

Hydrogen-bond configuration parameters for ferroelectrics isomorphic to KH_2PO_4

C. W. Fairall and W. Reese

Department of Physics and Chemistry, Naval Postgraduate School, Monterey, California 93940

(Received 23 September 1974)

The small tunneling approximation to the hydrogen-bond-ordering model of ferroelectrics of the KH_2PO_4 family has been fitted to experimental data for ferroelectrics with composition $X Y_2 Z O_4$, where X is K, Rb, or Cs, Y is the proton or deuteron, and Z is P or As. In almost all cases a quite satisfactory account of the thermodynamic parameters is obtained. The required tunneling parameters are 0, or nearly so, for the deuterated compounds and seem nearly independent of the cation. The hydrogen-bond occupation energy associated with the lowest-energy "disordered" state varies nearly linearly with cation radius for each series of compounds. The results are consistent with the suggestion that the energy parameters of deuterated and nondeuterated materials should scale as the square of the off-center distance.

The hydrogen-bond occupation configuration model of ferroelectrics isomorphic to KH_2PO_4 (KDP) was first developed by Slater.¹ It was then extended by Takagi² by the introduction of higher-energy configurations additional to those considered by Slater and further extended by Silsbee, Uehling, and Schmidt³ (SUS), who introduced a mean-field term to account for proton-lattice coupling. Although the SUS version of the model can be satisfactorily fitted to the curve of polarization versus temperature for KDP ferroelectrics, it frequently predicts a transition entropy in disagreement with experimental observations. In terms of the thermodynamic theory of ferroelectrics, such a failure is identical with a failure of the SUS model to correctly predict the Curie constant. Incorporation of tunneling into the model allows these discrepancies to be resolved.⁴ However, until recently the formulation of the tunneling theory was so computationally complex that detailed comparison between theory and experiment was seldom attempted. Recently Vaks and Zinenko⁵ have introduced a small-tunneling approximation to the full-tunneling model which seems both reasonably accurate and computationally attractive. As a consequence of the availability of this theory it was decided to use the small-tunneling approximation of the hydrogen-bond occupation model to examine changes in the parameters of the model with chemical substitution.

In addition to a tractable theory, such an endeavor requires a large body of experimental data. Based on work in a number of laboratories data are currently available for KH_2PO_4 ,⁶ KD_2PO_4 ,⁶ RbH_2PO_4 ,⁷ KH_2AsO_4 ,⁸ KD_2AsO_4 ,⁸ RbH_2AsO_4 ,⁸ CsH_2AsO_4 ,^{9,10} and CsD_2AsO_4 .¹⁰ For the most part these data consist of calorimetric data. Such data can be analyzed by separating the contribution to the heat capacity due to the ferroelectric transition from a slowly varying background. From such data the transition entropy ΔS can be computed as a function of temperature. Using the thermodynam-

ic theory of ferroelectrics the transition entropy can be converted to a curve of polarization versus temperature using the Curie constant, which is determined from susceptibility measurements. In a few cases, most notably for KDP, this procedure has been shown to give good agreement with direct polarization measurements.

The hydrogen-bond configuration model considers three important proton configurations. The ground state (energy zero) corresponds to two "top positions" or two "bottom positions" being occupied. The first excited state (energy ϵ_0) corresponds to occupation of one top and one bottom position. The next excited state (energy ϵ_1) corresponds to occupation of one or three positions. In addition to the two energy parameters the theory contains two other parameters, β , which describes the mean-field proton-lattice interaction, and Γ , which characterizes the tunneling.

Our procedure was to fit the small-tunneling theory of Vaks and Zinenko to the reduced polarization curve obtained from the transition entropy. This fit was subject to three subsidiary conditions which greatly reduced the flexibility in choosing parameters: (i) In reduced variables, the temperature was required to occur at $T/T_c = 1$; (ii) the polarization at T_c was required to match experiment; and (iii) the total transition entropy was required to match experiment.

In some cases our results differ from other^{5,7} attempts to apply the Vaks theory to KDP materials. These differences result primarily because of our strict adherence to condition (i). Initial parameter values were chosen by fitting the SUS theory ($\Gamma = 0$) to the reduced polarization curve subject to conditions (i) and (ii). Then Γ was increased, while maintaining conditions (i) and (ii), until condition (iii) was satisfied. In general this required only minor adjustments in the parameters ϵ_0 and β , which are most sensitive to the shape of the polarization curve. On the other hand, major in-

TABLE I. Results of fitting the small-tunneling version of the hydrogen-bond occupation model to the polarization of materials isomorphous to KDP. In this table experimental values are in parentheses and parameters fixed by the fitting procedure are underlined.

Property	$\text{KH}_2\text{AsO}_4^{\text{a}}$	$\text{RbH}_2\text{AsO}_4^{\text{a}}$	$\text{CsH}_2\text{AsO}_4^{\text{b}}$	$\text{KH}_2\text{PO}_4^{\text{c}}$	$\text{RbH}_2\text{PO}_4^{\text{d}}$	$\text{KD}_2\text{AsO}_4^{\text{a}}$	$\text{CsD}_2\text{AsO}_4^{\text{b}}$	$\text{KD}_2\text{PO}_4^{\text{c}}$
T_c (K)	<u>(96.15)</u>	<u>(109.75)</u>	<u>(146.23)</u>	<u>(122.)</u>	<u>(146.8)</u>	<u>(161.04)</u>	<u>(190.2)</u>	<u>(220)</u>
$\epsilon_0/K_B T_c$	0.361	0.405	0.455	0.494	0.510	0.345	0.440	0.513
$\epsilon_1/K_B T_c$	4.34	4.20	3.97	5.80	4.43	4.26	3.90	4.90
$\beta/K_B T_c$	0.205	0.185	0.154	0.160	0.135	0.208	0.158	0.102
$\Gamma/K_B T_c$	0.25	0.30	0.20	0.90	0.50	0	0	0
$\Delta S/R$	0.501	0.513	0.533	0.400	0.489	0.507	0.546	0.520
	<u>(0.506)</u>	<u>(0.502)</u>	<u>(0.530)</u>	<u>(0.40)</u>	<u>(0.488)</u>	<u>(0.500)</u>	<u>(0.521)</u>	<u>(0.46, 0.504)</u>
$P^2(0)V\alpha/2R$	0.528	0.530	0.526	0.498	0.513	0.522	0.526	0.513
$T_c - \Theta$ (K)	1.55	0.75	0.25	0.21	-0.08	3.63	1.13	0.70
	<u>(1.90)</u>	<u>(1.75)</u>		<u>(0.02)</u>		<u>(8.04)</u>		<u>(1.5)</u>
$P(T_c)/P(0)$	<u>0.862</u>	<u>0.755</u>	<u>0.625</u>	<u>0.365</u>	<u>0.300</u>	<u>0.922</u>	<u>0.701</u>	<u>0.724</u>

^aReference 8.

^bReferences 9 and 10.

^cReference 6.

^dReference 11.

creases in the parameter ϵ_1 were required. Thus the values of Γ and ϵ_1 are most sensitive to the total transition entropy. For the deuterated compounds, the SUS fit is satisfactory, so the results of previous SUS fits were used.

The results of the fitting are presented in Table I. Because of the fitting procedure, the best test of the success of the fits is in the prediction of the Curie constant. However, to evaluate the Curie constant from the theory one needs a value for the saturation polarization at 0 K. For the most part these values were obtained from transition entropy data using experimental values of the Curie constant. Thus, to avoid circularity the simplest test of the success of the theory is to test the equality

$$\frac{P^2(0)V\alpha}{2R} = \frac{\Delta S}{R}, \quad (1)$$

where V is the molar volume and α is the Curie constant. In almost all cases this equality is well satisfied. The difference between the Weiss temperature Θ and the transition temperature can be obtained from the calculation. This result is quite sensitive to the assumed parameters. Because of this sensitivity, the agreement observed in Table I is regarded as satisfying.

TABLE II. Comparison of the SUS parameters obtained from the small-tunneling fits to members of the KDP family. In this comparison values for deuterated materials are compared with values for the normal materials. It has been suggested that for a given material the parameter ratios should be constant.

Material	$\epsilon_{0d}/\epsilon_{0p}$	$\epsilon_{1d}/\epsilon_{1p}$	β_d/β_p	$P_d^2(0)/P_p^2(0)$
KH_2AsO_4	1.60	1.64	1.69	1.88
CsH_2AsO_4	1.27	1.30	1.35	1.40
KH_2PO_4	1.66	1.27	1.54	1.45

The least satisfactory comparison between the calculation and experiment occurs for the two materials with the most gradual transitions, KDP and RDP (RbH_2PO_4). For these materials the gradualness of the transition makes the separation of the heat capacity into a background and a ferroelectric part very uncertain. To obtain a consistent fit for RDP the data were reanalyzed using a background which was estimated self-consistently from the temperature dependence of polarization obtained from the model calculations. Vaks and Zinenko⁵ found it necessary to introduce an additional term in the model representing electrostriction to account for the data in KDP and RDP. We do not find such a term important for any of the other members of the KDP family and suggest that the difficulties in accounting for the data for KDP and RDP may represent problems in properly analyzing the data rather than limitations of the model.

The deuteron, because of its greater mass, is expected to have a much smaller tunneling integral than the proton in a similar potential. Since $\Gamma = 0$ allowed reasonable agreement for the deuterated compounds, this expectation is borne out. Additionally, the deuteron is expected to have a larger off-center distance (ξ_d) than the proton (ξ_p). It has been suggested⁴ that the configuration energies should satisfy

$$\frac{\xi_d^2}{\xi_p^2} = \frac{\epsilon_{0d}}{\epsilon_{0p}} = \frac{\epsilon_{1d}}{\epsilon_{1p}} = \frac{\beta_d}{\beta_p} = \frac{P_d^2(0)}{P_p^2(0)}. \quad (2)$$

This relationship cannot be checked unless the off-center distances determined below T_c are known. Such a measurement has been performed only in KDP.¹² However, the results of this investigation are consistent with the relationship of Eq. (2), as shown by Table II.

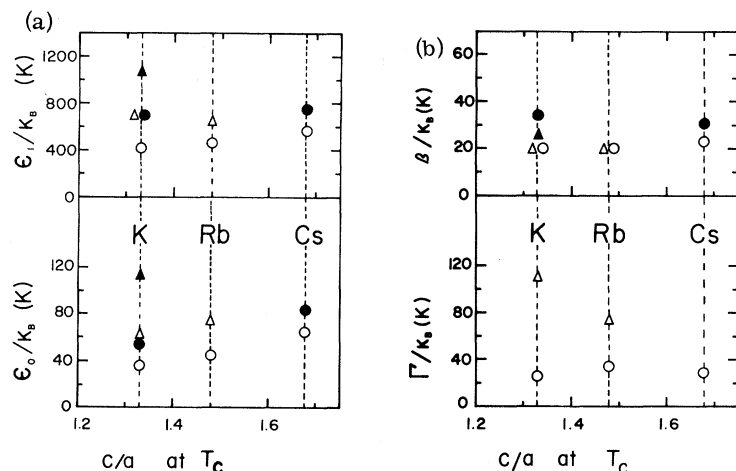


FIG. 1. Parameters of the small-tunneling version of the hydrogen-bond configuration model fitted to materials isomorphous to KDP as a function of the cation radius. Compounds with AsO_4 are shown as circles and compounds with PO_4 are shown as triangles. Filled symbols represent deuterated materials and open symbols represent normal materials.

The hydrogen-bond configuration parameters obtained in this study have been plotted against the cation radius in Fig. 1. This was done since these energy parameters should reflect an asymmetry between certain bonds relative to the polar direction. The most natural asymmetry parameter associated with the crystal is the c/a ratio. Cook¹³ has shown that the c/a ratio at the transition is proportional to the cation radius for each series of KDP isomorphs. The most significant result of such a comparison is that the parameter ϵ_0 ap-

pears to increase approximately linearly with cation radius. On the other hand, ϵ_1 seems almost independent of the cation radius. This can be interpreted as consistent with the idea that ϵ_1 represents an effective "ionization" state of the anion tetrahedron and hence should depend most strongly on the anion rather than the cation. The tunneling integral is nearly independent of the cation. Again, the observation is consistent with simple ideas since Γ should be most significantly influenced by anions to which the protons are bound.

¹J. C. Slater, *J. Chem. Phys.* **9**, 16 (1941).

²Y. Takagi, *J. Phys. Soc. Jpn.* **3**, 271, 273 (1948).

³H. B. Silsbee, E. A. Uehling, and V. H. Schmidt, *Phys. Rev.* **133**, A165 (1964).

⁴R. Blinc and S. Svetina, *Phys. Rev.* **147**, 430 (1966).

⁵V. G. Vaks and V. I. Zinenko, *Zh. Eksp. Teor. Fiz.* **64**, 650 (1973) [*Sov. Phys. -JETP* **37**, 330 (1973)].

⁶W. Reese, *Phys. Rev.* **181**, 905 (1969).

⁷B. A. Strukov, A. Baddur, V. I. Zinenko, V. K. Mikhailov, and V. A. Koptsik, *Fiz. Tverd. Tela* **15**, 1383, 2018 (1973) [*Sov. Phys. -Solid State* **15**, 939, 1347 (1973)].

⁸C. W. Fairall and W. Reese, *Phys. Rev. B* **6**, 193

(1972); **10**, 882 (1974).

⁹M. Deutsch and E. Litov, in *Proceedings of the Third International Conference on Ferroelectricity, 1973*, Edinburgh, Scotland (unpublished).

¹⁰B. A. Strukov, A. Baddur, and I. A. Velichko, *Fiz. Tverd. Tela* **13**, 2484 (1971) [*Sov. Phys. -Solid State* **13**, 2085 (1972)].

¹¹A. Amin and B. A. Strukov, *Fiz. Tverd. Tela* **10**, 3158 (1968) [*Sov. Phys. -Solid State* **10**, 2498 (1969)].

¹²G. E. Bacon and R. S. Pease, *Proc. R. Soc. Lond. A* **230**, 359 (1955).

¹³W. R. Cook, *J. Appl. Phys.* **38**, 1637 (1967).