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SLATER–SENKO MODEL FOR CsH₂PO₄

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Abstract This model for CsH₂PO₄ considers all six Slater H₂PO₄ 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 Tc.¹ In each a-axis chain, structural bias causes FE order but alternate chains are antialigned giving overall anti-ferroelectric (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 PO₄ to its neighbors, because there must be two protons close to each PO₄ and one proton in each bond. These six H₂PO₄ arrangements appear in Table I. The n⁺ and n⁻ groups predominate in positive and negative domains respectively. The n₀ and n₃ groups have higher energy ε₁ because their a-axis protons are in the wrong positions. The n₀ 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 $> |
|-------|---------|-------|--------|--------|--------|
| Fr. pop. | $n_+$ | $n_-$ | $n_u$ | $n_d$ | $n_o$ | $n_o$ |
| Moment | $\mu$ | $-\mu$ | $\mu$ | $-\mu$ | 0 | 0 |
| Energy | 0 | 0 | $\varepsilon_1$ | $\varepsilon_1$ | $\varepsilon_0$ | $\varepsilon_0$ |

Following Slater, 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 $n_+n_0+n_u=n_t$ of being compatible. This probability for the right or left neighbor is $n_+n_0+n_-=n_c$, so $c_+=n_t^2n_c^2$. Similarly, $c_-=-n_b^2n_c^2$, $c_u=-n_t^2n_w^2$, $c_d=n_b^2n_w^2$, and $c_o=n_tn_bn_cn_w$, where $n_b=n_++n_0+n_d$ and $n_w=n_u+n_o+n_d$.

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

$$1nW=N(-n_+ln n_+-n_-ln n_-2n_0ln n_0-n_u ln n_u-n_dln n_d$$
$$+n_tln n_t+n_b ln n_b+n_c ln n_c+n_wln n_w).$$

(1)

The internal energy $U$ is given by

$$U=N[(2\varepsilon_0-\varepsilon_1)n_0+\varepsilon_1n_w-\mu E(n_t-n_b)-\beta(n_t-n_b)^2],$$

(2)

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

The $n_i$ are found by minimizing the free energy $F=U-kTlnW$ 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 $n_s=n_c-n_w$ are
\[ n_o = (1 - n_a^2) / 2(1 + n_a \coth \tau), \]
\[ [n_a(n_a + \coth \tau) + n_f(1 + n_a \coth \tau)](1 - n_f) e^{-\rho/2} = [n_a(n_a + \coth \tau) - n_f(1 + n_a \coth \tau)](1 + n_f) e^{\rho/2}, \]
\[ n_f = [(n_a^2 - n_{ao}^2)/(1 - n_{ao}^2)]^{0.5}(n_a + \coth \tau)/(1 + n_a \coth \tau), \]
in which \( \rho = 2(bn_f + \varepsilon) \), \( \sigma = \varepsilon_0/kT \), \( \tau = \varepsilon_1/2kT \), \( b = 2\beta/kT \), \( \varepsilon = \mu E/kT \), and \( n_{ao} \)

is the value which \( n_a \) assumes when \( n_f = E = 0 \), given by
\[ n_{ao} = [1 + (1 + \coth \tau)^2/4e^2\sigma]^{-0.5}. \]

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

**COMPARISON WITH EXPERIMENT**

We calculate the three unknown model parameters \( \beta \), \( \varepsilon_0 \), and \( \varepsilon_1 \) from \( T_c = 153 \text{ K} \), Curie-Weiss constant \( C = 50,000 \text{ K} \), and \( dP_s^2/dT = -9.25 \times 10^{-5} \)

\( C^2/m^4 \text{K} \), the latter two measured near \( T_c \). To relate \( C \) to our model parameter \( \varepsilon/n_f \) we use \( \varepsilon/n_f = P_{\text{sat}} \mu(T - T_c)/\varepsilon_0 C kT \), where \( P_{\text{sat}} \)

is the saturation \( P_s \) of \( 3.3 \times 10^{-2} \text{ C/m}^2 \). \( \mu = P_{\text{sat}} / N \) is the moment \( 3.83 \times 10^{-30} \text{ C-m per molecule, and } \varepsilon_0 \)

is \( 8.85 \times 10^{-12} \text{ f/m} \).

To relate \( \varepsilon/n_f \) to our model we expand Eq. (4) in a power series in \( \varepsilon/n_f \), keep terms to first order, use Eq. (6) to eliminate \( n_a \) because \( n_a = n_{ao} \) here, and find
\[ \varepsilon/n_f = -b + a/c \text{ with } a = [(1 + \coth \tau)/2e^\sigma]^{0.5} \text{ coth} \tau. \]

At \( T_c \), \( \varepsilon/n_f = 0 \) and Eq. (7) reduces to \( a_e/c_e - b_e = 0 \).

We use \( dP_s^2/dT = P_{\text{sat}}^2 n_f^2/(T_c - T) \) 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 \( n_a = n_{ao} \) from Eq. (6), and obtain
\[ n_f^2 = (b - a/c)/b(1 + a/c + ab/2c). \]
These relations give $\epsilon/n_f = 0.0207 t$ and $n_f^2 = -13t$, where $t = (T-T_C)/T_C$. Then dividing Eq. (7) for $\epsilon/n_f$ 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 $n_o = 0.00101$ with error limits 0.0008 to 0.004.

The correlation length $\xi$ depends on $n_o$ because $H$-bonded chains reverse only at $n_o$ groups. In units of $H$-bond separation it is $\xi = -1/ln[1-4n_o/(1-n_o^2)]$. The correlation length along $b$ at $T_C$ is 250 lattice spaces or 800 Å, with error limits 200 to 1000 Å, consistent with the measured value at $T_C$ in CsD$_2$PO$_4$ of 600 Å.

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$_2$PO$_4$.

REFERENCES

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