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Modified strong-dipole proton-coupling model for hydrogen-bonded ferroelectrics

D. Merunka and B. Rakvin
Ruđer Bošković Institute, P.O. Box 1016, 10001 Zagreb, Croatia

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The ferroelectric phase transition of hydrogen-bonded ferroelectrics, KH_2PO_4-type, was investigated by employing a model of the strong-dipole proton coupling (SDPC). Besides the change of the dipolar component along the c axis, which was earlier considered within the original SDPC model, the continuous three-dimensional changes of the dipole were introduced in the model. The influence of these changes on the ferroelectric phase transition was examined by employing Monte Carlo calculation. It is shown that the experimental data for the spontaneous polarization along the polar c axis are better described with such a modified SDPC model in the vicinity of the ferroelectric transition temperature, T_C, than with the original SDPC model. The additional superiority of the modified model compared to the original is the ability to describe experimentally detected discontinuity in the transversal dielectric constant around T_C. It is also demonstrated that the modified SDPC model reduces the gap between the previously calculated and the experimentally detected T_C of KD_2PO_4 ferroelectric.

INTRODUCTION

The ferroelectric phase transition of the hydrogen-bonded ferroelectrics such as KH_2PO_4 (KDP) is not yet fully understood. One of the simplest, but a powerful test for the newly proposed theoretical models, is a simple $H \rightarrow D$ isotope exchange. When H is replaced by D, KDP-type crystal shows a large shift in the ferroelectric phase transition temperature, T_C, from 122 to 220 K. As is well known, the first suggested statistical theory[1] of the phase transition based on the order-disorder mechanism in the proton configurations is not able to describe this isotope effect. Later, the model of the proton tunneling in the double minima potential has been proposed by Blinc[2] and widely accepted. From the new detailed structural data for KDP-type lattices it is noted[3–6] that the bond length itself is related with the isotope effect. These facts have been used as a basis for a model known as ''geometrical model.'' However, this simple model cannot explain the absence of the phase transition in the so-called zero-dimensional hydrogen-bonded ferroelectrics.[7,8] Moreover, it was suggested that the phase transition arises due to the order-disorder mechanism of the tetrahedral PO_4 group.[9]

Recently, a model for the phase transition involving the geometrical properties and the strong dipole-proton coupling, SDPC model, was developed by Sugimoto and Ikeda.[10] In the model PO_4 tetrahedron was treated as a dipole. This involves that the proton dynamics is described in the asymmetric double-well type potential and the isotope effect is described without the effect of proton tunneling. Besides a new explanation for the isotope effect, the SDPC model was used to calculated the distribution of excitation energies of proton.[11] It was found that these energies are related to the excitation energies obtained by the inelastic neutron-scattering experiment. The same model was also adapted to solve a problem of the isotope effect detected by the paramagnetic probes in KDP-type of crystal.[12] By employing the SDPC model it was possible at least qualitatively to describe the changes of the polarization fluctuation in the vicinity of probe due to the isotope effect.[12]

Besides these successes, SDPC model exhibits some weaknesses.[10,11] For example, one cannot describe the temperature behavior of the transversal dielectric constant because the interaction of the proton and the dipole moment of PO_4 tetrahedron is considered only for the distortion of the tetrahedron, i, with the corresponding electric dipole moment, μ_i, along the c axis. It can be also noted[10] that the obtained value of T_C for KD_2PO_4 (DKDP) is shifted at much higher temperature (458 K) than is experimentally measured (220 K). In the process of theoretical considerations of the inelastic neutron-scattering in KDP and DKDP crystals[11] results of the SDPC model was improved by introducing Monte Carlo simulations, instead of simple mean field approximation (MFA) in the treatment of the dipoles along the c axis. Recently, Fujii[13] discussed importance of the interaction between dipolar components perpendicular to the c axis and protons. In the rotator-proton model suggested by Fujii[13] the electric polarization arises from tetrahedral groups which are described by orientation rotators with six directions and protons mediate interactions between the neighboring PO_4^{3-} groups. The parameters of the rotator-proton model are estimated by employing the MFA. Inside of the model the isotope effect was explained by assuming the difference of rotator-proton (deuteron) coupling constants, without introduction of tunneling. An important difference between the rotator-proton model and SDPC model should be pointed out. For the rotator-proton model the four configurational proton energies around PO_4 groups are deduced directly through the fitting procedure while in the SDPC model energies of proton states are obtained by quantum mechanical calculations in the double-well potential.[10]

The additional improvements of the SDPC model have been investigated in this study. From the above consideration it can be noted that one of the possible improvements of the model can be based on an unrestricted change of a dipole in all directions and not only along the c axis, as was proposed in the original SDPC model.[10] This expansion implies a more realistic description of the dipole network in the KDP-type lattice. The temperature behaviors of both components of

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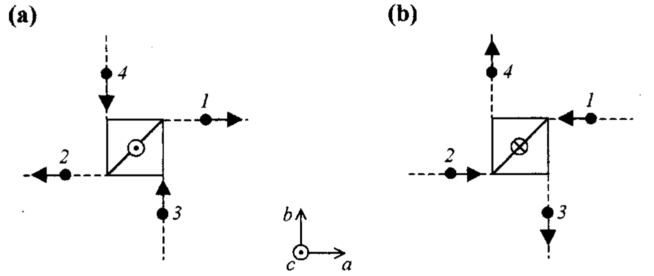

FIG. 1. Schematic structure of PO_4^{3-} tetrahedron and its dipole moment with the corresponding direction of the forces on neighbor protons: (a) tetrahedron dipole along the c direction; (b) tetrahedron dipole along the $-c$ direction.

polarization (along the c axis and perpendicular to the c axis) have been calculated and compared to the experimental values and also to the obtained values from the previously suggested models. It is shown that the obtained changes in this modified SDPC model leads to the significant decrease in the discrepancy between the measured and the calculated T_C for DKDP lattice.

PARAMETERS FOR THE MODIFIED STRONG-DIPOLE PROTON-COUPLING MODEL

Regarding the originally suggested SDPC model there are two major improvements which could lead to a more accurate thermodynamic parameters. The first possibility is to include the low lying excited proton states and the second is to introduce the unrestricted changes of a dipole in all directions. One expects that because of the high excitation energy levels in the proton potential the first effect will not give significant improvements for the thermodynamical properties of the model in the vicinity of phase transition. Therefore, the second improvement that allows the changes of a dipole in all directions has been chosen for the closer examination.

A spontaneous polarization in a three-dimensional hydrogen bond network such as KDP-type crystal appears along c axis while hopping and eventually localization of protons is along the a (or b) axis. In the SDPC model a dipole moment of PO_4 group contribute only along the c axis and for a possible contributions in other directions it will be described as a vector $\boldsymbol{\mu}_i = (\mu_i^a, \mu_i^b, \mu_i^c)$ with the components along the crystal axis (a, b, c). A polarization along the c axis can be simply related to the proton position around the tetrahedron,[14] as shown in Fig. 1. In the ferroelectric (FE) phase for the polarization along the positive direction of c, the lower protons (denoted as 3 and 4 in Fig. 1) are closer to oxygen atoms on the tetrahedron than the upper protons (denoted as 1 and 2 in Fig. 1). In the SDPC model[10] a proton position and ground-state energy directly depends on interaction with the two neighbor dipoles and it is described as the force, $F_{ij} = K(\mu_i + \mu_j)$, along oxygen-hydrogen-oxygen bond, x, with constant of proportionality, K. In terms of the interaction one can also conclude (Fig. 1) that a tetrahedron dipole repulses protons when it is pointed to the oxygen atoms to which these protons are bonded and attracts protons when it is pointed to the opposite direction. By the analogy for $\pm$c dipole directions the proton configurations and directions of the acting forces are also introduced for $\pm a$ and $\pm b$ dipole orientations, as shown in Fig. 2. According to the model[10] a new constant of proportionality, $K_\perp$, of the proton-dipole interaction can be introduced for these dipole directions.

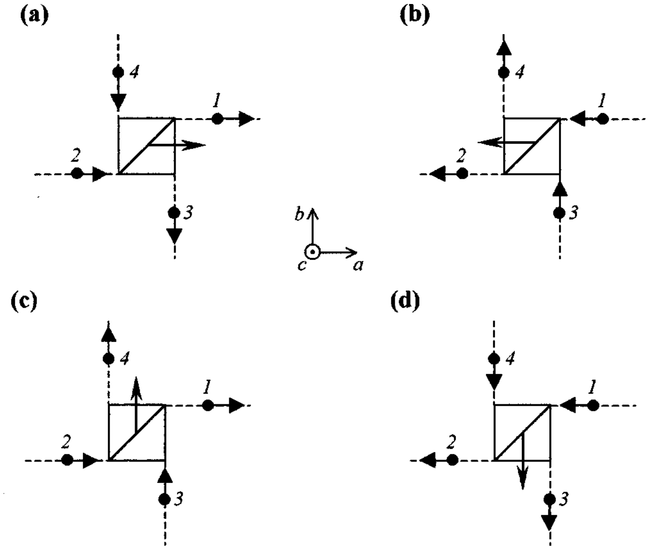

FIG. 2. Schematic structure of PO_4^{3-} tetrahedron and its dipole moment with the corresponding direction of the forces on the neighbor protons: (a) tetrahedron dipole along the a direction, (b) tetrahedron dipole along the $-a$ direction, (c) tetrahedron dipole along the b direction, and (d) tetrahedron dipole along the $-b$ direction.

In order to describe potential energy E_{pot} for such expanded model of N distorted tetrahedra connected with $2N$ hydrogen bonds, it is convenient to use schematic structure of KDP shown in Fig. 3. In Fig. 3 two types of tetrahedra (denoted as I and II) and four types of protons ($\rho = 1, 2, 3, 4$) can be noted. The tetrahedron I in the case of dipole direc-

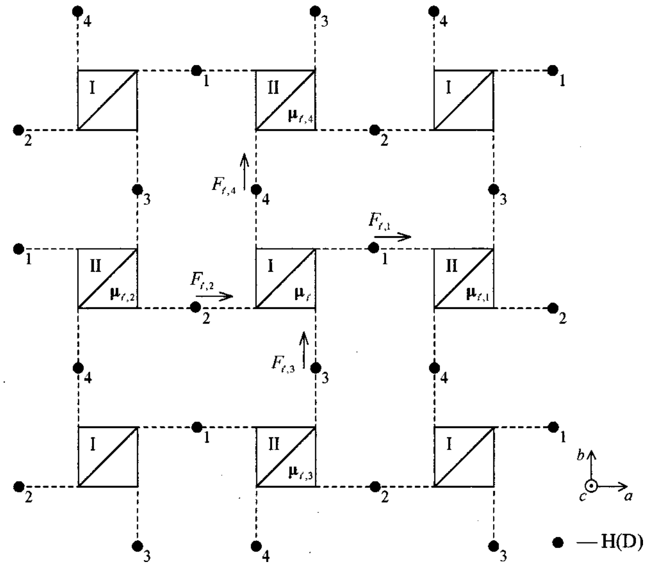

FIG. 3. Simplified projection of KH_2PO_4 structure on the ab plane. The two types of tetrahedron (I and II) with the corresponding neighbor protons ($\rho = 1,2,3,4$) are denoted. A dipole $\boldsymbol{\mu}_{i'}$ of type I tetrahedron i' is assigned together with dipoles $\boldsymbol{\mu}_{i',\rho}$ of four surrounding type II tetrahedra i', ρ. Arrows are pointed in the direction of positive forces on protons i', ρ due to induced dipoles.

TABLE I. Parameters and results of the modified SDPC model ($\mu_s^H = 4.8\times 10^{-30}$ C m).

	h eV	A $h^H/(\mu_s^H)^2$	IK h^H/μ_s^H	$A_\perp$ $h^H/(\mu_s^H)^2$	$IK_\perp$ h^H/μ_s^H	κ K	μ_s/μ_s^H	T_c K	C K
KDP	0.110	1.84	0.6	0.11	0.135	1948	1.0	120	2600
DKDP	0.058	1.84	0.6	0.11	0.135	1925	1.2	250	2900

tion along +a axis, repulses protons 1 and 3 and attracts protons 2 and 4. Similarly, the tetrahedron II repulses protons 2 and 3 and attracts protons 1 and 4 for the same dipole direction. Tetrahedra in the lattice are denoted as i, ($i = 1,...,N$), and type I tetrahedra are denoted as i', ($i' = 1,...,N/2$). Each tetrahedron of the type I is connected to four tetrahedra of the type II by the proton of type ρ. Therefore, the dipoles of type II can be described with the pair of the indices i',ρ. The same pair of the indices are used for the proton and for the force description.

For an arbitrary orientation of neighboring dipoles a force on proton is constructed from special cases showed in Fig. 1 and Fig. 2 and can be written in a form

$$\begin{aligned} F_{i',1} &= K(\mu_{i'}^c + \mu_{i',1}^c) + K_\perp(\mu_{i'}^a + \mu_{i'}^b + \mu_{i',1}^a - \mu_{i',1}^b),\\ F_{i',2} &= K(-\mu_{i'}^c - \mu_{i',2}^c) + K_\perp(\mu_{i'}^a + \mu_{i'}^b + \mu_{i',2}^a - \mu_{i',2}^b),\\ F_{i',3} &= K(\mu_{i'}^c + \mu_{i',3}^c) + K_\perp(-\mu_{i'}^a + \mu_{i'}^b + \mu_{i',3}^a + \mu_{i',3}^b),\\ F_{i',4} &= K(-\mu_{i'}^c - \mu_{i',4}^c) + K_\perp(-\mu_{i'}^a + \mu_{i'}^b + \mu_{i',4}^a + \mu_{i',4}^b). \end{aligned} \tag{1}$$

A force is positive when points to the positive *a* (or *b*) axis. For the induced dipole along the *c* axis an elastic deformation energy is described with the parameter A ($A > 0$).[10] In expanded model a new additional parameter $A_\perp$ for induction dipole in the perpendicular direction has been introduced. The importance of the effect of the transversal dipole interaction is emphasis in this study, therefore the previously introduced direct dipole-dipole interaction can be neglected in the comparison to the transverse contribution in further consideration. Thus, the potential energy for system of N dipoles and $2N$ hydrogen bonds in the modified model is obtained:

$$\begin{aligned} E_{\text{pot}} = {} & \sum_{i=1}^{N}\left[\frac{A_\perp}{2}(\mu_i^{a^2} + \mu_i^{b^2}) + \frac{A}{2}\mu_i^{c^2}\right]\\ & - \sum_{i'=1}^{N/2}\sum_{\rho=1}^{4}\left(\sqrt{h^2 + I^2F_{i',\rho}^2} - h\right). \end{aligned} \tag{2}$$

The first term describes the elastic deformation energy of the tetrahedra for an induction of dipole in the arbitrary direction (A, $A_\perp > 0$) and the second term describes the ground state energy of $2N$ protons or deuterons. The parameter h describes the effect of mass (H or D) and the geometric effect while the parameter I is approximately the same for the both lattice ($I = 0.22$ Å). The four parameters (A, $A_\perp$, IK, and $IK_\perp$) should be obtained from the experimental data for KDP lattice. It can be shown that A and IK can be easily deduced from the same experimental parameters as for the standard SDPC model. The perpendicular parameters $A_\perp$ and $IK_\perp$ are determined by condition that Monte Carlo simulation reproduced expected experimental data for KDP, $T_C \sim 120$ K and $\varepsilon_a \sim 59$ at 140 K.[15] All used and calculated parameters are collected in Table I.

Monte Carlo calculations have been employed for KDP and DKDP lattices with N dipoles by imposing periodic boundary conditions and by using Metropolis importance sampling method.[16] Dimensionless parameters s_a and s_c are used to define the polarization along the *a* and along the *c* direction and they are defined as

$$\begin{aligned} s_a &= \frac{1}{N\mu_s^H}\sum_{i=1}^{N}\mu_i^a,\\ s_c &= \frac{1}{N\mu_s^H}\sum_{i=1}^{N}\mu_i^c. \end{aligned} \tag{3}$$

By employing these parameters the polarization components are obtained: $P_\alpha = \mu_s^H s_\alpha / V_d (\alpha = a,b,c)$, where V_d represents the space occupied by one dipole and μ_s^H is saturated dipole moment for KDP. Monte Carlo calculation is used to evaluate the temperature dependent distribution functions $P_N(s_a)$ and $P_N(s_c)$. Average over the distribution functions for the absolute values is denoted as $\langle |s_c| \rangle_N$. In this notation the spontaneous polarization is defined as

$$P_c(T) = \frac{\mu_s^H}{V_d}\lim_{N\to\infty}\langle |s_c| \rangle_N. \tag{4}$$

It can be shown that the dielectric constant along the *a* axis is given:

$$\varepsilon_a(N,T) = \varepsilon_\infty + \frac{\kappa}{T}N\langle s_a^2 \rangle_N, \tag{5}$$

where κ is the constant depending on the lattice parameters (for KDP $\kappa = 1948$ K and for DKDP $\kappa = 1925$ K) and $\varepsilon_\infty = 12$ is the high frequency dielectric constant for KDP.[13] In the paraelectric (PE) phase a dielectric constant along the *c* axis is given as

$$\varepsilon_c(N,T) = \varepsilon_\infty + \frac{\kappa}{T}N\langle s_c^2 \rangle_N, \tag{6}$$

Similarly, in the FE phase where the order parameter is different from the zero ε_c is given as

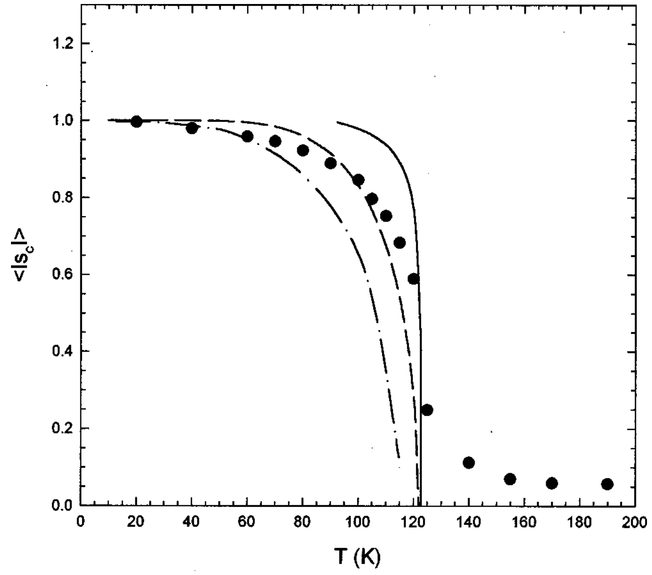

FIG. 4. Monte Carlo calculation of the temperature dependence of $\langle|s_c|\rangle$ parameter for the KH_2PO_4-type lattice with $N=500$ dipoles (full circles). The solid line represents the experimental data for the relative polarization of KH_2PO_4. The dashed line represents the order parameter calculated from the rotator-proton model and the dashed-dotted line represents the same parameter calculated from the original SDPC model.

$$\varepsilon_c(N,T)=\varepsilon_\infty+\frac{\kappa}{T}N(\langle s_c^2\rangle_N-\langle|s_c|\rangle_N^2). \tag{7}$$

Monte Carlo calculations were performed on the KDP lattice with $N=500$ dipoles. For the dipole components along the a axis and along the b axis the random values are taken between $-12\mu_s^H$ and $+12\mu_s^H$ and for the component along the c axis between $-3\mu_s{}^H$ and $+3\mu_s^H$. The average was calculated for a certain temperature from the data of 10^5 to 5×10^5 Monte Carlo steps.

The order parameter $\langle|s_c|\rangle$ exhibits temperature dependence as shown in Fig. 4 (full circles). In Fig. 4 the temperature dependence of the experimentally obtained relative polarization as well as the theoretically obtained order parameters from the rotator-proton model[13] and data from the previous Monte Carlo calculation in the SDPC model[11] are shown. The results from the modified SDPC model show better description of the experimental results than the earlier SDPC results. Moreover, in the near vicinity of T_C the modified SDPC model exhibits better agreement with experiment than the rotator-proton model.[13] A discontinuity at T_C indicates the first order type of phase transition behavior as was experimentally detected[14] and theoretically discussed earlier.[17]

For the same numbers of dipoles the temperature dependence of the transversal component of the dielectric constant is calculated by employing relation (5) and shown in Fig. 5. The model calculation shows a small discontinuity at T_C and a good agreement with the experiment[15] in the PE phase while a poor agreement can be seen in the FE phase. This is opposite to the rotator-proton model[13] where a better agreement is in the FE than in the PE phase.

Longitudinal dielectric constant is calculated from relation (6) for $T\geqslant125\,\mathrm{K}$ and with relation (7) for $T\leqslant120\,\mathrm{K}$. Results for ε_c and ε_c^{-1} are shown in Fig. 6 and in the PE phase these results can be fitted to Curie-Weiss law. The obtained constants ($C=2600\pm200\,\mathrm{K}$ and $T_0=121.5\pm0.3\,\mathrm{K}$) are in a good agreement with the experimental values.[14] In the FE phase one can also use the similar temperature dependence as for Curie-Weiss law with negative constant value ($C=-660\pm40\,\mathrm{K}$ and $T_1=130.9\pm0.8\,\mathrm{K}$). The discontinuity in the dielectric constant at T_C and the difference in T_0 and T_1 temperature where $T_0<T_C<T_1$ clearly support the first order of the phase transition.

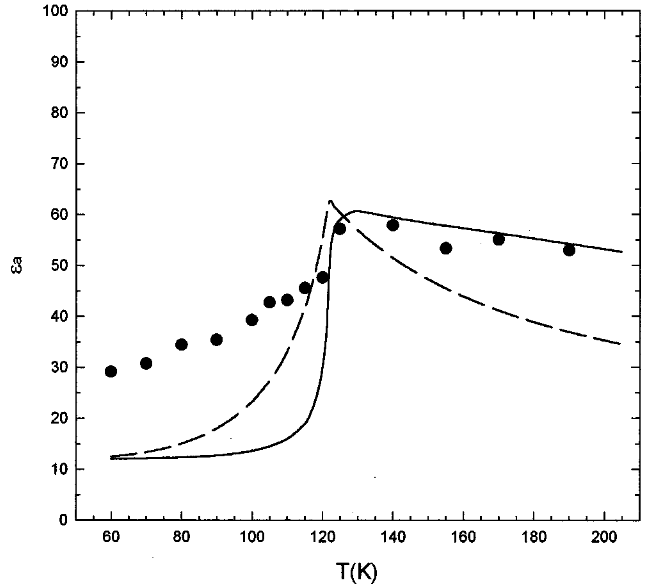

FIG. 5. Temperature dependence of the transversal dielectric constant for KH_2PO_4, calculated from the modified SDPC model (full circle), experimental data (solid line), and calculated from the rotator-proton model (dashed line).

Monte Carlo calculation for the DKDP lattice is provided on $N=846$ dipoles network. All parameters A, $A_\perp$, IK, and $IK_\perp$ are the same as for KDP except parameter h which was taken from the original SDPC model.[10] For the dipole components along the a axis and along the b axis the random values are taken between $-14\mu_s^H$ and $+14\mu_s^H$ and for the component along the c axis between $-4\mu_s^H$ and $+4\mu_s^H$. The number of Monte Carlo steps is $\sim10^5$. The simulated parameter $\langle|s_c|\rangle$ is shown in Fig. 7 and can be compared with the relative longitudinal polarization for DKDP. As is well known, the experimentally measured longitudinal polarization shows sharp phase transition at 220 K.[15] Comparing the calculated and the experimental results one notes that the calculated transition behavior does not exhibit sharp transition as experimental data in the temperature interval around T_C. However, the obtained phase transition temperature $T_C\sim250\,\mathrm{K}$ is significantly lower than the calculated one ($T_C=310\,\mathrm{K}$) in the standard SDPC model.[11] Similarly, as in the case of KDP, the longitudinal component of the dielectric constant can be calculated and Curie-Weiss constant is deduced ($C=2900\pm300\,\mathrm{K}$ and $T_0=245\pm1\,\mathrm{K}$). All employed and calculated parameters for KDP and DKDP lattices in this modified model are collected in Table I.

DISCUSSION AND CONCLUSION

It was shown[11] that if SDPC model were treated under the assumption of permanent dipoles, this would lead to an

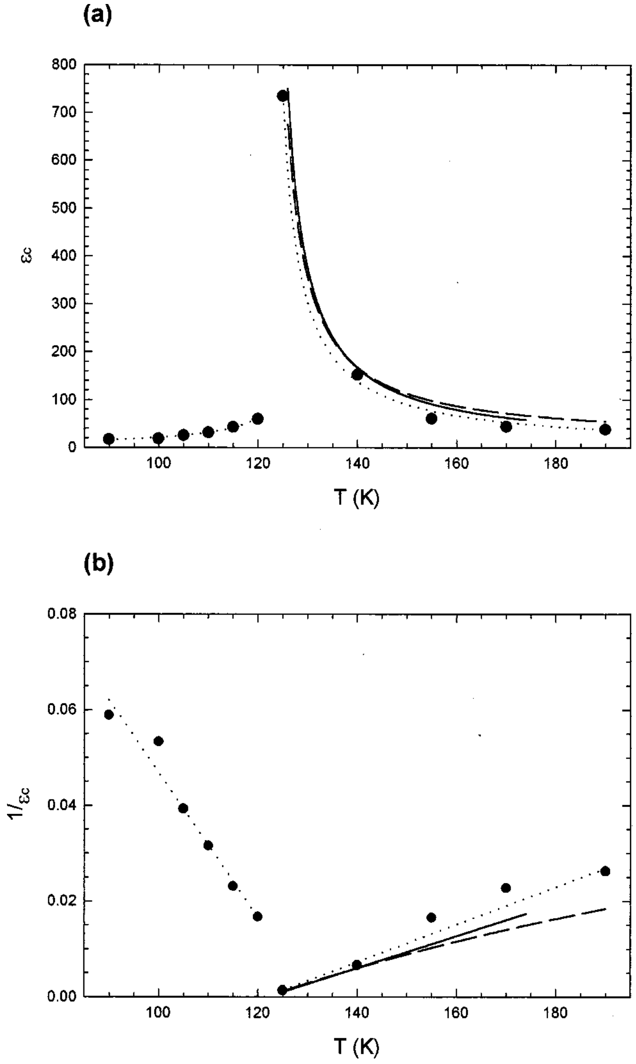

FIG. 6. Temperature dependence of the longitudinal dielectric constant (a) and the inverse of the longitudinal dielectric constant (b) for KH_2PO_4, obtained from the modified SDPC model (full circle), experimental data (solid line), obtained from the rotator-proton model (dashed line), and the best fit of the modified SDPC model (dotted line).

Ising-type model. Calculated results show that such a model is poor.[10,11] Therefore, the simple continuous change of dipoles along the c axis in the SDPC model should be taken into account. Besides the significant success of the SDPC model[10–12] such model shows no any lateral polarization effect. Further step in expansion of the model is to assume a change of dipole in the directions perpendicular to polar axis. In this study the model with the continuous three-dimensional changes of the dipole in KDP-type lattice was implanted in the SDPC model. The anomalous behavior of the transversal dielectric constant in the vicinity of T_C was qualitatively predicted by employing the modified SDPC model. Moreover, the calculated order parameter shows a discontinuity and better fit of the experimental data than the original SDPC model. This better fit to the experimental data indicates that coupling of order parameter to the transverse dipole components can be responsible for the first order nature of phase transition in KDP. It can be noted that the first order nature of phase transition in KDP crystals was explained as a consequence of the term in potential energy which comes from long-range polarization forces[18] or from the mechanical energy associated with the shear strain which accompanies the polarization.[17] However, for more detailed approach to order of phase transition more sophisticated Monte Carlo methods are required.[19]

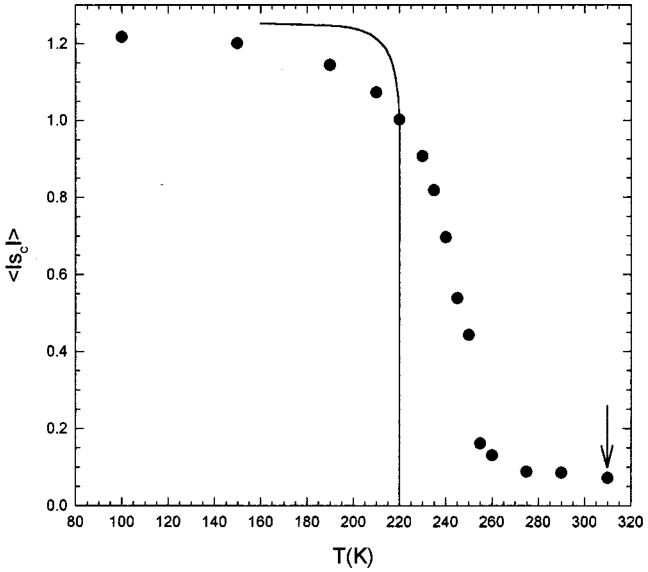

FIG. 7. Monte Carlo calculation of the temperature dependence of $\langle |s_c| \rangle$ parameter for the KD_2PO_4-type lattice with $N=864$ dipoles (full circles). The solid line represents experimental data for the relative dielectric constant of KD_2PO_4. The arrow denotes the temperature position of the phase transition obtained by the original SDPC model.

Improvements in the description of the critical effects in KDP lattice also have an impact on much accurate description of the isotope effect. Thus, the isotope effect can be seen as a strong support for the modified SDPC model. Employing similar criteria one can also tests the quality of the other alternative models. For example, in the recent model for the phase transition in KDP (DKDP) lattice,[20] which is based on the interplay between the tunneling motion of the protons (deuterons), the polarizability change of the neighboring PO_4 groups and the geometrical effects of hydrogen bonds the T_C for DKDP lattice is predicted on 168 K. Thus the obtained difference between predicted and experimentally obtained T_C in this model exhibits larger deviation (~ 55 K) than for the modified SDPC model.

Efficiency of the modified SDPC model to predict the isotope effect of the saturation of polarization, critical temperature and Curie-Weiss constant indicates that this model can be also used for more detailed descriptions of the short-range type interaction around the dipole. A paramagnetic probe is usually employed for the study of slow-motional dynamics in the PE phases of the hydrogen-bonded ferroelectrics. By applying the modified model a probe can be treated as a dipole with different parameters than the original one. One expects that such treatment would lead to more accurate description than it was obtained earlier by employing original SDPC model.[12]

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