Development and application of the modified strong dipole-proton coupling model for KDP-type crystals

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ABSTRACT

The modified strong dipole-proton coupling (MSDPC) model, which predicted several static and dynamic dielectric properties of KDP-type ferroelectrics, was used to investigate local properties of these crystals. The results showed both order-disorder and displacive characteristics of pure KDP and DKDP, as in many other experimental studies (NMR, neutron scattering) of local properties. Paramagnetic center SeO_4^{3-} introduced in KDP and DKDP lattice as a local probe in EPR technique was treated within MSDPC model as a "soft" impurity. Simulated dipole reorientational dynamics of the impurity showed characteristics similar to the slow local dynamics of the probe detected in an EPR experiment. Additionally, the MSDPC model was adapted to describe dielectric properties of KDP-type antiferroelectrics. Antiferroelectric phase transition of the first order and isotopic shift in T_c were reproduced.

INTRODUCTION

The origin of a large isotopic effect on T_c when H→D and a phase transition mechanism for ferroelectrics of KH_2PO_4 or KDP-type are still unclear. The proton tunneling model, the first model that explained the isotopic effect, predicted the displacive mechanism [1]. However, more recent lattice dynamics measurements have indicated the order-disorder mechanism. According to the strong dipole-proton coupling (SDPC) model, a difference in ground-state energy between H and D causes the isotopic effect [2]. This model was modified (MSDPC model) by inclusion of transversal (perpendicular to the ferroelectric *c*-axis) dipole components, which reproduced better value of T_c for KD_2PO_4 (DKDP) and the transversal dielectric constant anomaly [3]. The molecular dynamics (MD) simulations performed to study longitudinal ("soft mode") and transversal polarization dynamics in KDP and DKDP yielded the results similar to experimental data [4]. In this study local static and dynamic properties of these systems were investigated by applying MSDPC model. The obtained results were compared with experimental data from NMR, EPR, and neutron scattering measurements. In addition, MSDPC model was adapted to describe antiferroelectrics of KDP-type i.e. $NH_4H_2PO_4$ (ADP) and $ND_4D_2PO_4$ (DADP).

LOCAL STATIC PROPERTIES

MD simulations and model parameters defined earlier [2-4] were used to investigate the local properties of MSDPC model. The induction of PO_4 dipole is related to the shift of P atom and mean-square deviation from the mean value of the *c*-component of PO_4 dipole $\langle (c - \langle c \rangle)^2 \rangle$ (Figure 1) can be correlated with the mean-square thermal motion u^{33}(P) obtained in the neutron scattering experiment [5]. The calculated temperature dependence

of the mean-square of the *c*-component of PO_4 dipole $\langle c^2 \rangle$ can be approximated with $\langle c^2 \rangle \approx \Delta + \gamma T$ well above T_c and the fast decrease of $\langle (c - \langle c \rangle)^2 \rangle$ below T_c occurs (Figure 1). This behavior supports existence of the temperature-independent constant Δ, which has larger value for DKDP than for KDP and disappears in the ferroelectric phase in accordance with the order-disorder type of phase transition. Similar temperature behavior and isotopic effect in Δ shows u^{33}(P) [5]. The value of $\langle c^2 \rangle$ shows anomalous increase by lowering temperature towards T_c and continues to increase below T_c. Experimental parameters that can be related to $\langle c^2 \rangle$, such as ^{31}P isotropic chemical shift [6] and ^{75}As quadrupole coupling constant in KH_2AsO_4 [1], show similar temperature behavior. These experimental data indicate a displacive component in the phase transition mechanism [6].

PARAMAGNETIC PROBE

The PO_4^{3-} group of the KDP lattice can be replaced with the paramagnetic probe SeO_4^{3-} to study local lattice dynamics by EPR spectroscopy. The probe exhibits a local low-frequency polarization fluctuation mode at EPR time scale (10^7-10^{10} Hz) in the paraelectric phase. The obtained motional dynamics was usually described by simple Arrhenius-type correlation time $\tau = \tau_0 \exp(\Delta E/kT)$ [7]. In the MSDPC model, the SeO_4^{3-} probe is described as "soft" impurity with A_{probe} value of the elastic constant for the dipole *c*-component induction lower than the *A* value for the original PO_4^{3-} group. For $A_{probe} = 0.45A$, the MD simulations in the paraelectric phase of KDP and DKDP show the effective local double-well potential of the probe and the temperature dependence of calculated correlation times τ for the dipole reorientational jumps over the barrier can be fitted to the Arrhenius law (Figure 2). The fitted parameters for KDP are close to the

experimental ones, and the experimentally detected higher activation energy (ΔE) in DKDP is also reproduced [7].

ANTIFERROELECTRICS OF KDP-TYPE

By replacing K ions in the KDP lattice with NH_4 group, the obtained crystal lattice exhibits antiferroelectric (AFE) phase transition of the first order and the isotope effect in T_c [8]. The ordered phase is characterized by the four types of AFE domains having transversal unit dipoles. The effect of the NH_4 group in ADP is introduced in the MSDPC model by additional force, which is induced by the transversal PO_4 dipole and acts on the next nearest H(D). The force is proportional to the dipole with the constant $L_\perp$ and its orientation is chosen so that dipole orientation at T=0 K corresponds to one of the AFE domains. Due to similarity of hydrogen bond lengths, the parameters h and I have the same value for ADP (DADP) as for KDP (DKDP) [2]. To reproduce experimental values of dielectric constants ε_a and ε_c along the a and c-axis, the values of the previously defined parameters for KDP (DKDP) [3] are adjusted for ADP (DADP), as follows: $A=2.474h^{\mathrm{H}}/(\mu_s^{\mathrm{H}})^2$, $A_\perp=0.174h^{\mathrm{H}}/(\mu_s^{\mathrm{H}})^2$, $IK=0.847h^{\mathrm{H}}/\mu_s^{\mathrm{H}}$, $IK_\perp=0.226h^{\mathrm{H}}/\mu_s^{\mathrm{H}}$, with the new parameter value $IL_\perp=0.0023h^{\mathrm{H}}/\mu_s^{\mathrm{H}}$. Calculated results for ε_a and ε_c in ADP and DADP show sharp discontinuity at T_c as expected for the first order transition, as well as isotopic shift in T_c (Figure 3).

CONCLUSION

Several dielectric and local properties as well as isotope effects for KDP can be predicted and fairly good described with MSDPC model without including proton tunneling. This model can also predict the first order AFE phase transition in ADP by including an additional interaction between dipole and the second nearest protons.

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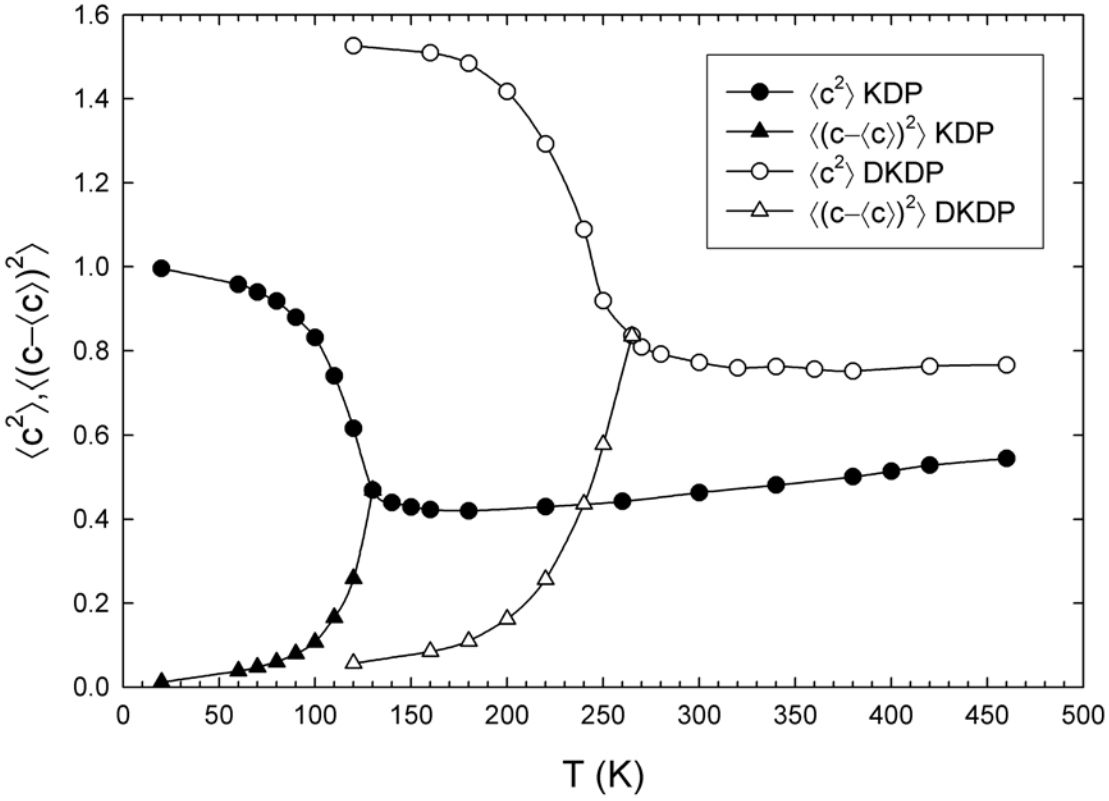
FIGURE CAPTIONS

Figure 1. Temperature dependence of $\langle c^2 \rangle$ and $\langle (c - \langle c \rangle)^2 \rangle$ obtained from the MD simulation on KDP and DKDP system of 256 PO_4 dipoles, where c is value of PO_4 dipole component along c-axis relative to the saturated value $\mu_s^{\mathrm{H}}=4.8\times10^{-30}$ C m for KDP.

Figure 2. The MD simulation results for inverse reorientational correlation time of the "soft" impurity with $A_{probe}=0.45A$ embedded in KDP and DKDP system of 107 PO_4 dipoles in paraelectric phase. Lines denote the best fits to the Arhhenius law.

Figure 3. Results obtained from the MD simulation for **(a)** ε_a and **(b)** ε_c on the ADP and DADP system of 108 PO_4 dipoles. Lines denote experimental values [8].

D. Merunka and B. Rakvin, Figure 1.



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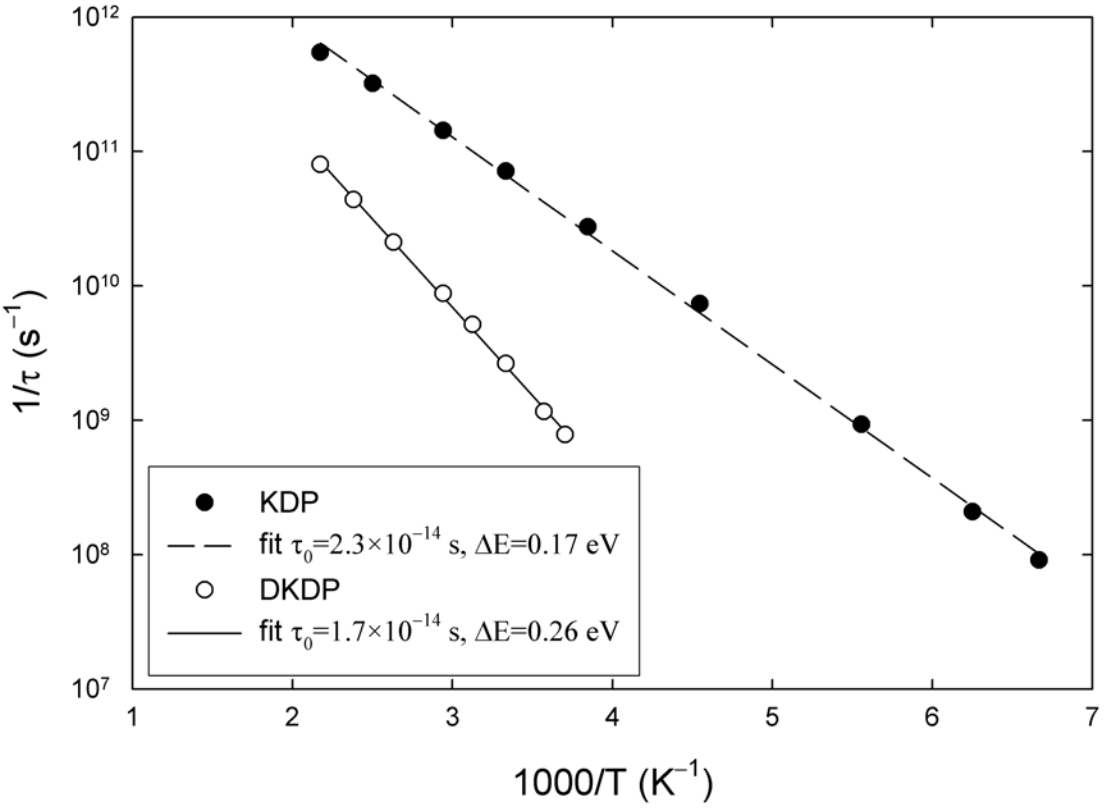
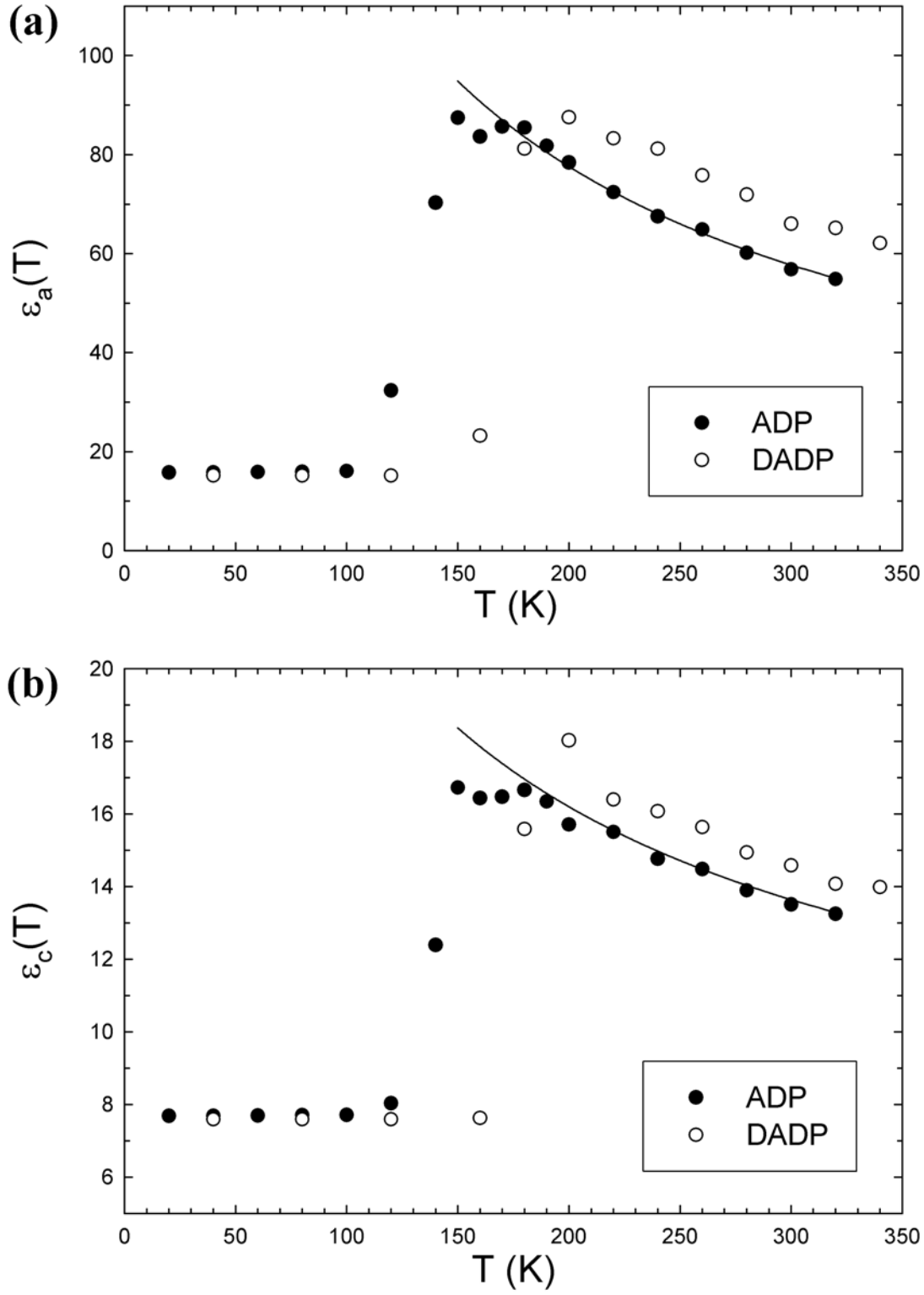
D. Merunka and B. Rakvin, Figure 3.