



Slater-senko model for CsH_2PO_4

Author: V. Hugo Schmidt

This is an Accepted Manuscript of an article published in Ferroelectrics in 1984, available online:
<http://www.tandfonline.com/1080/00150198408245052>. [Ferroelectrics](#)

V.H. Schmidt, "Slater-Senko model for CsH_2PO_4 ," Ferroelectrics 53, 223-226 (1984).
<http://dx.doi.org/10.1080/00150198408245052>

Made available through Montana State University's [ScholarWorks](#)
scholarworks.montana.edu

SLATER-SENKO MODEL FOR CsH_2PO_4 *

V. HUGO SCHMIDT

Department of Physics, Montana State University, Bozeman,
Montana 59717, U.S.A.

Abstract This model for CsH_2PO_4 considers all six Slater H_2PO_4 configurations and employs the Senko long-range interaction to obtain a ferroelectric transition above 0 K. Model predictions are compared with experimental results for susceptibility, spontaneous polarization, and correlation length.

INTRODUCTION

Cesium dihydrogen phosphate (CDP) is called a one-dimensional ferroelectric (FE) because its hydrogen (H) bonds form a square lattice in which only the b-axis bonds order into aligned FE chains below T_c .¹ In each a-axis chain, structural bias causes FE order but alternate chains are antialigned giving overall antiferroelectric (AFE) order along a. The present model considers all six Slater group types and thus allows partial a-bond disorder.

MODEL

The Slater model² allows six proton arrangements in the four H-bonds linking each PO_4 to its neighbors, because there must be two protons close to each PO_4 and one proton in each bond. These six H_2PO_4 arrangements appear in Table I. The n_+ and n_- groups predominate in positive and negative domains respectively. The n_u and n_d groups have higher energy ϵ_1 because their a-axis protons are in the wrong positions. The n_0 groups occur where a- and b-axis chains both reverse, so one a-axis proton is in the wrong position.

TABLE I Slater H_2PO_4 group configurations for CDP (a axis horizontal and b vertical) and their fractional populations, b-axis electric dipole moments, and energies.

Group	H < > H	H H < > H	< > H H	H < > H H	H < > H	H < > H
Fr. pop.	n_+	n_-	n_u	n_d	n_o	n_o
Moment	μ	$-\mu$	μ	$-\mu$	0	0
Energy	0	0	ε_1	ε_1	ε_0	ε_0

Following Slater,² we count all Slater group distributions over the lattice sites without considering compatibility and then multiply by compatibility factors c_i . For example, the neighbor above or below an n_+ group has probability $n_+ + n_o + n_u = n_t$ of being compatible. This probability for the right or left neighbor is $n_+ + n_o + n_- = n_c$, so $c_+ = n_t^2 n_c^2$. Similarly, $c_- = n_b^2 n_c^2$, $c_u = n_t^2 n_w^2$, $c_d = n_b^2 n_w^2$, and $c_o = n_t n_b n_c n_w$, where $n_b = n_- + n_o + n_d$ and $n_w = n_u + n_o + n_d$.

The number W of ways of arranging N groups compatibly is $W = N! \pi_i (c_i^{N_i/2} / N_i!)$, where the 2 prevents double counting. Using the Stirling approximation and taking the logarithm, we obtain

$$\ln W = N(-n_+ \ln n_+ - n_- \ln n_- - 2n_o \ln n_o - n_u \ln n_u - n_d \ln n_d + n_t \ln n_t + n_b \ln n_b + n_c \ln n_c + n_w \ln n_w). \quad (1)$$

The internal energy U is given by

$$U = N[(2\varepsilon_0 - \varepsilon_1)n_o + \varepsilon_1 n_w - \mu E(n_t - n_b) - \beta(n_t - n_b)^2], \quad (2)$$

where E is electric field. In CDP (unlike KDP) the term with the Senko long-range interaction parameter β is essential for the FE transition.

The n_i are found by minimizing the free energy $F = U - kT \ln W$ with respect to these n_i , using Lagrange undetermined multipliers. The results for n_o and the FE and AFE order parameters $n_f = n_t - n_b$ and $n_a = n_c - n_w$ are

$$n_o = (1 - n_a^2) / 2(1 + n_a \coth \tau), \quad (3)$$

$$\begin{aligned} & [n_a(n_a + \coth \tau) + n_f(1 + n_a \coth \tau)](1 - n_f)e^{-\rho/2} \\ & = [n_a(n_a + \coth \tau) - n_f(1 + n_a \coth \tau)](1 + n_f)e^{\rho/2}, \end{aligned} \quad (4)$$

$$n_f = [(n_a^2 - n_{a0}^2) / (1 - n_{a0}^2)]^{0.5} (n_a + \coth \tau) / (1 + n_a \coth \tau), \quad (5)$$

in which $\rho = 2(bn_f + \varepsilon)$, $\sigma = \varepsilon_0/kT$, $\tau = \varepsilon_1/2kT$, $b = 2\beta/kT$, $\varepsilon = \mu E/kT$, and n_{a0} is the value which n_a assumes when $n_f = E = 0$, given by

$$n_{a0} = [1 + (1 + \coth \tau)^2 / 4e^{2\sigma}]^{-0.5}. \quad (6)$$

Eqs. (4) and (5) are solved simultaneously to find n_f and n_a .

COMPARISON WITH EXPERIMENT

We calculate the three unknown model parameters β , ε_0 , and ε_1 from $T_c = 153$ K, Curie-Weiss constant $C = 50,000$ K, and $dP_s^2/dT = -9.25 \times 10^{-5}$ C^2/m^4K , the latter two measured near T_c .³ To relate C to our model parameter ε/n_f we use $\varepsilon/n_f = P_{sat}\mu(T - T_c)/\varepsilon_0 CkT$, where P_{sat} is the saturation P_s of 3.3×10^{-2} C/m², $\mu = P_{sat}/N$ is the moment 3.83×10^{-30} C-m per molecule, and ε_0 is 8.85×10^{-12} f/m.

To relate ε/n_f to our model we expand Eq. (4) in a power series in ε/n_f , keep terms to first order, use Eq. (6) to eliminate n_a because $n_a = n_{a0}$ here, and find

$$\varepsilon/n_f = -b + a/c \text{ with } a = [(1 + \coth \tau)/2e^\sigma]^2, \quad c = 1 + (1 + a)^{0.5} \coth \tau. \quad (7)$$

At T_c , $\varepsilon/n_f = 0$ and Eq. (7) reduces to $a_c/c_c - b_c = 0$.

We use $dP_s^2/dT = -P_{sat}^2 n_f^2 / (T_c - T)$ to relate dP_s^2/dT to our model. We find n_f^2 by expanding Eq. (5) to third order in n_f with $E = 0$, substituting for $n_a = n_{a0}$ from Eq. (6), and obtain

$$n_f^2 = (b - a/c) / b(1 + a/c + ab/2c). \quad (8)$$

These relations give $\epsilon/n_f = 0.0207t$ and $n_f^2 = -13t$, where $t = (T - T_c)/T_c$. Then dividing Eq. (7) for ϵ/n_f by Eq. (8) for n_f^2 at reduced temperatures t and $-t$ respectively, we obtain $b(1+b+b^2/2) = 0.0207/13 = 0.00159$ which at T_c gives $b_c = 0.00159$ or $\beta/k = 0.145 \pm 0.015$ K. Solving Eqs. (7) and (8) yields $\epsilon_0/k = 640 \pm 150$ K and $\epsilon_1/k = 4.4$ K with error limits 0.9 K to 90 K, while Eqs. (6) and (3) evaluated at T_c yield $n_{a0} = 0.93$ with error limits 0.56 to 0.98, and $n_0 = 0.00101$ with error limits 0.0008 to 0.004.

The correlation length ξ depends on n_0 because H-bonded chains reverse only at n_0 groups. In units of H-bond separation it is $\xi = -1/\ln[1 - 4n_0/(1 - n_f^2)]$. The correlation length along b at T_c is 250 lattice spaces or $800 \text{ \AA}$, with error limits 200 to $1000 \text{ \AA}$, consistent with the measured⁴ value at T_c in CsD_2PO_4 of $600 \text{ \AA}$.

CONCLUSIONS

This model accounts for susceptibility, polarization, and correlation length phenomena in CDP quite well, and provides the first estimate of the interaction which aligns protons in a -axis chains. This interaction is quite weak, so 1) partial disorder in such chains might be observable in neutron diffraction experiments, and 2), a -bond intrabond motion should cause observable effects, such as in deuteron spin-lattice relaxation in CsD_2PO_4 .⁵

REFERENCES

1. H. Matsunaga, K. Itoh, and E. Nakamura, J. Phys. Soc. Japan, **48**, 2011 (1980).
2. H. B. Silsbee, E. A. Uehling, and V. H. Schmidt, Phys. Rev., **133**, A165 (1964), describe the Slater and Senko models.
3. N. Yasuda, S. Fujimoto, M. Okamoto, H. Shimizu, K. Yoshino, and Y. Inuishi, Phys. Rev., **B20**, 2755 (1979).
4. B. C. Frazer, D. Semmingsen, W. D. Ellenson, and G. Shirane, Phys. Rev., **B20**, 2745 (1979).
5. B. Topic, V. Rutar, J. Slak, M. I. Burgar, S. Zumer, and R. Blinc, Phys. Rev., **B21**, 2695 (1980).

* Work supported in part by NSF Grant DMR8205280.