Displacive and order–disorder behavior of KDP-type ferroelectrics on the local scale

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Abstract

The modified strong dipole–proton coupling (MSDPC) model, which predicted several static and dynamic dielectric properties of KH_2PO_4 or KDP-type ferroelectrics, was used to investigate the properties of these crystals on the local scale. Results calculated by molecular dynamics (MD) simulation show that both order–disorder and displacive characteristics of one PO_4 dipole are present in KDP and KD_2PO_4 (DKDP). These results correlate with experimental data from NMR and neutron scattering studies of local properties.
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1. Introduction

The real nature of the ferroelectric phase transition and the isotope effect on T_c for $H \rightarrow D$ exchange in KH_2PO_4 or KDP-type ferroelectrics has not been fully explained [1–3]. The proton tunneling model [4], the earliest model used to explain the isotope effect, predicted the displacive type of phase transition. More recent crystal lattice dynamics measurements, on the other hand, have suggested the order–disorder mechanism of phase transition, as extensively discussed elsewhere [2,3].

It was early recognized that pure protonic models are not sufficient to explain ferroelectric properties of KDP and KD_2PO_4 (DKDP). As recently shown by ab initio calculation [5], motion of heavy atoms coupled to protons or deuterons has to be taken into account to obtain more realistic model. Moreover, several experiments clearly supported the existence and importance of the PO_4 dipole order–disorder motion [2,3]. One of such experiments was the neutron diffraction measurement of refined thermal parameters for heavy atoms [6], as pointed out in Ref. [3]. Temperature dependence of mean square displacement of central P atom along ferroelectric c-axis indicates moving of P atom between two sites in paraelectric phase and thus suggests order–disorder motion of the whole PO_4 tetrahedron. On the other hand, an order–disorder model for PO_4 dipoles does not provide an explanation of the isotope effect in T_c; therefore, it is usually assumed that so called 'geometric' isotope effect, or the change of hydrogen bond geometry by deuteration, is responsible for that effect. Additionally, a pure (Ising-type) order–disorder model for PO_4 dipoles cannot explain chemical shift measurements of ^{31}P by high resolution NMR, which indicates that the displacive component, apart from the order–disorder one, is also involved in phase transitions [7].

According to the new strong dipole–proton coupling (SDPC) model, protons adiabatically follow dynamics of PO_4-dipoles aligned along c-axis, without tunneling motion [8]. The isotope effect in T_c is attributed to the difference in calculated ground state energy between proton and deuteron in the hydrogen bond potential due to different masses and hydrogen bond lengths in the two cases. By involving the change of the PO_4-dipole in all directions, the SDPC model has been additionally improved [9]. This modified strong

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dipole–proton coupling (MSDPC) model describes the static dielectric properties of the crystal better than the original SDPC model. By employing molecular dynamics (MD) simulation based on the MSDPC model for KDP and DKDP, the major inconsistencies [2] are removed between the lattice dynamics experiments and theoretical predictions for the 'soft mode' dynamics, which characterize the proton tunneling model [10]. Furthermore, this model can reproduce some additional experimental features, such as transversal (perpendicular to c-axis) polarization dynamics and pressure-induced change of the central peak (CP) lineshape [10].

The MSDPC model predicts mixed order–disorder and displacive behavior of polarization dynamics in KDP and DKDP. The order–disorder behavior is dominant near T_c and crossover to dominant displacive behavior appears at temperatures far from T_c [10]. The purpose of this letter is to examine properties of the MSDPC model on the local scale, i.e. properties of one PO_4 dipole, and to compare calculated data with investigations of local properties by neutron scattering [6], NQR [11] and recent NMR [7] experiments.

2. Results and discussion

The MSDPC model with parameters defined previously [9,10] is used to investigate the local properties of KDP and DKDP. MD simulation, whose details are described in Ref. [10], is performed on the cubic sample of the crystals of KDP and DKDP with $n \times n \times n$ unit cells or $4n^3$ PO_4 dipoles.

The local order parameter for PO_4 dipole at site i is defined as the quantity $c_i = \mu_i^c / \mu_s^H$, i.e. as the ratio of dipole c-component μ_i^c and the saturated dipole value for KDP $\mu_s^H = 4.8 \times 10^{-30}$ C m. The thermal distribution of local order parameter for one PO_4 dipole c_i is calculated in KDP and DKDP. In the paraelectric phase above T_c ($T_c \approx 120$ K for KDP and $T_c \approx 250$ K for DKDP in the MSDPC model), calculated distributions show maximum on zero value of c_i, which is one of the characteristics of displacive behavior. Mean-square deviation of quantity c_i from the mean value $\langle c_i \rangle$ or $\langle \Delta c_i^2 \rangle = \langle (c_i - \langle c_i \rangle)^2 \rangle$ is calculated for the KDP and DKDP systems with $n = 4$ or 256 PO_4 dipoles (Fig. 1). The calculated temperature dependence of $\langle \Delta c_i^2 \rangle$ can be approximated with the linear temperature dependence $\langle \Delta c_i^2 \rangle \approx \Delta + \gamma T$ well above T_c (Fig. 1). This behavior supports existence of the temperature-independent constant Δ, which has a larger value for DKDP than for KDP ($\Delta^D / \Delta^H \approx 2.2$). The fast decrease in $\langle \Delta c_i^2 \rangle$ below T_c can be interpreted as the loss of temperature-independent constant Δ in the ferroelectric phase. These characteristics of temperature dependence of $\langle \Delta c_i^2 \rangle$ support the order–disorder type of phase transition.

It can be assumed that induction of PO_4 dipole along ferroelectric c-axis is related to the shift of central P atom

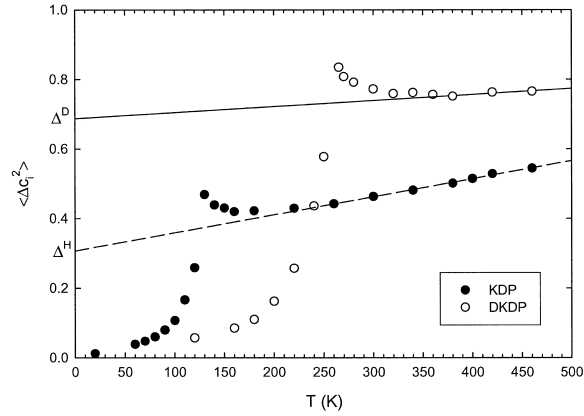
Fig. 1. Temperature dependence of $\langle \Delta c_i^2 \rangle$ obtained by the molecular dynamics simulation on KDP and DKDP system with $n = 4$. Lines denote best fits to the linear temperature dependence at high temperatures.

along the same axis. As neutron scattering experiments provide information on the thermal distribution of motion of this atom, calculated results for $\langle \Delta c_i^2 \rangle$ can be compared with the results for the mean-square thermal motion of P atom along c-axis $u^{33}(P)$ obtained by the neutron scattering experiment [6]. Parameter $u^{33}(P)$ shows linear temperature dependence in paraelectric phase with non-zero extrapolated value at $T = 0$ K, which is larger in DKDP than in KDP by a factor of about 2, indicating that P atom moves between two sites. Obviously, this non-zero extrapolated value can be related to parameter Δ from the MSDPC model. In such an order–disorder picture for motion of P atom, it is expected that below T_c P atom is placed at one site, which results in the decrease of $u^{33}(P)$ below T_c. Experimental data for $u^{33}(P)$ confirmed the predicted behavior on cooling through T_c [6], which was also in accordance with calculations from the MSDPC model.

In the rigid order–disorder model of the Ising type for KDP, the PO_4 dipole can have two values: $c_i = +1$ or -1. In such an extreme order–disorder situation, the mean-square value of c_i or $\langle c_i^2 \rangle$ has a temperature independent value, i.e. $\langle c_i^2 \rangle = 1$ for all temperatures. In a more realistic model, this value would be temperature dependent and sensitive to the ferroelectric phase transition. In the MSDPC model, the calculated values of $\langle c_i^2 \rangle$ in the paraelectric phase of KDP and DKDP near T_c (Fig. 2) show anomalous deviation from high temperature linear dependence and increase by lowering temperature towards T_c. Values of $\langle c_i^2 \rangle$ continue to increase below T_c to the saturated value at $T = 0$ K. In the MSDPC model, PO_4 dipole is not considered a rigid dipole, as it is in an Ising type model. Thus, the decrease in the temperature to T_c and below T_c leads not only to ordering of PO_4 dipoles, but also an additional inducing of PO_4 dipole because of local ordering.

The ^{31}P chemical shift tensor of PO_4 group at site i depends on the c-component of PO_4 dipole or local order parameter variable c_i. By reversing the sign of c_i, the
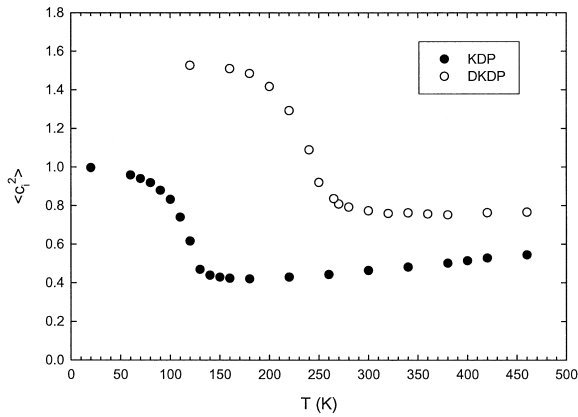
Fig. 2. Temperature dependence of $\langle c_i^2 \rangle$ obtained by the molecular dynamics simulation on KDP and DKDP system with $n = 4$.

orientation of the principal axes is changed, while the eigenvalues of the tensor are kept constant. Accordingly, the isotropic part of the ^{31}P chemical shift tensor σ_{iso} has to be even function of the local order parameter, i.e. $\sigma_{iso}(c_i) = \sigma_{iso}(-c_i)$. Thus, the term quadratic in c_i is the lowest order term in expansion of the ^{31}P isotropic chemical shift in local order parameter variable c_i. In the simple approximation, experimental temperature dependence of the ^{31}P isotropic chemical shift occurs due to temperature dependence of $\langle c_i^2 \rangle$. Temperature dependence of ^{31}P isotropic chemical shift in NMR experiment showed an S-shape anomaly around T_c similar to quantity $\langle c_i^2 \rangle$ [7]. In an Ising type model, ^{31}P isotropic chemical shift has to be temperature independent because $\sigma_{iso}(c_i = 1) = \sigma_{iso}(c_i = -1)$. This is the reason why experimental data for ^{31}P isotropic chemical shift were taken as evidence for the existence of the displacive component in the phase transition mechanism [7].

Anomalous temperature increase by lowering temperature to T_c in the paraelectric phase also showed ^{75}As quadrupole coupling constant in KH_2AsO_4 measured by NQR technique [1,11]. This coupling constant is proportional to the electric field gradient tensor component V_{zz}, which also has to be even function of c_i, so that the temperature dependence of the coupling constant can be qualitatively explained by the temperature dependence of $\langle c_i^2 \rangle$. Since this increase cannot be explained by an Ising type model, Slater model is used to explain this behavior. The source of this anomaly is the change in population between lateral and polar Slater configurations caused by a decrease in the temperature toward T_c [1,11]. Experimental results and results calculated from the MSDPC model for fluctuations of transversal polarization suggest that there are locally induced transversal PO_4 dipole configurations in paraelectric phase, which correspond to lateral Slater configurations [10]. Since they disappear as the temperature decreases through T_c, a part of the increase of $\langle c_i^2 \rangle$ can be related to this effect, which is in accordance with the Slater

model approach [11]. It seems that two different approaches to the explanation of anomalous behavior of the isotropic ^{31}P chemical shift and the ^{75}As quadrupole coupling constant are reconciliated in the MSDPC model. One part of this effect can be attributed to the non-rigidity (or displacive component) of elementary PO_4 dipole and the other part to the changing relative population between transversal and longitudinal PO_4 dipole configurations.

3. Summary

MD simulations of the MSDPC model are performed to describe local properties of KDP and DKDP. Distributions of local order parameter fluctuations for one PO_4 dipole in KDP and DKDP show displacive characteristics in para-electric phase, but temperature dependences of the distribution widths indicate existence of temperature independent constant, which is an order–disorder characteristic. This temperature independent constant is larger in DKDP, which is in accordance with neutron scattering experiments.

On the other hand, mean square of local order parameter shows S-shape anomaly on T_c for both KDP and DKDP, which could not be reproduced by an Ising type of the order–disorder model. This anomaly is akin to the experimental anomalous behavior of isotropic ^{31}P chemical shift and ^{75}As quadrupole coupling constant around T_c, which are differently interpreted. The first feature is interpreted as the direct evidence of existence of the displacive component in phase transition mechanism and the latter as the effect of local lateral Slater configurations. Although the first interpretation seems to be in accordance with the novel findings that pure order–disorder models are too simple to describe behavior of hydrogen bond materials, the latter interpretation should not be rejected. The MSDPC model indicates that both effects can contribute to these anomalies.

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