperature interval around T^* in the PE phase, leading to temperature dependence of the barrier. Thus, the barrier can not be simply approximated to ΔE, which is nearly constant for the same temperature interval.

The purpose of this investigation is to deduce local potentials and τ based on modified SDPC model for a paramagnetic probe in KDP host lattice. The obtained theoretical results will be tested by comparing the experimentally measured and calculated τ by employing LMF and modified SDPC models in the wide temperature interval around T^*.

2. *Strong dipole-proton coupling model*

The SDPC model for KDP and DKDP ferroelectrics involves strong coupling between electric dipole moments induced by a distortion of PO_4 tetrahedra and surrounding protons (deuterons) [16,17]. Potential energy of the system of N distorted tetrahedra and $2N$ protons has the form

$$E_{\rm pot} = \frac{A}{2}\sum_{i=1}^{N}\mu_i^2 + \frac{B}{4}\sum_{\langle ij\rangle}^{2N}\mu_i\mu_j + \sum_{\langle ij\rangle}^{2N} E_{ij}^0(\mu_i,\mu_j)\,, \tag{1}$$

where μ_i is the dipole moment of the tetrahedron i $(= 1, ..., N)$ which lies along ferroelectric c-axis. The first term is the elastic energy due to the mechanical deformations of tetrahedra, the second term is the interaction energy between neighbouring dipoles, and the last term is the energy of protons. The ground-state energy E_{ij}^0 of proton connecting two neighbouring tetrahedra (i and j) depends on a force F_{ij}, which acts along the hydrogen bond due to induced dipoles of tetrahedra. Quantum-mechanical calculations for proton and deuteron in the empirical potential of the hydrogen bond affected with this force give the ground-state energy of the form

$$E_{ij}^0 = -\sqrt{h^2 + I^2F_{ij}^2} + h\,, \tag{2}$$

where h shows isotopic effect ($h^H = 110$ meV, $h^D = 58$ meV), and $I(= 0.22\,10^{-10}$ m) has the same value for both materials. The force is assumed to depend on dipole moments as $F_{ij} = K(\mu_i + \mu_j)$, where K is a dipole-proton coupling constant. Parameters A, B and K are adjusted to reproduce experimental data for the transition temperature, saturated polarization and protonic vibrational frequencies in KDP. By using the same values for all parameters except h, results obtained for DKDP predict an isotopic effect in qualitative agreement with the experiment.

SDPC model shows some weaknesses. The obtained $T_c \approx 310$ K for DKDP is much larger than the experimental one and there is no information about the transversal dielectric constant which shows anomaly near T_c. This model was improved recently by introducing 3-dimensional change of the dipole moment [19]. In such modified SDPC model, a dipole of the tetrahedron i is described as a vector $\vec{\mu}_i = (\mu_i^a, \mu_i^b, \mu_i^c)$ with components along crystal axes (a, b, c) [19]. Direct dipole-dipole interaction is neglected, so that neighbouring dipoles which are connected with proton interact only via the ground-state energy of this proton. In the modified SDPC model, two types of tetrahedra (I and II) and four types of protons $(\rho = 1, ..., 4)$ can be distinguished. Tetrahedron of type I can be assigned with index $i'(= 1, ..., N/2)$ and surrounding four protons and tetrahedra of type II with a pair of indices i', ρ. A force $F_{i',\rho}$, which acts on the proton i', ρ along the hydrogen bond has positive value when it points to the positive a or b axis. This is shown in Fig. 1.

The potential energy of the system in the modified SDPC model has the form

$$E_{\rm pot} = \sum_{i=1}^{N}\left[\frac{A_\perp}{2}\left(\mu_i^{a^2} + \mu_i^{b^2}\right) + \frac{A}{2}\mu_i^{c^2}\right] + \sum_{i'=1}^{N/2}\sum_{\rho=1}^{4} E_{i',\rho}^0(\mu_{i'}, \mu_{i',\rho})\,, \tag{3}$$

where $A_\perp$ describes the deformation energy of the tetrahedron when the dipole is induced in the transversal ($\perp c$) direction. The ground-state energy $E_{i',\rho}^0$ depends on the force $F_{i',\rho}$, according to relation (2) from the original SDPC model, while $F_{i',\rho}$ has the form

$$\begin{aligned}
F_{i',1} &= K(\mu^c_{i'} + \mu^c_{i',1}) + K_\perp(\mu^a_{i'} + \mu^b_{i'} + \mu^a_{i',1} - \mu^b_{i',1}) \\
F_{i',2} &= K(-\mu^c_{i'} - \mu^c_{i',2}) + K_\perp(\mu^a_{i'} + \mu^b_{i'} + \mu^a_{i',2} - \mu^b_{i',2}) \\
F_{i',3} &= K(\mu^c_{i'} + \mu^c_{i',3}) + K_\perp(-\mu^a_{i'} + \mu^b_{i'} + \mu^a_{i',3} + \mu^b_{i',3}) \\
F_{i',4} &= K(-\mu^c_{i'} - \mu^c_{i',4}) + K_\perp(-\mu^a_{i'} + \mu^b_{i'} + \mu^a_{i',4} + \mu^b_{i',4})
\end{aligned} \tag{4}$$

where $K_\perp$ is the transversal dipole-proton coupling constant. Using values of parameters A, $A_\perp$, K and $K_\perp$ adjusted to reproduce experimental data for KDP, and by changing only the parameter h, a better value of $T_c \approx 250$ K for DKDP is obtained from Monte Carlo simulation [19]. Also, the anomaly in the transversal dielectric constant is qualitatively reproduced for both materials [19].

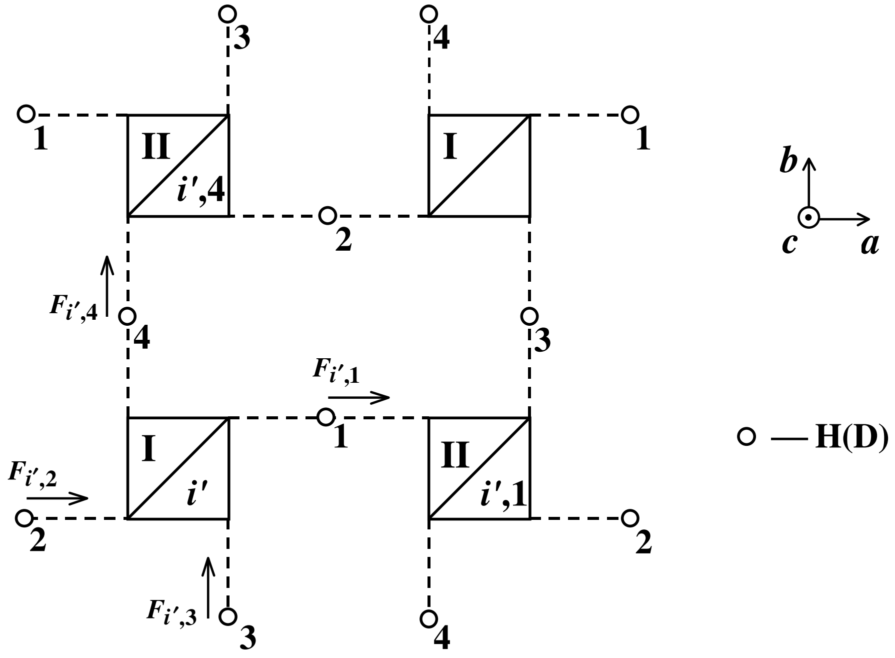

Fig. 1. Simplified projection of KH_2PO_4 *structure on the ab plane. The two types of tetrahedron (I and II) with the corresponding neighbouring protons ($\rho = 1, 2, 3, 4$) are marked. Tetrahedron i' of type I is linked by protons i', ρ to four surrounding tetrahedra i', ρ of type II. Arrows are pointed in the direction of positive forces on protons i', ρ due to induced dipoles.*

3. Model for paramagnetic probes: probe as “soft” impurity

As discussed above, the modified SDPC model has been successfully employed to describe behaviour of hydrogen-bonded ferroelectrics in the vicinity of phase transition and one expects that dynamic properties of paramagnetic impurities in these systems can also be treated within the same model. In the modified SDPC model, anionic paramagnetic probe, such as SeO_4^{3-}, can be described as a dipole moment $\vec{\mu}_0 = (\mu_0^a, \mu_0^b, \mu_0^c)$ which is “soft” for its c component. This means that the tetrahedron of the probe has a more susceptible dipole in c direction than other original tetrahedra. Precisely, parameter A has a lower value for the tetrahedron of the probe ($A_{\mathrm{probe}} = \alpha A, \alpha < 1$), while other parameters are the same as in the original KDP lattice.

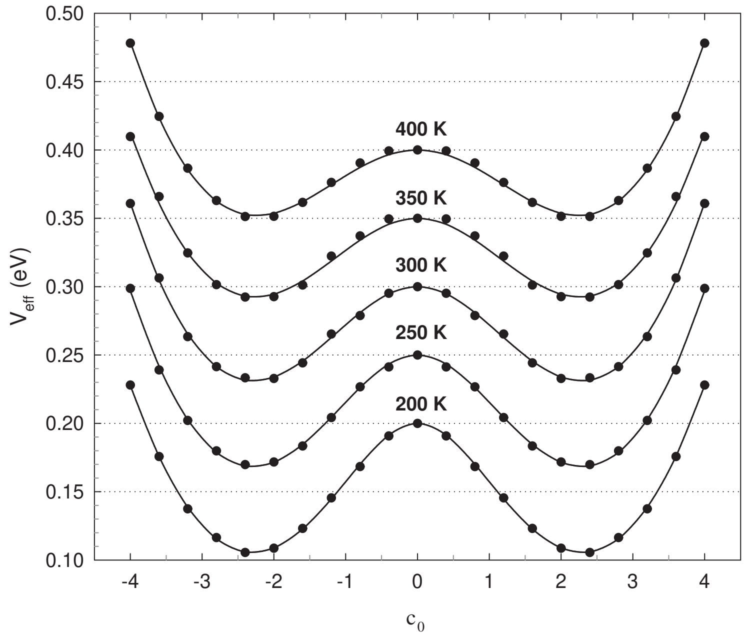

Fig. 2 Effective potentials of the “soft” probe ($\alpha = 0.5$) in modified SDPC model calculated from Monte Carlo simulation (circles) and fitting double-well potentials (full lines).

The Monte Carlo simulation is performed for the “soft” probes described with three different characteristic parameters ($\alpha = 0.6, \alpha = 0.5, \alpha = 0.4$) in the PE phase. The KDP system with the probe was approximated with $N = 108$ dipoles in the lattice network. The probability distribution of the local coordinate $c_0 = \mu_0^c/\mu_s^H$ (μ_s^H is a saturated dipole in KDP) has the form: $\rho(c_0) = Z^{-1}\exp(V_{\mathrm{eff}}(c_0)/kT)$, where $V_{\mathrm{eff}}(c_0)$ is the effective potential. Results for effective potentials are shown in Fig. 2. It can be seen that the effective potential is of the double-well type in a wide temperature range above T_c. The effective potential is well approximated by a double-well potential of form $V_{app}(c_0) = ac_0^2 - \sqrt{d + ic_0^2} + d$, where parameters a, d and i are obtained from best-fit procedure for each temperature. The temperature dependence of energy of barrier can be seen in Fig. 3. The energies become larger as temperature is decreased to T_c.

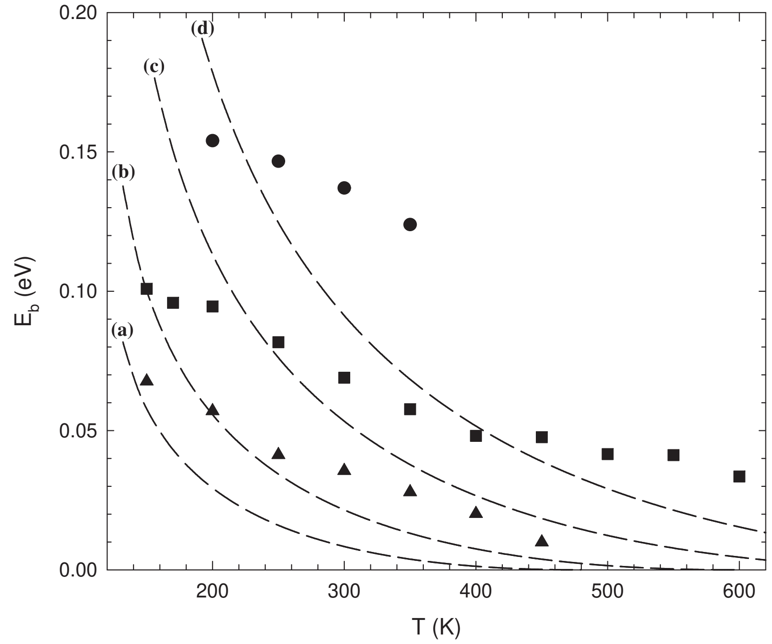

Fig. 3 Energy of barrier in modified SDPC model for $\alpha = 0.6$ *(triangles),* $\alpha = 0.5$ *(squares) and* $\alpha = 0.4$ *(circles). Dashed lines represent the energy of the barrier as a function of temperature in the LMF model for values of parameter (a)* $\widetilde{J}_{q=0} = 0.40$ eV, *(b)* $\widetilde{J}_{q=0} = 0.50$ eV, *(c)* $\widetilde{J}_{q=0} = 0.66$ eV *and (d)* $\widetilde{J}_{q=0} = 0.80$ eV.

The relation $\nu(T) = \omega_0(T)/(2\pi)\exp(-E_b(T)/kT)$ is assumed to be valid for the reorientational frequency of the probe. $E_b(T)$ is the energy of the barrier between two minima and $\omega_0(T)$ is the vibration frequency around the minima ($c_0 = c_{\rm min}$). This leads to

$$\nu(T) = \nu_M \sqrt{f(T)}\, \exp(-E_b(T)/kT)\,, \tag{5}$$

where $2\pi\nu_M = \sqrt{h^{\rm H}/(M\mu_S^{\rm H2})}$ and $h^{\rm H} f(T) = d^2V_{\rm eff}/(dc_0^2)$ for $c_0 = c_{\rm min}$. Here, M is effective mass for the c component of the dipole of the probe. Values of $f(T)$ and $E_b(T)$ are obtained from parameters of the fitting potential. Value of the temperature independent frequency ν_M is adjusted for every α so that $\nu(350\ {\rm K}) = 1/\tau_{\rm exp}(350\ {\rm K})$. Here, $\tau_{\rm exp}$ is the experimentally obtained correlation time for KDP:SeO_4^{3-} system, which follows Arrhenius law with $\tau_0 = 10^{-14}$ s and

$E = 0.19$ eV in the region 130 – 350 K [13]. The results for $\nu(T)$ and $1/\tau_{\rm exp}$ are shown in Fig. 4. The temperature behaviour of frequency $\nu(T)$ can be well described with the Arrhenius law $\nu(T) = \nu_0 \exp(\Delta E/kT)$ in a wide temperature range. ΔE is the activation energy (effective) and ν_0 is the preexponential factor.

To compare the modified SDPC and LMF model for the description of the paramagnetic probe (SeO_4^{3-}) in the KDP lattice the LMF model [10] was employed to evaluate temperature dependence of the energy barrier. These energies are estimated by taking parameters from Ref. [10] and for various values of the interaction between the probe and the lattice dipoles (pseudospins) with which it is coupled ($\widetilde{J}_{q=0}$) (see Fig. 3). The temperature dependence of the reorientational frequency can be also evaluated for this model assuming the relation $\nu(T) = \Omega \exp(E_b(T)/kT)$ with temperature-independent isolated-pseudospin frequency Ω [10]. This frequency is taken as a free parameter to obtain $\nu(350{\rm K}) = 1/\tau_{\rm exp}(350\ {\rm K})$. The results are shown in Fig. 4.

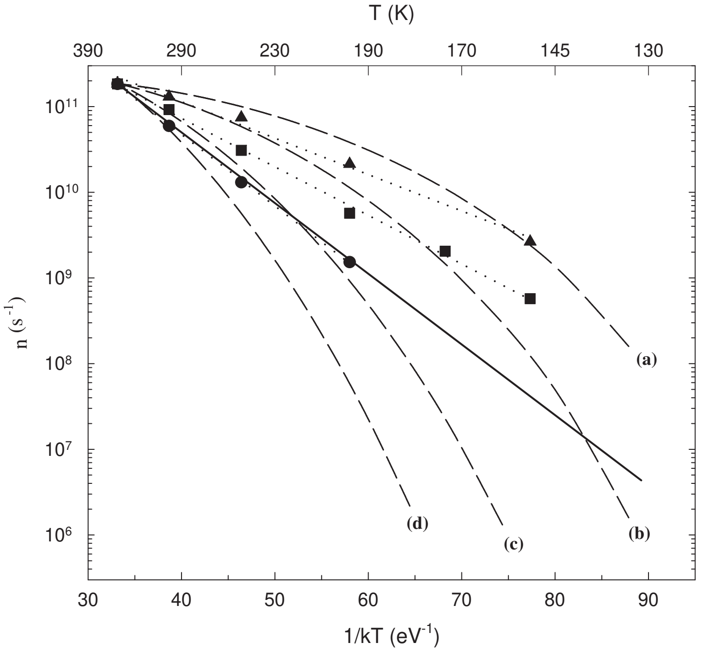

Fig. 4 Reorientational frequency calculated from the effective potential of probe in modified SDPC model for $\alpha = 0.6$, $\nu_M = 6.06\,10^{11}$ s^{-1} (triangles), $\alpha = 0.5$, $\nu_M = 1.64\,10^{12}$ s^{-1} (squares) and $\alpha = 0.4$, $\nu_M = 1.47\,10^{13}$ s^{-1} (circles). Dotted lines represent a fit by the Arrhenius law: $\nu_0 \exp(\Delta E/kT)$. Dashed lines represent reorientational frequency in the LMF model for values of parameters (a) $\widetilde{J}_{q=0} = 0.40$ eV, $\Omega = 2.10\,10^{11}$ s^{-1}, (b) $\widetilde{J}_{q=0} = 0.50$ eV, $\Omega = 2.88\,10^{11}$ s^{-1}, (c) $\widetilde{J}_{q=0} = 0.66$ eV, $\Omega = 6.60\,10^{11}$ s^{-1} and (d) $\widetilde{J}_{q=0} = 0.80$ eV, $\Omega = 1.84\,10^{12}$ s^{-1}. Full line represents experimentally obtained value of $1/\tau$ in the region 130 – 350 K for SeO_4^{-3} in KDP (taken from Ref. [13]).

4. *Discussion and conclusion*

In the early study [20] of the thermal fluctuations of impurities in the ferroelectric crystals, two major types of impurities are classified. In the PE phase, one distinguishes on-center and off-center type of impurities. The first type of impurities is characterized by a single-peaked probability distribution, and a single time scale governs its dynamics. The second type of impurities shows multiple-peaked distribution and a dynamics governed by two time scales which is connected with the oscillation in the off-center minimum and thermally activated hopping. The anionic probe, such as SeO_4^{3-}, can be treated as an off-center type impurity, which fluctuates between the off-center positions with an Arrhenius behaviour at temperature $T > T_c$. On the other side, the earlier proposed LMF model [10] for SeO_4^{3-}, which includes strongly temperature dependent activation energy, is less suitable to describe dynamical behaviour of the probe as can be seen in Fig. 4. The experimentally detected inverse correlation time exhibits nearly constant value of activation energy (within 10% of experimental error) in a wide temperature interval ($T > T_c$) and strongly deviate from the calculated LMF values of the reorientational frequency. In this model, ferroelectric crystal and paramagnetic defect are described as systems of pseudospins (Ising-type) where mean-field approximation was introduced to obtain the statistical properties of the system. In order to reach temperature dependence of activation energy, one should employ strong short-range forces which couple a defect and surrounding pseudospins. These forces are significantly stronger (about 13 times for $\widetilde{J}_{q=0} = 0.66$ eV) than the interaction forces in the undisturbed lattice. According to the modified SDPC model, the largest part of the activation energy arises from the local potential of the probe produced by strongly coupled protons, and a smaller part has a source in the temperature-dependent contribution. The temperature-dependent contribution is expected due to the interaction with other neighbouring dipoles. In Fig. 4, it is shown that, by changing the essential dipole coupling parameter ($\widetilde{J}_{q=0}$) and dipole deformation parameter (a) for the corresponding model, the experimental data can be better approximated within the modified SDPC model.

As it was clearly demonstrated, a polarization fluctuation in PE phase is detected as an effective activation process by the anionic probe. In this process ΔE is a temperature independent parameter and can not be simply decomposed to $f(T)$ and $E_b(T)$, temperature dependent parameters of the effective potential of the probe. This is the important finding and gives us the possibilities to reach more reliable dynamical parameters detected by the EPR probe in KDP-type of ferroelectrics.

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MODEL PARAMAGNETSKE PROBE U FEROELEKTRICIMA S VODIKOVIM VEZANJEM

Primijenili smo izmijenjeni model jakog vezanja i Monte Carlo račun za opis paramagnetskog defekta vodikom-vezanog feroelektika. U ovom se modelu proba uzima kao "meka" dipolna nečistoća u sustavu $N = 108$ dipola. Izvodi se efektivan potencijal tipa dvojne jame i proučava njegova temperaturna ovisnost u paraelektričnoj fazi. Pokazuje se kako se eksperimentalno opažena aktivacijska energija polarizacijske fluktuacije probe SeO_4^{3-} može povezati s efektivnom aktivacijskom energijom. Ovaj se model uspoređuje s ranije predloženim modelom lokalnog "pseudo zamrzavanja" koji pokazuje veća odstupanja od eksperimentalnih podataka nego predloženi izmijenjen model jakog vezanja dipol-proton.