

**Modified strong dipole-proton coupling model and local properties of
EPR probe in the KDP-type ferroelectrics**

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ABSTRACT

The modified strong dipole-proton coupling (MSDPC) model, which predicts several static and dynamic dielectric properties of KDP-type ferroelectrics, is used to investigate properties of paramagnetic center SeO_4^{3-} introduced in KH_2PO_4 (KDP) and KD_2PO_4 (DKDP) lattice as a local probe in EPR experiment. Paramagnetic center is treated within MSDPC model as a “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 time τ for the dipole reorientational jumps over the barrier can be fitted by the Arrhenius law. The obtained Arrhenius parameters for KDP are close to the experimental ones, and the experimentally detected higher activation energy in DKDP is reproduced. Also, the high-temperature line broadening and the temperature dependence of ^{77}Se hyperfine coupling observed in experiment are discussed within the MSDPC model.

INTRODUCTION

The real nature of the ferroelectric phase transition and the isotope effect on T_c for H→D exchange in KH_2PO_4 or KDP-type ferroelectrics has not been fully explained [1]. The proton tunneling model [2], the earliest model used to explain the isotope effect, predicts the displacive type of phase transition, but more recent measurements on crystal lattice dynamics suggest the order-disorder mechanism. On the other side, by applying an Ising-type of the order-disorder model one cannot explain the isotope effect and other experiments, such as chemical shift measurements of ^{31}P , which indicate that both types of mechanism are involved in phase transitions [3].

In the new strong dipole-proton coupling (SDPC) model [4], protons adiabatically follow dynamics of PO_4 dipoles and the isotopic effect is described without proton tunneling. An additional improvement of the SDPC model, as recently suggested, can be obtained by involving the change of the PO_4 dipole in all directions [5]. This modified SDPC (MSDPC) model describes the static dielectric properties of the crystal better than the original SDPC model. The MSDPC model was employed to describe the polarization dynamics of KDP in the paraelectric phase. An order-disorder mechanism near T_c and crossover to a displacive mechanism at higher temperatures were predicted [6].

In the typical EPR experiment, the response of the paramagnetic probe inside the crystal lattice is measured. In the KDP lattice, SeO_4^{3-} was used to replace the PO_4^{3-} unit and the local disturbance produced by the probe could be seen in the form of order-disorder dynamics, slower than the dynamics of the PO_4^{3-} group. Although several

experimental and theoretical investigations of the probe dynamics have been carried out, the question remains whether the correlation time τ of this dynamics exhibits only pure Arrhenius-type ($\tau = \tau_0 \exp(\Delta E/kT)$) temperature dependence [7] or a deviation from such behavior in accordance with the pseudo-freeze-out model [8]. Another question is the microscopic origin of the activation energy ΔE that has larger value in deuterated lattice.

The purpose of this study is to deduce local parameters within the MSDPC model, which can describe SeO_4^{3-} probe in KDP. In the MSDPC model, the probe is treated as a “soft” impurity in the crystal lattice. The simulated dynamics is tested by comparing the experimentally measured and calculated τ . Also, the MSDPC model is employed to discuss the high-temperature line broadening and the temperature dependence of ^{77}Se hyperfine coupling observed in EPR experiment.

RESULTS AND DISCUSSION

Molecular dynamics (MD) simulations and MSDPC model parameters defined earlier [6] are used to investigate the local properties of SeO_4^{3-} probe in KDP and KD_2PO_4 (DKDP). Numerical simulations are performed on the cubic sample of KDP and DKDP crystals with $n \times n \times n$ unit cells or $4n^3$ PO_4 dipoles. For PO_4 dipole on site i , the quantity $c_i = \mu_i^c / \mu_s^H$ is defined 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 SeO_4^{3-} probe is described as a “soft” impurity on site $i=0$ 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, i.e. $A_{probe} = \alpha A$ ($\alpha < 1$). In accordance with previous MD simulations [6], the value of damping constant is chosen to be $\Gamma_0 = 26.5 \text{ cm}^{-1}$.

For KDP system with $n=2$ at $T=340$ K, the distribution $f(c_0)$ of the local order-parameter or the dipole c -component for the impurity is calculated. The distribution shows one peak when the impurity is identical ($\alpha=1$) to the original dipole (Fig. 1). The original KDP system at this temperature thus shows a displacive behavior. By decreasing parameter α , the dipole distribution $f(c_0)$ broadens and two peaks appear for $\alpha=0.7$. These peaks become more separated by lowering the value of α below 0.7 (Fig. 1). Thus, by softening of the impurity the system locally shows more order-disorder characteristics.

Calculated correlation functions $G_1(t) = \langle c_0(0)c_0(t) \rangle / \langle c_0(0) \rangle^2$ of the local order parameter fluctuations in KDP show oscillatory and relaxational contributions (Fig. 2). By decreasing α , oscillatory contribution decreases and relaxational one increases, reflecting the fact that local dynamics becomes more order-disorder-like. Thermally

activated jumps between local minima described with correlation time τ contribute to the relaxational part and small oscillations about one minimum contribute to the oscillatory part of correlation functions. Relaxation correlation time τ increases as α decreases, reaching the value of 7×10^{-12} s for $\alpha = 0.45$, which is close to the value of 6.5×10^{-12} s obtained for SeO_4^{3-} in KDP at 340 K, by using Arrhenius relation for correlation time and experimental values: $\tau_0 = 1 \times 10^{-14}$ s and $\Delta E = 0.19$ eV for SeO_4^{3-} in KDP [7]. Thus, SeO_4^{3-} probe in the MSDPC model is described as the “soft” dipole impurity with $\alpha = 0.45$, embedded in KDP or DKDP system.

For the obtained value of α , the calculated distributions $f(c_0)$ in KDP and DKDP show two peaks in temperature range from T_c up to 460 K. Effective local potential $V_{eff}(c_0)$ defined by relation: $f(c_0) = f_0 \exp(-V_{eff}(c_0)/kT)$ is the double well potential with the barrier energy E_{bar} . Temperature dependence of calculated barrier energy in paraelectric phase of KDP and DKDP exhibits two features (Fig. 3). The first feature is that the barrier energy increases by lowering temperature to T_c in accordance with the pseudo-freeze-out model [8], but without such strong temperature dependence as predicted by the same model (Fig. 3). The second feature is that the barrier energy is larger in DKDP than in KDP. Similar increase of calculated barrier energy from 135 meV in KDP to 192 meV in DKDP at $T = 500$ K was already predicted for AsO_4^{4-} probe by employing MFA of the original SDPC model [9]. The isotopic effect in barrier energy has the same origin as the isotopic effect in T_c of pure KDP, i.e. the difference in parameter h , which describes ground-state energy of H(D) depending on values of neighboring PO_4 dipoles.

Calculated correlation functions $G_1(t)$ for the probe with $\alpha = 0.45$ in KDP and DKDP can be approximated with a simple sum of the damped harmonic oscillator

correlation function describing oscillations about minimum of the potential well and the relaxational exponential function describing dipole jumps between wells, proportional to $\exp(-t/\tau)$, where τ is correlation time. Values for inverse correlation times obtained by such fitting procedure are shown in Figure 4. The value of correlation time does not change with increase in the size of model system from $n=2$ to $n=3$, and $\log(1/\tau)$ nearly linearly depends on $1000/T$ for both systems and can be fitted by the Arrhenius law. Obtained Arrhenius parameters are: $\tau_0=2\times 10^{-14}$ s, $\Delta E=0.17$ eV for KDP and $\tau_0=2\times 10^{-14}$ s, $\Delta E=0.26$ eV for DKDP. Values for parameters in KDP correspond with experimental values for SeO_4^{3-} in KDP [7]. The isotopic shift of 0.09 eV in activation energy ΔE is larger than experimental shift (0.03 eV) and experimentally obtained isotopic effect in preexponential factor τ_0 is not reproduced. It is interesting that the activation energy ΔE has larger value than the barrier energy E_{bar} and has to be considered as the effective energy, not corresponding to any energy of the system measured by other experimental techniques (proton and deuteron excitation energy or similar).

By increasing the temperature in paraelectric phase, jumping frequency of the probe increases and becomes higher than a separation frequency of EPR lines corresponding to two potential wells at the temperature T^* . At this temperature, the EPR spectrum shows transition from the low-temperature to the high-temperature symmetry. Above T^* , the probe is in the fast exchange region and EPR lines narrow as the temperature and jumping frequency increase (motional narrowing regime). More precisely, the relaxation time T_2 that is responsible for linewidth depends on spectral density of correlation function of local order parameter:

$$G(\omega) = \int_{-\infty}^{\infty} dt \langle c_0(0)c_0(t) \rangle e^{-i\omega t} \quad (1)$$

for $\omega=0$ [10,11]. Relaxational contribution to the correlation function is dominant and the spectral density has the following form:

$$G(\omega) = G_0 \tau / (1 + \omega^2 \tau^2) \quad (2),$$

where G_0 is nearly independent on T , while the correlation time τ , according to Figure 4, follows Arrhenius law. Since the linewidth is proportional to $1/T_2 \propto G(\omega=0) \propto \tau \propto \exp(\Delta E/kT)$, it becomes smaller as the temperature increases.

Interestingly, at temperatures above the motional narrowing region, the EPR lines of SeO_4^{3-} probe in KDP and DKDP start to broaden, following exponential temperature dependence, i.e. $\exp(-\Delta E/kT)$, with the same activation energy ΔE as in Arrhenius dependence of τ . It has been proposed that this broadening results from decreasing of spin-lattice relaxation time T_1 by increasing temperature [7]. This relaxation time depends on the spectral density $G(\omega)$ for the electron Larmor frequency $\omega=\omega_0$, which corresponds to X-band frequency ($\nu_X=9.5$ GHz) in usual EPR-experiment. One can see from (2) that exponential increase in $G(\omega_0)$ is possible for the limit $\omega_0^2 \tau^2 \gg 1$, where $G(\omega_0) \cong G_0 / (\omega_0^2 \tau) \propto \exp(-\Delta E/kT)$. However, this temperature range is below $T=300$ K, the temperature where $G(\omega_0)$ reaches maximum value for experimental values of parameters for SeO_4^{3-} probe in KDP. Experimentally, only the exponential increase in linewidth up to 370 K is observed, without any maximum [7]. Additionally, the value of $G(\omega)$ from (2) is always lower for $\omega=\omega_0$ than for $\omega=0$, which is why line broadening is difficult to explain by using relation (2).

Generally, in the spin Hamiltonian for the paramagnetic probe the function $F(t)$, which depends on lattice variables and is responsible for spin-lattice relaxation, can be expanded in the local order parameter variable: $F=F_0+a_1\cdot c_0+a_2\cdot c_0^2+\dots$ [11]. The spectral density (2) corresponds to the one-phonon (direct) relaxation process and the spectral density of the correlation function $\langle c_0^2(0)c_0^2(t) \rangle$ to the two-phonon (Raman) relaxation process. The calculated correlation function $G_2(t)=\langle c_0^2(0)c_0^2(t) \rangle / \langle c_0^4 \rangle$ for the probe in KDP (Fig. 5) shows oscillatory character in paraelectric phase without relaxational contribution and can be fitted by the damped harmonic oscillator correlation function. Fast jumps of the dipole of the probe from one minimum $c_0=c_{\min}$ to another $c_0=-c_{\min}$ and vice versa do not change the square of the local parameter value, so only oscillatory motion about minima is visible in the correlation function. Nevertheless, these jumps affect an effective oscillatory mode damping. Temperature dependence of the effective damping constant $\Gamma(T)$ obtained by fitting procedure and subtracted by $\Gamma_0=26.5 \text{ cm}^{-1}$ (Fig. 6(a)) exhibits Arrhenius behavior at high temperatures, similar to the Arrhenius behavior of the correlation time τ , but with slightly lower activation energy. Additionally, as for the correlation time, the isotopic effect in activation energy is also visible. These results indicate that thermally activated jumping of the probe can affect vibration modes responsible for the spin-lattice relaxation, increasing the damping of these modes and leading to the high-temperature line broadening observed in the experiment (Fig. 6(b)).

Regarding the static properties of the SeO_4^{3-} probe, the temperature dependence of the hyperfine interaction between unpaired electron and ^{77}Se ($I=1/2$) nucleus was measured in KDP and DKDP [12]. Hyperfine tensor component A_{\parallel} , where direction \parallel is

along c -axis, exhibits larger value for DKDP than for KDP and jumps at T_c for DKDP. In paraelectric phase, temperature dependence of this component can be approximated by relation: $A_{\parallel}(T)=A_{\parallel}(0)-B\coth(T_0/T)$, where T_0 (≈ 570 K for both crystals) corresponds to the frequency of the vibration mode responsible for the change of the tensor component.

In the expansion of $A_{\parallel}(T)$ in local parameter variable c_0 ($A_{\parallel}=a_0+a_2\cdot c_0^2+\dots$), the lowest order term is the quadratic term in c_0 because of the symmetry requirements. In the simple approximation, only the temperature dependence of $\langle c_0^2 \rangle$ would contribute to the temperature dependence of $A_{\parallel}(T)$. The calculated values of $\langle c_0^2 \rangle$, $\langle c_0^2 \rangle_0$, where $\langle c_0^2 \rangle_0$ is the value of $\langle c_0^2 \rangle$ at $T=0$ K in KDP, are shown in Figure 7. As a result of the additional local ordering by lowering the temperature below T_c , the small increase in $\langle c_0^2 \rangle$ can be seen for KDP. Above T_c the temperature dependence can be approximated by the same relation as in the experiment with $T_0 \approx 370$ K. The value of $\langle c_0^2 \rangle$ is larger in DKDP, which is in accordance with the experiment. However, the temperature dependence of $\langle c_0^2 \rangle$ is weak and there is no jump at T_c , which is contrary to the experiment. These results can lead to the conclusion that temperature dependence of the mean square of local order parameter, beside other mechanisms, can affect the dependence of the hyperfine interaction on temperature and deuteration.

CONCLUSION

According to the MSDPC model, the distribution function of the local order parameter for one PO_4 dipole exhibits a single peak in the paraelectric phase of KDP system, indicating displacive behavior of pure KDP lattice. By decreasing the value of the c -dipole induction elastic constant for the impurity in KDP system, the local order parameter potential on the impurity site becomes of the double well type and the system locally becomes more order-disorder-like.

Such “soft” impurity with 0.45 of the original PO_4 dipole, elastic constant value can be used to simulate SeO_4^{3-} paramagnetic probe, because the inter-well jumping frequency at $T=340$ K has the same value as the local dynamics frequency measured by EPR spectroscopy on SeO_4^{3-} probe in KDP. The energy of the barrier between two wells for this impurity in KDP and DKDP increases as the temperature decreases to T_c , as predicted by pseudo-freeze out model, but the temperature dependence of jumping correlation time can be approximated by the Arrhenius law, contrary to this model and in accordance with the most recent EPR experiments. The parameters in approximated Arrhenius dependence for the impurity in KDP have values similar to the experimental ones and the larger value of effective activation energy in DKDP than in KDP correlates with the experiment. This is another isotopic effect predicted by the MSDPC model, with the same origin as the isotopic effect in T_c of pure crystals i.e. ground-state energy difference between proton and deuteron.

Results for the fluctuations of the square of the local order parameter indicate that jumping dynamics of the impurity can affect damping of vibration modes responsible for the spin-lattice relaxation leading to the high-temperature line broadening observed in experiment and characterized by the same activation energy as jumping correlation time.

Furthermore, the results indicate that temperature dependence of the mean square of local order parameter on the impurity site can contribute to the temperature dependence of an experimentally measured local quantity, such as ^{77}Se hyperfine coupling.

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FIGURE LEGENDS

Figure 1. Calculated distribution of the local order parameter for the “soft” impurity in the KDP system at $T=340$ K for several values of parameter α .

Figure 2. Calculated correlation functions of local order parameter fluctuations for the “soft” impurity in the KDP system at $T=340$ K for several values of parameter α and $t_0=2\times 10^{-14}$ s.

Figure 3. Calculated energy of the barrier in the double well effective local potential for the “soft” impurity with $\alpha=0.45$ in the KDP and DKDP system with $n=3$. Dashed line denotes temperature dependence of the barrier height of SeO_4^{3-} center in KDP predicted by the pseudo-freeze-out model [8].

Figure 4. Obtained inverse correlation times of the “soft” impurity with $\alpha=0.45$ in the KDP and DKDP system. Lines denote fits to Arrhenius law.

Figure 5. Calculated correlation functions for fluctuations in the square of the local order parameter for the “soft” impurity with $\alpha=0.45$ in the KDP system with $n=3$ at several different temperature values.

Figure 6. Temperature dependence of (a) obtained effective damping constant for oscillations of the square of local order parameter for the “soft” impurity with $\alpha=0.45$ in

the KDP and DKDP system, subtracted by the value of $\Gamma_0=26.5 \text{ cm}^{-1}$, and of (b) the exponential high-temperature line broadening contribution to the EPR linewidth: $\Delta\Gamma=B\exp(-\Delta E/kT)$, with experimental parameters B and ΔE for SeO_4^{3-} center in KDP and DKDP taken from Table I in Ref. 7.

Figure 7. Calculated mean square values of local order parameter for the “soft” impurity with $\alpha=0.45$ in the KDP and DKDP system, relative to $T=0 \text{ K}$ value in KDP.

Figure 1.

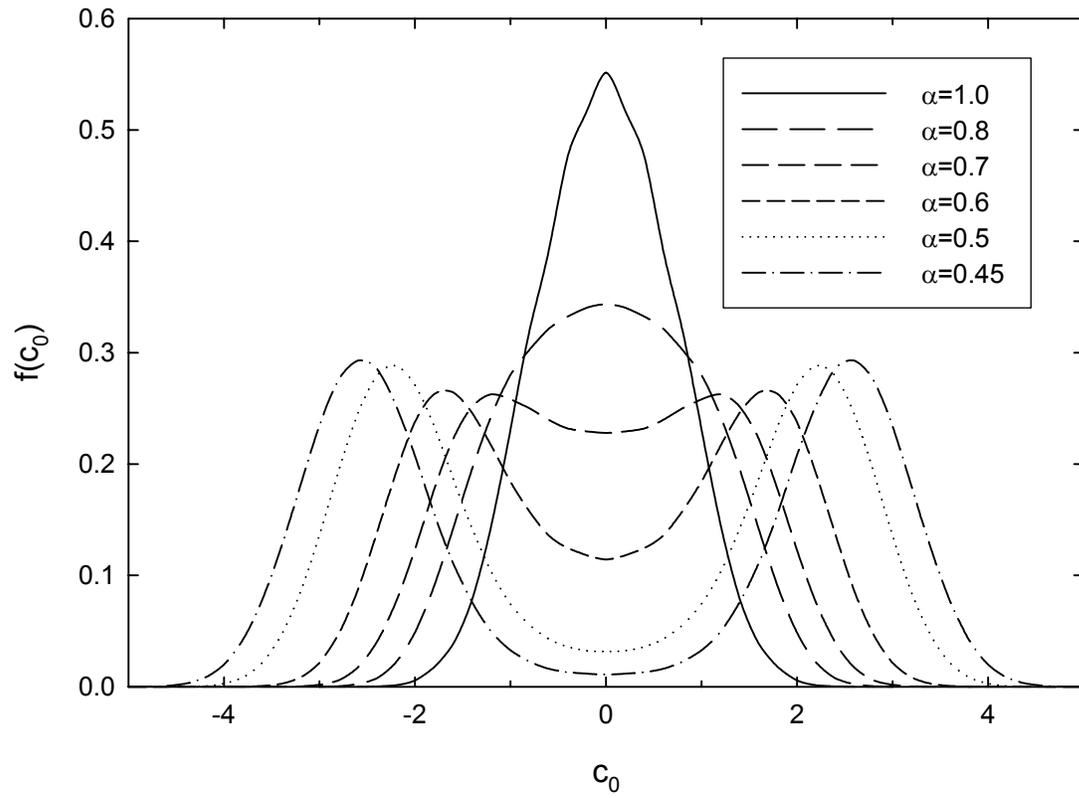


Figure 2.

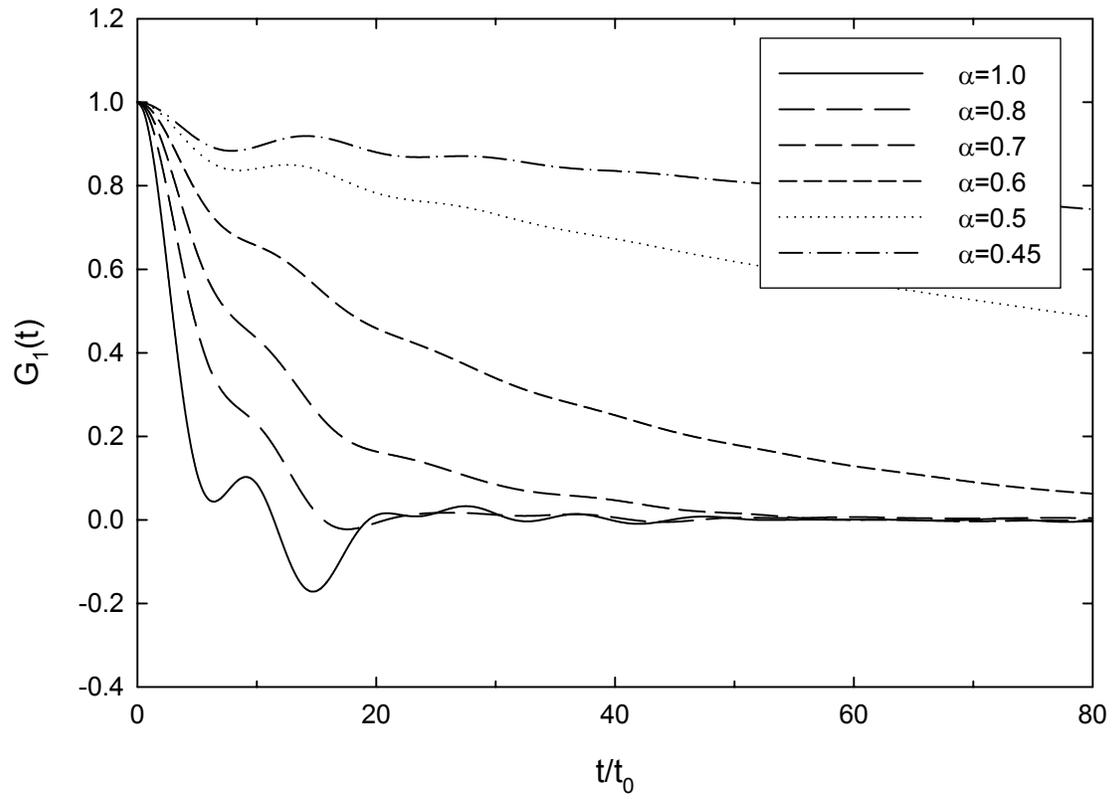


Figure 3.

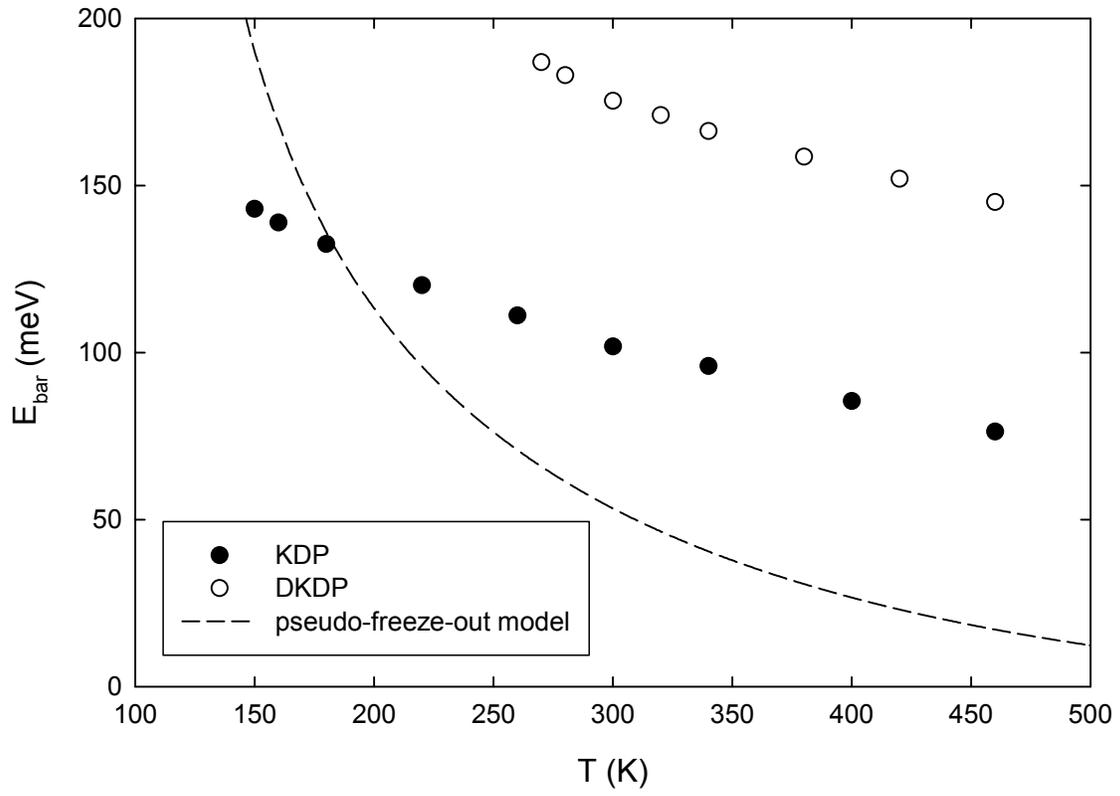


Figure 4.

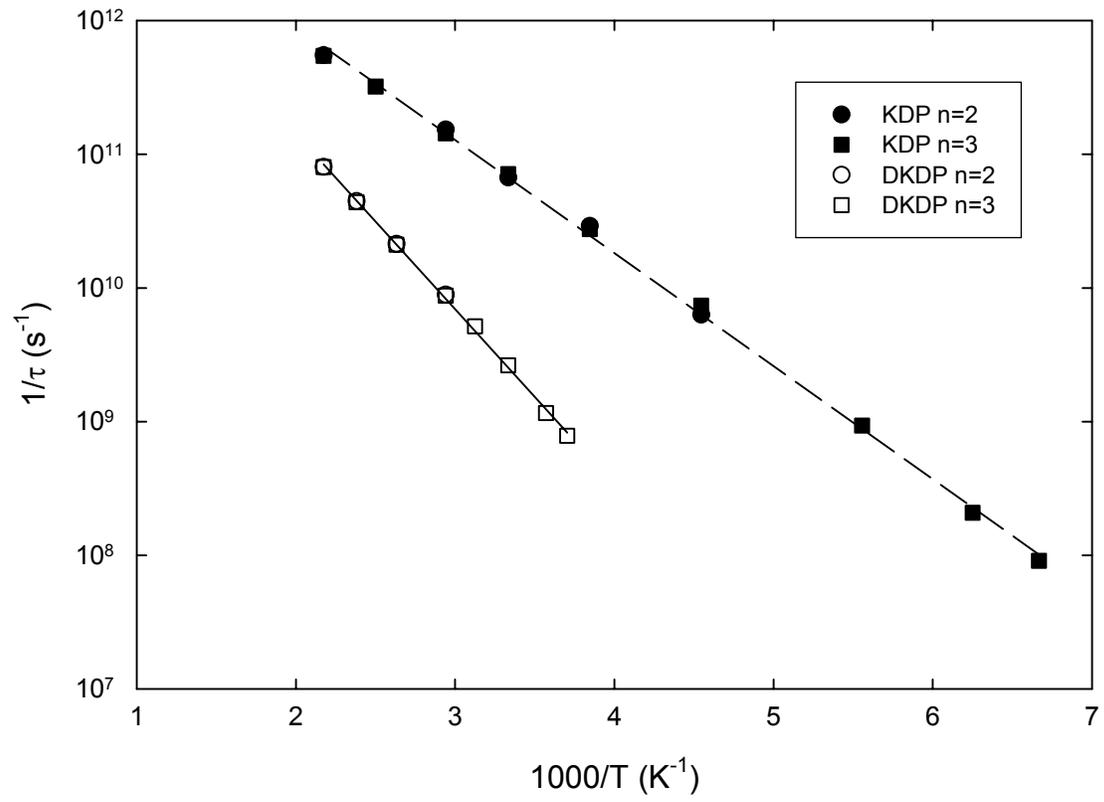


Figure 5.

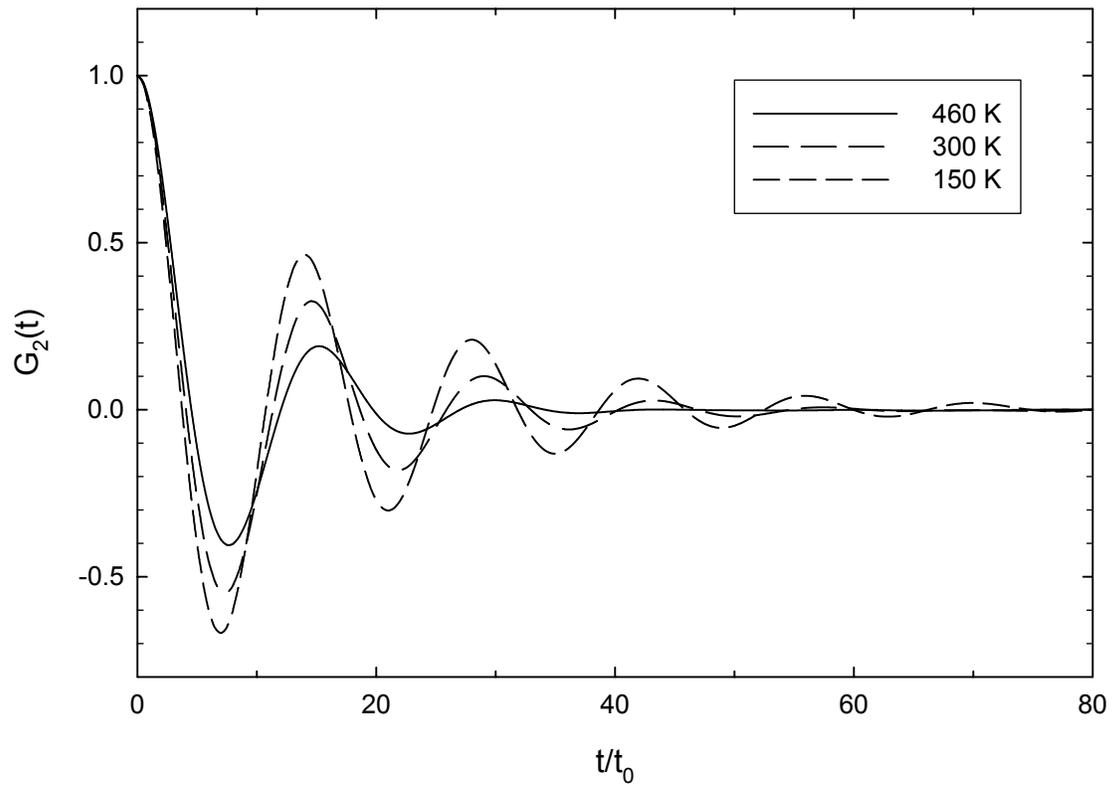


Figure 6.

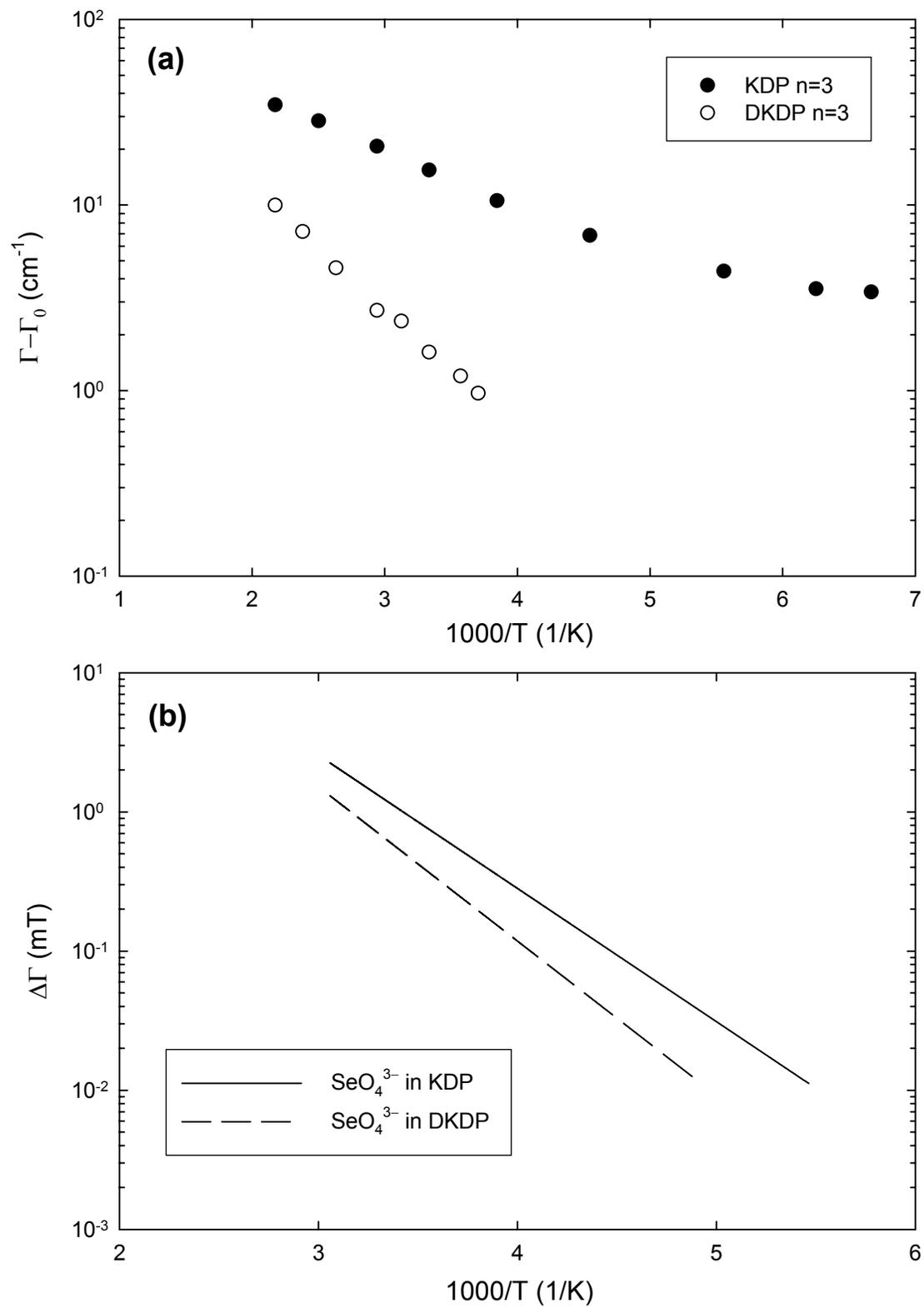


Figure 7.

