



Theory of pressure and deuteration effects in the ferroelectric potassium dihydrogen phosphate
by Steven Marshall Torstveit

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF
PHILOSOPHY in PHYSICS

Montana State University

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Abstract:

We examine the phenomenological and microscopic theories of ferroelectricity in KH_2PO_4 (KDP), both for the case of a perfectly rigid lattice and for the case where the lattice is allowed to deform either spontaneously or under applied pressure. We make a formal connection between the phenomenological and microscopic theories of pressure dependence, thus permitting a systematic examination of the predictions of particular microscopic models. By examining the undeuterated and deuterated crystals within the same framework we achieve an economy of assumptions and free parameters.

In particular, we construct a model for the pressure and deuteration dependence of the parameters which occur in Blinc and Svetina's treatment of the four-particle cluster approximation to the tunneling model, and find that the theory is in quantitative agreement with the body of experimental evidence provided that the long-range interaction parameter γ is negative, corresponding to antipolar long-range coupling. The possibility of applying the methods used here to the study of other crystals of the KDP class is also discussed.

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DIHYDROGEN PHOSPHATE

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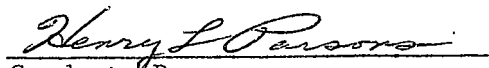
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TABLE OF CONTENTS

	Page
VITA	ii
ACKNOWLEDGMENTS	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
ABSTRACT	viii
I. INTRODUCTION	1
II. STRAIN-INDEPENDENT THEORY	7
A. Phenomenological Theory of Landau	7
B. Microscopic Theories	22
1. Slater-Takagi-Senko-SUS Theory	22
2. Tunneling Models	30
a. Transverse Ising Model	30
b. Four-Particle Cluster Approximation	43
3. Relations Among the Microscopic Theories	53
III. STRAIN-DEPENDENT THEORY	59
A. Phenomenological Theory	59
B. Microscopic Theories	68
1. Introduction	68
2. Model for Pressure and Deuteration Dependence in the FPCA	69
a. General Remarks	69

	Page
b. The Parameter d	72
c. Pressure Dependence	76
d. Connection with Phenomenological Theory	78
3. Fitting Procedure	79
a. Ambient Pressure	79
b. Applied Pressure	87
4. Results	90
IV. CLOSING REMARKS	92
1. Conclusions	92
2. Recommendations for Further Study	92
REFERENCES	96
APPENDIX - Calculation of γ_H	101

LIST OF TABLES

Table	Page
I. Experimental Values for Landau Parameters in KDP	20
II. Some Experimental Lattice Dimensions for KDP and DKDP at Various Temperatures.	74
III. Results for Four-Particle Cluster Approximation Models . .	83
III. A. Ambient Pressure.	84
III. B. Applied Pressure.	85

LIST OF FIGURES

Figure	Page
1. Structure of KH_2PO_4 (KDP)	3
2. Gibbs Potential for Second Order Case ($B > 0$)	9
3. Polarization and Susceptibility for $B > 0$ Case	11
4. Gibbs Potential for $E = 0$ for First Order Case ($B < 0$)	12
5. Polarization and Susceptibility for $B < 0$ Case	14
6. Gibbs Potential for $B < 0$ Case in Applied E Field	15
7. Phase Diagram for KDP in E, T, p Space	16
8. Polarization and Susceptibility for Critical Case ($B = 0$)	18
9. Configurational Energies and Dipole Moments for KDP	24
10. Schematic Behavior of Gibbs Potential in Slater-Takagi Type Theories	28
11. Energy and Eigenfunctions for Particle in Double Well	33
12. Relation of Slater-Takagi and Ising-like Energies	56
13. Free Energy as a Function of Strain and Polarization	62
14. Projection of KDP Structure on xy Plane	70
15. Polarization vs. Temperature for KDP and DKDP	81

ABSTRACT

We examine the phenomenological and microscopic theories of ferroelectricity in KH_2PO_4 (KDP), both for the case of a perfectly rigid lattice and for the case where the lattice is allowed to deform either spontaneously or under applied pressure. We make a formal connection between the phenomenological and microscopic theories of pressure dependence, thus permitting a systematic examination of the predictions of particular microscopic models. By examining the undeuterated and deuterated crystals within the same framework we achieve an economy of assumptions and free parameters. In particular, we construct a model for the pressure and deuteration dependence of the parameters which occur in Blinc and Svetina's treatment of the four-particle cluster approximation to the tunneling model, and find that the theory is in quantitative agreement with the body of experimental evidence provided that the long-range interaction parameter γ is negative, corresponding to antipolar long-range coupling. The possibility of applying the methods used here to the study of other crystals of the KDP class is also discussed.

I. INTRODUCTION

Potassium dihydrogen phosphate (KDP) and its isomorphs form an important class of hydrogen-bonded order-disorder ferroelectrics. A ferroelectric material is one which below a certain temperature (called the Curie temperature, T_c) develops a spontaneous electric dipole moment whose direction can be reversed by the application of an electric field. In an order-disorder ferroelectric the macroscopic polarization is in some sense due to the ordering of elementary dipoles, whereas for a displacive ferroelectric the polarization is caused by the displacement of the ions of the lattice in such a way that the positive and negative centers of charge no longer coincide. In terms of the soft-mode description (see, e.g., Ref. [1]), the ferroelectric transition is seen as a result of the temperature dependence of the frequency of one of the natural modes of the lattice, causing the mode displacements to become "frozen in" when the frequency becomes zero. An order-disorder transition can thus be thought of as the freezing in of a normal mode of the pseudo-spin system into which one has transformed the large nonlinearity of the problem, while a displacive transition is due to the instability of an optical phonon. In the KDP problem, one is actually dealing with a coupled pseudo-spin-phonon system, inasmuch as the ordering of the protons (represented by the pseudo-spins) does not in itself produce a dipole moment in the direction of the ferroelectric axis, since their motion along the

hydrogen bonds is nearly perpendicular to it (see Fig. 1), but rather triggers a displacement of the heavy ions in the lattice. For this reason KDP belongs to the class of improper ferroelectrics (those for which the order parameter is not identical with the polarization) in which the order parameter nevertheless has the same symmetry as the polarization. Since we will be concerned in this thesis with the static ferroelectric properties of KDP, this distinction will be of no consequence, and we can as well take the order parameter to be the polarization itself¹.

Since the discovery of ferroelectricity in KDP in 1935³, this crystal and its isomorphs have been the subjects of hundreds of experimental and theoretical papers. An early theoretical paper by J. C. Slater⁴ successfully explained qualitatively many of the features of the ferroelectric transition using only the assumptions that the hydrogens occupied off-center positions in the hydrogen bonds in such a way that each bond was singly occupied and that every phosphate radical had exactly two protons close to it (the ice rule). Unlike the case of ice, however, certain of the configurations were associated with dipole moments; these configurations were assumed to have a lower energy. This approach received further development in the ensuing years, and progress up to 1964 was summarized in a paper by Silsbee, Uehling, and Schmidt (SUS)⁵. The model was extended by Blinc and Svetina in 1966 to include the effects of the quantum mechanical tunneling of the proton across the potential barrier between the off-

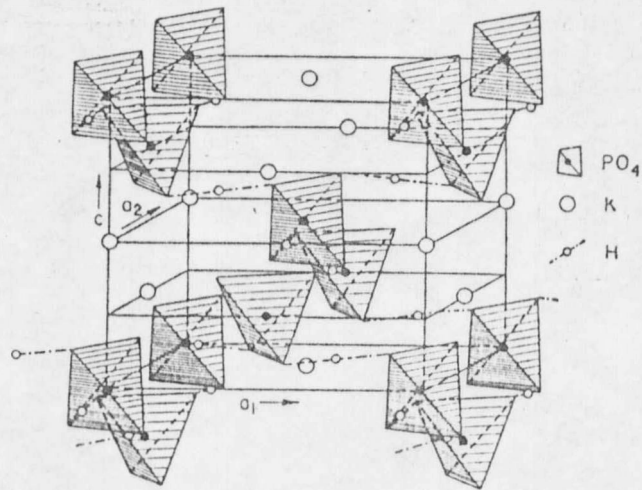


Fig. 1. The structure of KH_2PO_4 (after West²). For a projection of this structure onto the a_1a_2 plane, see Fig. 14.

center positions in the hydrogen bonds⁶. The theory by this time had become capable of quantitative description of the ferroelectric properties of KDP.

Another line of development which has been pursued with some success has been the description in terms of the Blinc-deGennes Hamiltonian^{7,8}, which comprises an Ising Hamiltonian in a transverse (tunneling) field, the z components of the pseudo-spins being coupled by an exchange-like interaction. This model has proven useful for analyzing dynamical phenomena, particularly in connection with the soft-mode description¹. The coupling of the pseudo-spins to the optical phonon responsible for the ferroelectric displacements was treated by K. K. Kobayashi⁹ in 1968; this coupling leads to a renormalization of the exchange-like interaction constant. There is a formal connection¹⁰ between the transverse Ising model and that of the Slater-type models; this connection is discussed in Section II.3.

Although the pure Slater model can be solved exactly in two dimensions¹¹, the practical solution of any of the above models in three dimensions requires at some stage the application of a mean-field approximation. For this reason, the microscopic models admit description in terms of the phenomenological theory of Landau, in which the free energy is expanded in powers of the order parameter--in this case, the polarization. Landau theory has proven useful for summarizing and comparing the results of a variety of experiments, and it has been

shown experimentally to be applicable even very close to the transition temperature in KDP. There are excellent theoretical reasons for this as well^{12,13}. We will therefore express the main predictions of the microscopic theories in terms of the coefficients in the Landau expansion, thus facilitating comparison of the theory with experiment.

Isotopic and isovalent substitution and the application of pressure are some of the most important tools for elucidating the nature of the microscopic interactions which lead to ferroelectricity in various substances. This is especially true of crystals of the KDP class. In this work we will take pressure and deuteration effects into account in a consistent way, thereby reducing the total number of free parameters needed to describe the ferroelectric behavior of KDP and DKDP (KD_2PO_4) and providing a more rigorous test of the theory than would otherwise be obtained.

This paper is divided into two main sections: the first deals with the theoretical description of KDP as would apply to a rigid lattice, and the second describes strain-related effects. Each of these is in turn divided into subsections dealing with the phenomenological and microscopic theories. It will be seen that a detailed phenomenological description is of great utility in the construction of a proper microscopic theory of the strain-related effects.

Insofar as the experimental data for KDP can be reduced to a consistent set of Landau coefficients, the theory developed here is in

quantitative agreement with the body of experimental evidence. The possibility of extending the model to other crystals of the KDP class seems promising, and we will discuss this possibility in Section IV.3.

II. STRAIN-INDEPENDENT THEORY

A. Phenomenological Theory of Landau

In this section we will review some of the main features of the phenomenological theory of Landau^{14,15} as it applies to a uniaxial ferroelectric¹⁶. One assumes that the Helmholtz free energy $F(P,T)$ can be expanded in powers of the order parameter, which is in this case the polarization P :

$$F = F_0 + \frac{1}{2}AP^2 + \frac{1}{4}BP^4 + \frac{1}{6}CP^6 + \frac{1}{8}DP^8 + \dots, \quad (1)$$

the coefficients of which are in general functions of the temperature T (due to the requirement of symmetry under $P \rightarrow -P$, only even powers of P occur). A phase transition will occur if A has a zero at some temperature T_0 ; for cases of interest here we will keep the leading term in the expansion of the coefficient A in powers of $T - T_0$, writing the P dependence as

$$F = \frac{1}{2}A_0(T - T_0)P^2 + \frac{1}{4}BP^4 + \frac{1}{6}CP^6 + \dots, \quad (2)$$

The equation of state is found by differentiation with respect to the polarization

$$E = \frac{\partial F}{\partial P} = A_0(T - T_0)P + BP^3 + CP^5 + \dots, \quad (3)$$

where E is the applied field along the polarization axis. The inverse isothermal susceptibility is then given by

$$\chi^{-1}_T = \left. \frac{\partial E}{\partial P} \right|_T = A_0(T - T_0) + 3BP^2 + \dots \Big|_{E=0} \quad (4)$$

For cases where E is to be held constant, it is useful to introduce the Gibbs potential, related to the free energy F by the Legendre transform $G = F - EP$. Then the polarization will be a parameter chosen in such a way as to minimize the function G for any particular value of E . The condition for an equilibrium value of P is that G be an absolute minimum. This, of course, implies that

$$\frac{\partial G}{\partial P} = \frac{\partial F}{\partial P} - E = A_0(T-T_0)P + BP^3 + CP^5 - E = 0 \quad (5)$$

and one obtains the same equation of state as before (Eq. (3)).

At this point, assuming that $C > 0$, it is useful to distinguish three cases, viz., $B > 0$, $B < 0$, and $B = 0$.

Case 1: $B > 0$.

For this case, Eq. (5) has two real solutions for $E = 0$. One of these, $P = 0$, will minimize the function $G(T, 0)$ for $T > T_0$ and will be a relative maximum for $T < T_0$; this solution represents a paraelectric (nonpolar) state. The other solution, representing a ferroelectric (polar) state, will minimize G below T_0 . This solution is given by

$$P = \pm \left[\frac{-B + (B^2 - 4A_0(T-T_0)C)^{1/2}}{2C} \right]^{1/2}. \quad (6)$$

(The Gibbs potential $G(T, 0)$ is plotted for this case as a function of the parameter P for various fixed temperatures in Fig. 2.) For T near T_0 , one finds that $|P| \sim (T_0 - T)^{1/2}$, rising continuously as the temperature is decreased below T_0 . This type of transition, for which the order parameter is continuous, is referred to as a second order

