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ISOTOPIC EFFECT DETECTED BY A PARAMAGNETIC PROBE IN THE KH_2PO_4-TYPE FERROELECTRIC

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Based on strong proton coupling to the AsO_4^{4-} probe, a model for the isotopic effect detected by a paramagnetic probe in the KH_2PO_4-type ferroelectric has been suggested. In accordance with earlier measurements this model predicts higher activation energy and smaller preexponential factors than the non-deuterated lattices. © 1998 Elsevier Science Ltd. All rights reserved

1. INTRODUCTION

Paramagnetic probes such as AsO_4^{4-}, SeO_4^{3-} or CrO_4^{4-} have been extensively studied in hydrogen bonded ferroelectrics KH_2PO_4 (KDP), KH_2AsO_4 (KDA) and antiferroelectric $NH_4H_2AsO_4$ (ADA) during the two past decades [1–3]. These centers have been employed as probes to study slow lattice dynamics and low-frequency (10^7- 10^{10} Hz) polarization fluctuations in the vicinity of the paraelectric-ferroelectric phase transition temperature, T_c. In some reports [4, 5] the motional dynamics is described by a simple Arrhenius-type correlation time $\tau = \tau_0 \exp(\Delta E/kT)$, whereas in other studies [6, 7] a non-Arrhenius behavior is suggested. A deviation from the Arrhenius law is interpreted by theoretical models which predict the local motional freezing of a spin probe in the paraelectric phase [9]. According to the model in [8], ΔE for the probe should increase as $(a - b(T - T_c)^{1/2})$ with $a > b$. Subsequently, it has been shown that some of non-Arrhenius behavior can be ascribed to at least two processes: a) line broadening which depends on temperature exponentially [10, 11] and b) inhomogeneous broadening due to the proton spin-flip transition [12]. By employing the EPR and ENDOR techniques [13], this has been found indeed to be the case for the KDP:AsO_4^{4-} system, where down to T_c ΔE is mostly independent of temperature.

Since the model in [8] for the temperature dependence of ΔE has not been supported by recent experimental results [10–13], the important question of the microscopic origin of ΔE still remains open. One of the experimental observations which can help to describe the microscopic origin of ΔE is the fact that τ obtained in a deuterated ferroelectric (in which ^1H is replaced by ^2H) exhibits the same Arrhenius behavior with larger ΔE and τ_0 values lower than those in non-deuterated lattices [10–12]. This general type of isotope effect is experimentally detected in several hydrogen bonded ferroelectrics and antiferroelectrics by employing different probes (Table 1). From the data in Table 1, one concludes that the EPR probes are sensitive to the isotope effect in the KDP-type materials despite their local behavior in the host lattice, *i.e.* the AsO_4^{4-} probe exhibits different Arrhenius parameters in different lattices.

The purpose of this investigation is to deduce a possible model so as to describe ΔE and τ_0 in both normal and deuterated lattices by using the corresponding lattice parameters. In addition, such an investigation is carried out since the origin of the large isotope effect

Table 1. Activation energies, Δ E, and preexponential factors, τ_0, for paraelectric probes in ferroelectric and antiferroelectric lattices. The experimental errors for Δ E are within 10% and for τ_0 within an order of magnitude

lattice	probe	$\Delta E/eV$	τ_0/s	reference
KDP	AsO_4^{4-}	0.16	1.0×10^{-12}	13
DKDP	AsO_4^{4-}	0.20	2.0×10^{-14}	3
KDA	AsO_4^{4-}	0.20	3.2×10^{-13}	12
DKDA	AsO_4^{4-}	0.26	3.7×10^{-14}	12
KDP	SeO_4^{3-}	0.19	1.0×10^{-14}	11
DKDP	SeO_4^{3-}	0.22	6.0×10^{-15}	11
ADA	CrO_4^{3-}	0.19	8.3×10^{-14}	10
DADA	CrO_4^{3-}	0.23	1.3×10^{-14}	10

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on the T_C of the KDP-type materials is not yet fully understood. It has been noted [14, 15] that the traditional tunneling model [16,17] can not explain some of the new experimental observations, such as the linear relation between T_C and the $O-O$ distance in these ferroelectric materials. These observations have been used as a basis for the newly proposed model known as the "geometrical model". According to this model, the geometrical properties of $O-H\cdots O$ bonding determine the ferroelectric properties including the isotope effect on T_C [18]. The strong coupling model, which has been slightly modified by Sugimoto and Ikeda [18–21], will be used as a basis for explaining the isotope effect detected by the paraelectric probe in the KDP-type lattices.

2. PROPOSED MODEL FOR STRONG COUPLING BETWEEN PROTONS AND THE PROBE TETRAHEDRON

Essentially, a paramagnetic probe in the crystal lattice is a defect (or impurity) with its own vibrational modes that can be quite different from the molecular fragments which the probe substitutes. If the probe mode (called local mode) is significantly different from those of the lattice, and if the local mode can couple with the lattice modes, then the probe dynamics would involve both local and lattice mode. It is known [22] that the "local" modes become significant in at least two cases: (a) When the probe has a mass lighter than that of the nominal atoms at the site (i.e. before doping). (b) The probe is bonded to the neighbouring atoms with forces stronger than those normally present in the lattice. Since, the differences in the mass between these probes and similar anionic groups in the lattice are insignificant (*i.e.*, practically there are none for the AsO_4^{4-} center in KDA) one expects that only the second case can be responsible for the local behavior of the probe. Thus, a strong coupling between protons and PO_4 tetrahedra in the geometrical model for the isotope effect in KDP should be replaced with even stronger coupling between the probe tetrahedra and the neighbouring protons. According to the model [18–20], the H-bond potential is of an asymmetric double-well type and the proton is strongly localized near one oxygen in the ferroelectric phase. The asymmetry term, which is proportional to the local force between neighbouring protons and PO_4, strongly decreases the ground state with small change of the $O-O$ atomic distance. Due to the presence of stronger forces in the vicinity of the probe than in the host lattice, one would expect a larger contribution of the asymmetry term.

In order to introduce a strong coupling model which describes the behavior of the probe in the lattice, we can employ the previously developed [20] adiabatic potential of a system containing N distorted tetrahedra and 2N protons.

$$E_{pot} = \frac{A}{2}\sum_{i=1}^{N}\mu_i^2 + \frac{B}{4}\sum_{(i,j)}^{2N}\mu_i\mu_j - \sum_{(i,j)}^{2N}E_{ij}^0 \qquad (1)$$

where the distortion of tetrahedron i is proportional to its electric dipole moment μ_i. The first term is the elastic energy present due to mechanical deformations of the tetrahedra. The second term is the interaction energy between dipoles, and the last term is the energy of 2N protons. E_{ij}^0 represents the ground-state energy of a proton connecting two neighboring tetrahedra. The ground-state energy is given by:

$$E_{ij}^0 = [h^2 + I^2K^2(\mu_i + \mu_j)^2]^{1/2} - h \qquad (2)$$

where K is a coupling constant, h and I represent parameters for the KDP and DKDP lattices [18–21]. In this calculation the hydrogen potential is taken as a double minima potential along the $O-O$ bond with an asymmetric contribution arising from the $-K(\mu_i + \mu_j)x$ term. The parameter x represents the position of a proton measured from the center of the $O-O$ bond. Assuming the probe in the lattice can occupy the position at $i = 0$ and the neighbouring protons are coupled with a constant $K_0 > K$, the adiabatic potential from Eq. (1) can be obtained as follows:

$$E_{pot}^0 = \frac{A}{2}\mu_0^2 + \frac{B}{4}\sum_{j=1}^{4}\mu_0\mu_j - \sum_{j=1}^{4}[h^2 + I^2(K_0\mu_0 + K\mu_j)^2]^{1/2} - h \qquad (3)$$

where, because of simplicity, the summation is taken only over the nearest neighbouring tetrahedra. In this approximation one can also assume that in the paraelectric phase $\mu_j = <\mu> = 0$, and the potential can be obtained by:

$$E_{pot}^0 \simeq \frac{A}{2}\mu_0^2 - 4\{[h^2 + I^2K_0^2\mu_0^2]^{1/2} - h\}. \qquad (4)$$

This type of potential also exhibits double well type behavior with the minima at the positions $\mu_0 = \pm\mu_0^s$ with a barrier height, E_B between these minima. Both of these parameters, as well as the dipole frequency, ($\omega_0 = \sqrt{f/M}$ where $f = \partial^2E/\partial\mu^2\ |_{\mu=\mu_0^s}$), are functions of the proton coupling to the probe represented by K_0. Using previously proposed parameters [18–21] for KDP and DKDP (Table 2) and $K_0 = 1.236K$, the

parameters for double-minima potentials are calculated (Table 3) and shown in Fig. 1. The plots represent the profile of dipole potentials of the probe (solid line) and one of the PO_4^{3-} tetrahedron from the host (dashed line) in the KDP (Fig. 1a) and DKDP (Fig. 1b) lattice (calculated under the approximation that the contributions of other neighbouring dipoles are neglected). K_0 has been chosen assuming that the corresponding E_B is equal to the activation energy of the AsO_4^{4-} probe in KDP. It can be noted that the energy barrier obtained for DKDP is higher than that for KDP. Although the calculated value $E_B = 0.30$ eV exceeds the measured value for DKDP, $\Delta E = 0.20$ eV, it is important to point out the same general behavior, *i.e.* an increase in E_B with the deuteration of lattices. Therefore, by using the model of strong proton coupling one obtains an activation energy for polarization fluctuation around the paramagnetic probe in DKDP higher than in the KDP lattice (Table 1). Moreover, the Arrhenius-type of polarization fluctuation in the paraelectric phase can be easily explained by the double minima potential which exhibits a ground-state energy for protons slightly lower in the vicinity of the probe than in the ordinary lattice. A preexponential factor in the Arrhenius-type of dynamics which is related to the oscillation of dipole around minima exhibits higher frequency in the DKDP lattice than in the KDP lattice (Table 3). The same trend in the change of τ_0 for deuterated and non-deuterated lattices can be noted in Table 1. The dipole minima oscillation calculated from the data in Table 3 ($2\pi/\omega_0 = 1.4 \times 10^{-13}$ s) can be found in the region within experimentally detected τ_0 for AsO_4^{4-} in the KDP and in the DKDP lattices.

In order to qualitatively predict the effect of neighbouring dipoles on the probe, the temperature dependences of dipole moment distributions are calculated for the KDP lattice by a mean-field approximation to the potential (Eq.(3)). Different forms of the dipole moment distribution can be expected in the ferroelectric and in the paraelectric phase. By introducing the parameters for the KDP lattice used earlier [21], the distribution of dipolar moments is obtained for each phase (Fig. 2). The shapes of these distributions are very similar to the shapes performed by the Monte Carlo calculation [21]. In further calculations the dipole moment distributions and Eq. (3) were used to evaluate the data (Table 4) for the probe with $K_0 = 1.35K$ in the KDP lattice in the paraelectric phase at two different temperatures. From these data, two important effects of the neighbouring dipoles can be observed: a) a small change (less than 15%) of E_B in the wide temperature interval in the paraelectric phase, and b) a decreased difference between the barrier in DKDP and the barrier in KDP at $(E_B)^D - (E_B)^H = 0.057$ eV. Since the average difference between barriers due to the isotope effect is ~ 0.05 eV (Table 1), an agreement with the experiments better than in the model in which the effect of neighbouring dipole moments is neglected has been obtained.

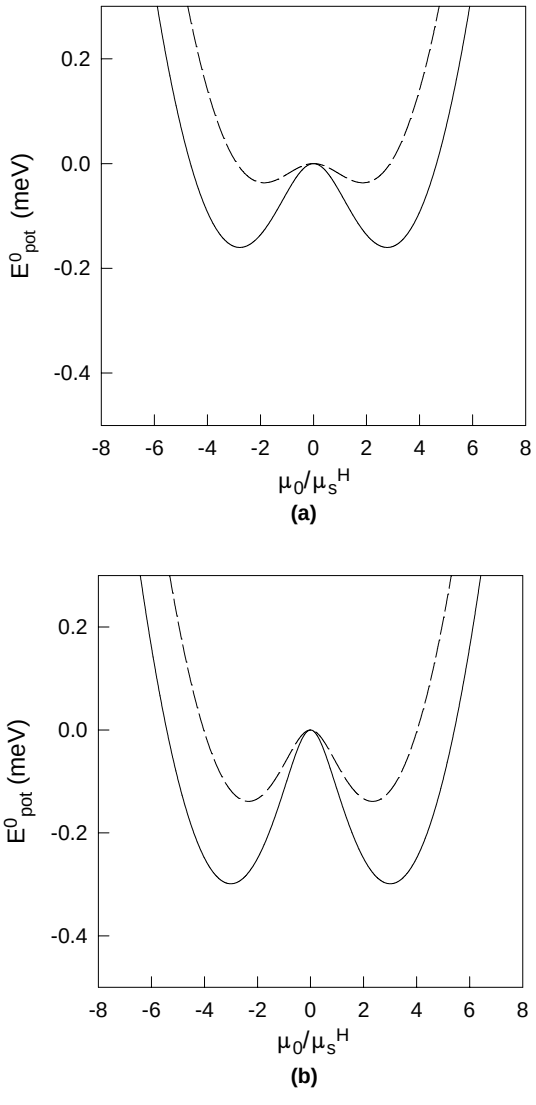

Fig. 1. Profile of dipole potentials of the probe ($K_0 = 1.236K$), solid line, and one of the PO_4^{3-} tetrahedra from the host ($K_0 = K$), dashed line, in the KDP (a) and DKDP (b) lattice vs relative dipole moment μ_0^s/μ_s^H calculated from Eq. 4 with the parameters given in Tables 2 and 3.

Table 3. Parameters for a local potential in the vicinity of a probe calculated for $K_0/K = 1.236$, and $\mu_s^H = 4.8 \times 10^{-22}\mu$ Ccm, in the KDP and DKDP lattices

	K_0/K	μ_0^s/μ_s^H	E_B/eV	$\hbar\omega/meV$
KDP	1.236	2.8	0.16	29.4
DKDP	1.236	3.0	0.30	31.3

Table 2. Values of the parameters h, IK, A and M used in Eqs (1, 2 and 3) for the KDP and DKDP lattices [18–21]

	h/eV	$IK/10^{20}\frac{eV}{\mu Ccm^2}$	$A/10^{41}\frac{eV}{\mu Ccm}$	$M/10^{14}\frac{eVs^2}{\mu C^2cm^2}$
KDP	0.110	1.375	4.58	1.91
DKDP	0.058	1.375	4.58	1.91

Table 4. Parameters for local potential in the vicinity of the probe in the KDP and DKDP lattices calculated at different temperatures in the paraelectric phase

	T/K	K_0/K	μ_0^s/μ_s^H	E_B/eV	$\hbar\omega/meV$
KDP	200	1.35	3.1	0.160	28.6
KDP	500	1.35	3.0	0.135	27.9
DKDP	500	1.35	3.3	0.192	29.4

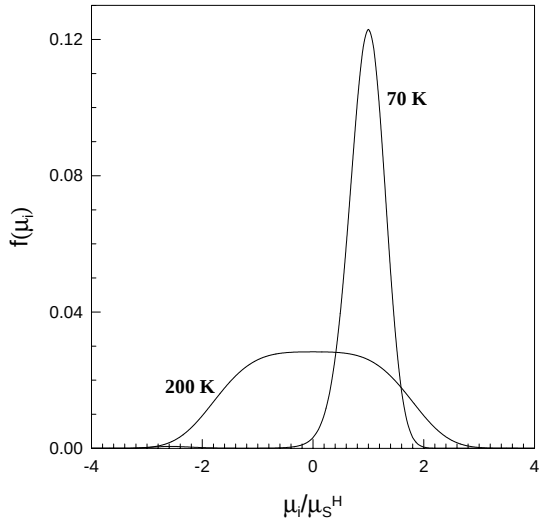

Fig. 2. Calculated distribution of the dipole moments in the paraelectric and in the ferroelectric phases.

3. DISCUSSION AND CONCLUSIONS

It has been observed that the earlier discussion of the isotope effect detected by a paramagnetic probe, which was based only on proton dynamics in the isolated double well-type potential [23] along $O-O$ bonds was not successful [11]. This failure was caused by the harmonic potential approximation according to which for any proton excited state replaced by a deuteron (or possible tunneling splitting) one would expect lower values for the same states. This leads to the effect in ΔE opposite to the one experimentally detected. According to the strong coupling model [20], the proton transfer along the $O-O$ bond can be approximated by an Arrhenius behavior since the activation energy in the paraelectric phase exhibits slightly lower value than the value of E_B in the adiabatic potential shown in Fig. 1a. A similar type of coupling between dipolar fluctuations and proton transfer has been also observed in the case of the AsO_4^{4-} probe within which the activation process for the proton hopping exhibits the same activation energy as the process for the polarization fluctuation in the paraelectric phase [3].

The agreements obtained between the proposed model and the experimental results open a new opportunity for more detailed microscopic description of the local probe behavior in the KDP-type of lattice. As noted earlier [19], the strong coupling model can describe the isotopic effect qualitatively. For a more sophisticated description of some of the experiments (*i.e.* inelastic neutron scattering experiments), one needs to include the long-range part of the direct interaction between dipole moments. In a more quantitative description of the isotope effect related to each particular probe and lattice we expect an additional correction due to the strong correlation between neighbouring dipoles even in paraelectric phase. Finally, we conclude that the consistency of the isotope effect in both the strong coupling model and in the proposed model for the isotope effect detected by paramagnetic probes now confirm a clear origin of the Arrhenius parameters of the probe dynamics.

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