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 KH2PO4 (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 y 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.
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

Approved:

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Chairman, Graduate Committee
Head, Major Department
Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana
August, 1979
## ACKNOWLEDGEMENTS

The author expresses his appreciation to:

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*for:*

Michael Kinnersley, Alexander Schalm, Robert Western, G. A. Samara, David Robinson, Michael Dixon, Fran Calvin.
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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 itself.

Since the discovery of ferroelectricity in KDP in 1935, this crystal and its isomorphs have been the subjects of hundreds of experimental and theoretical papers. An early theoretical paper by J. C. Slater 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). 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 $\text{KH}_2\text{PO}_4$ (after West$^2$). For a projection of this structure onto the $a_1 a_2$ plane, see Fig. 14.
center positions in the hydrogen bonds. 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, 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 description. The coupling of the pseudo-spins to the optical phonon responsible for the ferroelectric displacements was treated by K. K. Kobayashi in 1968; this coupling leads to a renormalization of the exchange-like interaction constant. There is a formal connection 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 dimensions, 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\textsuperscript{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\textsubscript{2}PO\textsubscript{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 as it applies to a uniaxial ferroelectric. 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 \( P \):

\[
F = F_0 + \frac{1}{2} AP^2 + \frac{1}{4} BP^4 + \frac{1}{6} CP^6 + \frac{1}{8} DP^8 + \ldots \ \ (1)
\]

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

\[
F = \frac{1}{2} A_0 (T - T_0) P^2 + \frac{1}{4} BP^4 + \frac{1}{6} CP^6 + \ldots \ \ (2)
\]

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

\[
\mathcal{E} = \frac{\partial F}{\partial P} = A_0 (T - T_0) P + BP^3 + CP^5 + \ldots \ \ (3)
\]

where \( \mathcal{E} \) is the applied field along the polarization axis. The inverse isothermal susceptibility is then given by

\[
\chi_{\mathcal{E}}^{-1} = \mathcal{E} \left. \frac{\partial \mathcal{E}}{\partial P} \right|_{\mathcal{E} = 0} = A_0 (T - T_0) + BP^2 + \ldots \ \ (4)
\]
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 I: \( B > 0 \).

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

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

(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
Fig. 2. The Gibbs potential as a function of the parameter P for various fixed temperatures for the case $B > 0$. 
transition.

The inverse susceptibility in the two phases is found by substituting the appropriate value of $P$ for $E = 0$ into Eq. (4), yielding

$$\chi^{-1}_T = \begin{cases} \frac{A_0}{2}(T - T_0) & T > T_0 \\ 2A_0(T_0 - T) & T < T_0 \end{cases}.$$

These results are shown schematically in Fig. 3.

Case 2: $B < 0$.

In this case one again has the paraelectric solution $P = 0$, which will be at least a local minimum of $G(T, 0)$ above $T_0$. However, below a temperature $T_c > T_0$ there will be an absolute minimum in $G$ at a nonzero $P$ (see Fig. 4). This temperature, known as the Curie temperature, becomes the stability limit of the high-temperature phase. The Curie temperature is determined by the solution of the set of equations:

$$G = O = \frac{1}{2}A_0(T_c - T_0)P^2 + \frac{1}{4}BP^4 + \frac{1}{6}CP^6,$$

$$E = O = A_0(T_c - T_0)P + BP^3 + CP^5. \quad (8)$$

One can eliminate the terms in $A_0$ to find

$$P(T_c) = \pm \left(-\frac{3B}{4C}\right)^{1/2}. \quad (9)$$

Thus the polarization jumps discontinuously at $T = T_c$ from $P = 0$ to the value $(-3B/4C)^{1/2}$. A transition in which the order parameter displays such a discontinuity is known as a first order transition.
Fig. 3. The polarization (a) and inverse isothermal susceptibility (b) as functions of temperature for the case $B > 0$. 
Fig. 4. The Gibbs potential for \( E = 0 \) as a function of the parameter \( P \) for the case \( B < 0 \). The curves shown are the isotherms at the indicated temperatures \( T \). \( T_{cr} \) is the critical temperature, \( T_1 \) the upper metastability limit, \( T_c \) the Curie temperature, and \( T_0 \) the Curie-Weiss temperature. The dots indicate inflection points.
Substituting the value of $P(T_c)$ from Eq. (9) into Eq. (8) gives

$$T_c = T_0 + \frac{3B^2}{16A_0 C}. \quad (10)$$

The spontaneous polarization at arbitrary $T < T_c$ is given by the solution of Eq. (3) for $E = 0$

$$P^2 = \frac{-B}{4C} \left( 2 + \left( 1 - 16A_0 C(T-T_c)/B^2 \right)^\frac{1}{2} \right) \quad (11)$$

The inverse dielectric susceptibility for the two phases is found as before by substituting the appropriate value of $P$ into Eq. (4). The resulting function is depicted schematically in Fig. 5.

For the case of a nonzero applied field $E$, the Gibbs potential $G = F - EP$ will have a term linear in $P$ subtracted from it (see Fig. 6). There will continue to be a jump in the polarization at a temperature $T_c(E)$ up until this temperature reaches the critical temperature $T_{cr} = T_c(E_{cr})$, at which the two inflection points in the $T_c(E)$ isotherm (indicated by dots in Fig. 6) come together. This will occur at

$$T_{cr} = T_0 + \frac{9B^2}{20A_0 C}, \quad P_{cr} = \pm \frac{-3B}{10C} \quad (12)$$

$$E_{cr} = \pm \left( \frac{2(-B/5)^{\frac{1}{2}}}{(C/3)^{\frac{1}{2}}} \right)^\frac{1}{2} \quad (12)$$

The phase diagram in the ET plane is shown in Fig. 7.

There is yet another temperature of interest for the first order case—the metastability limit $T_1$, above which the ferroelectric state can no longer persist temporarily as the temperature is raised from
Fig. 5. The polarization (a) and inverse isothermal susceptibility (b) as functions of temperature for the case $B < 0$. The dots indicate the critical points (cf. Fig. 7(a)).
Fig. 6. The Gibbs potential as a function of the parameter $P$ for the case of $B < 0$ with a nonzero applied field $E$. The dots indicate the inflection points which merge when $T$ equals the critical temperature $T_{cr}$. $T_c(E)$ is the transition temperature in the applied field $E$. 
Fig. 7. Phase diagram for KDP. (a) is a projection on a plane where the pressure $p = \text{const} < p_t$; (b) is a projection on a plane where $T = \text{const} < T_t$. First order lines and the triple point (TP) line are solid, and lines of critical points (CP) are shown by dashed lines.
below $T_c$ due to the trapping of the system in one of the outer local
minima (see Fig. 4). This temperature is the one at which the slope
is zero at the outer inflection point. Solving for the temperature at
which the first and second derivatives of the free energy are both zero,
we find

$$T_2 = T_0 + \frac{B^2}{4A_0C}. \quad (13)$$

Using the value of $T_c - T_0$ from Eq. (10), we find that $T_1$ is given in
terms of the Curie temperature $T_c$ as

$$T_1 = T_c + \frac{B^2}{16A_0C}. \quad (14)$$

Similarly, the high temperature phase can persist temporarily above $T_0$.
The limits of possible thermal hysteresis are thus $T_0 < T < T_1$.

Case 3. $B = 0$.

In this case one has a so-called critical transition at $T = T_c = T_0$. At this temperature the free energy curve is flat at
$P = 0$, and it follows from Eq. (3) for $E = 0$ and $B = 0$ that the spontaneous polarization increases continuously with decreasing temperature as $(T_0 - T)^{\frac{1}{2}}$, rather than as $(T_0 - T)^{\frac{1}{4}}$ as in the second order ($B > 0$)
case. The curves $P(T)$ and $\chi^{-1}(T)$ for this case are shown in Fig. 8.

Having solved for the various physical quantities in terms of the
Landau coefficients, one can use experimental results of various kinds
to determine the Landau coefficients for a given system. Some recent
Fig. 8. The polarization (a) and inverse isothermal susceptibility (b) for the case $B = 0$. 
experimentally determined values of the Landau coefficients for KDP are shown in Table I. It can be seen that at ambient pressure the coefficient \( B \) is negative, so we are dealing with a first order transition (case 2). However, it has been shown experimentally that the value of \( B \) at the transition temperature depends on the pressure \( p \) in such a way that at \( p = 2.3 \) kbar the coefficient \( B \) becomes zero (case 3), and that above this pressure \( B \) is positive (case 1). Therefore, at some pressure or other each of the three cases will apply to KDP. It will be one of the tasks of the microscopic theory to predict \( \frac{dB}{dp} \) at the transition temperature.

It is instructive to examine the phase diagram of KDP in the three dimensional space of variables \( E, T, \) and \( p \) (see Fig. 7). As \( p \) is increased and \( |B| \) decreases, the critical points given by Eq. (12) will begin to converge, and the two lines of critical points join together smoothly at the point \( B(p_c, T_c) = 0 \), merging into a single line of critical points in the \( E = 0 \) plane. Such a junction of three lines of critical points is called a tricritical point, a point of some topical interest.

The Landau coefficients provide a convenient way of summarizing the results of many different experiments on KDP, and so should be extremely useful for expressing the theoretical predictions of the various microscopic models as well, since this will permit direct comparison of the theory with the body of experimental evidence. As was
TABLE I. Some recent published values of the parameters in the Landau expansion of the free energy \( F = \frac{1}{2} A_0 (T - T_0)^2 + \frac{1}{4} B P^4 + \frac{1}{6} C P^6 + \frac{1}{8} D P^8 \) at ambient pressure\(^a\).

<table>
<thead>
<tr>
<th>Ref., (1(\text{st}) Author)</th>
<th>(A_0) (10^{-3}) esu</th>
<th>(B) (10^{-11}) esu</th>
<th>(C) (10^{-19}) esu</th>
<th>(D) (10^{-27}) esu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strukov(^{19})</td>
<td>3.9</td>
<td>-1.9</td>
<td>6.3</td>
<td>0</td>
</tr>
<tr>
<td>Sidnenko(^{20})</td>
<td>3.8±0.1</td>
<td>-3.0±0.8</td>
<td>6.5±1.1</td>
<td>0</td>
</tr>
<tr>
<td>Valladé(^{21})</td>
<td>3.8±0.1</td>
<td>-0.5±0.3</td>
<td>0</td>
<td>3.8±0.4</td>
</tr>
<tr>
<td>Okada(^{22})</td>
<td>3.9</td>
<td>-0.54±0.05</td>
<td>0</td>
<td>2.8±0.10</td>
</tr>
<tr>
<td>Benepe(^{23})</td>
<td>3.9</td>
<td>-1.85±0.25</td>
<td>3.3±0.5</td>
<td>0.87±0.5</td>
</tr>
<tr>
<td>Okada(^{22})</td>
<td>4.2±0.1</td>
<td>-1.9±0.1</td>
<td>5.4±0.4</td>
<td>0</td>
</tr>
<tr>
<td>Kobayashi(^{24})</td>
<td>(3.81)</td>
<td>-0.44</td>
<td>0.75</td>
<td>2.96</td>
</tr>
<tr>
<td>Matsuda(^{25})</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Eberhard(^{26})</td>
<td>(7.3)</td>
<td>-2.2</td>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>Schmidt(^{17}) Sample 1</td>
<td>4.3±0.2</td>
<td>-2.35±0.4</td>
<td>5.9±1.5</td>
<td>0</td>
</tr>
<tr>
<td>Sample 2</td>
<td>4.0±0.2</td>
<td>-1.48±0.2</td>
<td>3.1±0.4</td>
<td>0</td>
</tr>
<tr>
<td>Sample 3</td>
<td>3.91±0.2</td>
<td>-1.26±0.05</td>
<td>3.2±0.1</td>
<td>0</td>
</tr>
<tr>
<td>Weighted Average</td>
<td>4.0±0.2</td>
<td>-2.0±0.05</td>
<td>4.8±1.6</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\)Numbers in parentheses were obtained from source other than primary reference. Table reproduced from Western et al.\(^{17}\) by permission.
pointed out in the Introduction, this reduction of the microscopic
theories into Landau coefficients is practical because we will at some
point be forced to make a mean field approximation in order to solve
the models in three dimensions; the assumption of a mean field im-
plies that the thermodynamic potentials are analytic functions and are
thus expansible in powers of their arguments. Furthermore, in a uni-
axial ferroelectric one expects mean-field-like critical behavior with
possible logarithmic corrections\textsuperscript{12,13}. The mean-field approximation and
the Landau description should therefore be applicable even very close
to the transition.
B. Microscopic Theory

1. Slater-Takagi-Senko-SUS Model. In 1941, J. C. Slater proposed and solved a simple model for KDP which successfully explained in a qualitative way many of the features of the ferroelectric transition in this crystal. Subsequent extensions by Takagi and Senko improved the agreement with experiment. Developments up to 1964 were summarized by H. B. Silsbee, E. A. Uehling, and V. H. Schmidt, who also used the result of the measured activation energy of deuteron intrabond hopping to limit the value of one of the parameters of the theory as it applies to the deuterated crystal DKDP. Because each of the developments of the theory contains the previous ones as limiting cases, it is convenient for our purposes to follow the exposition of the SUS paper, changing some of the notation to conform with that of a still later paper by Blinc and Svetina, which will be discussed in part 2.b of this section. The treatment by Blinc and Svetina includes the effect of the quantum mechanical tunneling of the proton between the equilibrium positions in the hydrogen bond in addition to the effects treated by SUS, and so contains in turn the SUS theory as a limiting case. There are three reasons, however, that the SUS theory warrants treatment in its own right. First, the tunneling integral for the deuterated crystal is very much smaller than it is in the undeuterated crystal and can be neglected for DKDP. Second, the free energy in the SUS theory can be written in analytic form, whereas this
is not possible if the tunneling integral is finite. Third, the different mathematical approach used in the SUS paper provides another perspective on the physical problem.

The SUS model assumes that there is exactly one hydrogen in each bond and that it can occupy one of two equilibrium positions—near the top or near the bottom of a neighboring PO$_4$ ion. There are various possible configurations of the four protons surrounding a given PO$_4$ ion. Each of these configurations is assigned a contribution to the energy and z axis dipole moment, as shown in Fig. 9 (cf. Fig. 14).

The internal energy is assumed to have the form

$$U = U_{SR} - \frac{1}{8} P^2,$$

where \( P = (N\mu/V)\sigma + \chi_0 E \) is the polarization and \( \gamma \) describes long-range dipolar interactions, \( U_{SR} \) is the energy of the short-range terms (given by a sum of the configurational energies), \( \chi_0 \) is the polarizability of the lattice; \( \sigma \) is the fractional polarization or order parameter, given in terms of the fractional populations of Fig. 9 as \( \sigma = x_2 - x_2^2 + 2(x_1 - x_1^2) \). We find \( U \) as

$$U - EP = (N/V) \left[ 4\chi_0 \varepsilon + 4(\chi_4 + \chi_2)\varepsilon + 2\chi_4 \varepsilon + \frac{\mu_1 E \sigma}{-\sigma^2 - \alpha E^2} \right]$$

where \( \mu_1 = \mu + 2\chi_0 \gamma / N\mu = \mu (1 + 2\chi_0 \gamma) \). The \( E^2 \) term plays no significant role and will be dropped.

One finds the entropy by examining the ways a group can be added
<table>
<thead>
<tr>
<th>Configuration</th>
<th>Energy</th>
<th>Moment</th>
<th>Fractional Population</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>(\mu)</td>
<td>(x_2) each</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>(-\mu)</td>
<td>(x_{-2}) each</td>
</tr>
<tr>
<td></td>
<td>(e)</td>
<td>0</td>
<td>(x_0) each</td>
</tr>
<tr>
<td></td>
<td>(w)</td>
<td>(\frac{1}{2}\mu)</td>
<td>(x_1) each</td>
</tr>
<tr>
<td></td>
<td>(w)</td>
<td>(-\frac{1}{2}\mu)</td>
<td>(x_{-1}) each</td>
</tr>
<tr>
<td></td>
<td>(w_1)</td>
<td>0</td>
<td>(x_4) each</td>
</tr>
</tbody>
</table>

Fig. 9. Schematic representation of proton configurations around a \(\text{PO}_4\) group and the associated energy and dipole moment parameters. A square represents a \(\text{PO}_4\) tetrahedron; the close protons are indicated by dots.
to the crystal consistent with the neighboring groups, since each proton is shared by two PO₄ groups. By a slight generalization of Takagi's result, the entropy for our problem is

$$S = Nk \log \frac{b_+^{2b_+}}{x_2^x_2} - \frac{b_-^{2b_-}}{x_2^x_2}$$

(17)

where $b_+ = x_2 + 2x_0 + 3x_1 + x_4 = \frac{1}{2}(1+\sigma)$ is the fraction of protons close to the bottom of a PO₄ group, and $b_- = 1 - b_+$.

Minimizing the free energy with respect to the populations for a given $\sigma$ yields

$$x_{12} = Ke^{\frac{12\sigma}{9}}, \quad x_{21} = K\Theta_1 e^{\frac{\sigma}{9}}, \quad x_0 = K\Theta_0, \quad x_4 = K\Theta_2$$

(18)

where

$$\Theta_0 = e^{-\frac{2}{kT}}, \quad \Theta_1 = e^{-\frac{1}{kT}}, \quad \Theta_2 = e^{-\frac{w_1}{kT}}$$

$$\Theta = \Theta_0 + \frac{1}{2}\Theta_2 - \frac{1}{2}$$

$$K = \frac{1}{4} \left( \cosh^2 \lambda + 2\Theta_1 \cosh \lambda + \Theta \right)^{-1}$$

and $\lambda$ is to be determined from the equation

$$\sigma = 4K \sinh \lambda (\cosh \lambda + \Theta_1) \equiv \frac{\tanh \lambda (1 + \Theta_1 \text{sech} \lambda)}{1 + 2\Theta_1 \text{sech} \lambda + \Theta \text{sech}^2 \lambda}$$

(20)

Substituting these populations into the expressions for $U$ and $S$, we find for the Gibbs potential $G = U - TS - EP$ (parameterized by $\sigma$).
\[ G(\sigma) = -(N/V) \left\{ \mu_1 E \sigma + \gamma \sigma^2 + kT \left( \log \left[ (1-\sigma^2)/4k \right] \right) + 2\sigma \left[ \tanh^{-1} \sigma - \lambda \right] \right\} \]  

(21)

and for its derivatives

\[ \frac{\partial G}{\partial \sigma} = -(N/V) \left\{ \mu_1 E + 2kT \left[ \gamma \sigma/kT + \tanh^{-1} \sigma - \lambda \right] \right\} \]  

(22)

\[ \frac{\partial^2 G}{\partial \sigma^2} = 2(N/V) kT \left[ \frac{d\lambda}{d\sigma} - \frac{1}{1-\sigma^2} - \frac{\gamma}{kT} \right] \]  

(23)

where \( d\lambda/d\sigma \) is determined by Eq. (20). As discussed in part A, the equilibrium polarization is that which minimizes the Gibbs potential.

The minimum of \( G(\sigma) \) can occur at a zero of (22) with (23) positive, giving

\[ \sigma = \tanh \left( \lambda - \frac{\gamma \sigma}{kT} - \frac{\mu_1 E}{2kT} \right) \]  

(24)

(which must be solved simultaneously with Eq. (20)), or the minimum might occur for a completely polarized state with \( \sigma = 1 \). If \( w \) is finite, however, it is easily shown that \( \partial G/\partial \sigma \rightarrow +\infty \), so \( G(1) \) cannot be a minimum. In this case one could substitute the value of \( \lambda \) from Eq. (24) into Eq. (21) and obtain an expression in closed form for \( G(\sigma) \).

In the unpolarized state \( \sigma = \lambda = E = 0 \), we have

\[ G(0) = -NkT \log \left( 1 + 2\Theta_1 + \Theta \right) \]  

(25)
At this point we will consider some special cases (at zero field):

(a) \( w = c^0, A = 0 \). This is the original Slater model. Equations (20) and (24) give only \( \sigma = \lambda = 0 \) for \( \theta_1 = 0 \), except at the critical temperature \( \theta = 0 \), where any value of \( \sigma \) will work. Figure 10(a) shows qualitatively the situation for the Slater model, in which the polarization rises infinitely steeply (but not discontinuously) at \( T_c = \varepsilon/(k \log 2) \) (for \( w_1 = \infty \)), and just above \( T_c \) one gets \( S_c = \frac{1}{2}kN \log 2 \) from Eq. (26).

(b) \( w = \infty, \gamma \neq 0 \). The additional \(-\gamma^2\) term gives the situation in Fig. 10(b). A transition to \( \sigma = 1 \) will occur when \( G(1) = -N\gamma/V \) becomes equal to \( G(0) \) given by Eq. (25), at a higher temperature and therefore higher entropy than in case (a).

(c) \( \gamma = 0, w \) finite. This is Takagi's model. At high temperatures \( \sigma = \lambda = 0 \) is the only solution of Eqs. (20) and (24); \( G(0) \) is a minimum for \( \theta > -\theta_1 \), as can be seen from Eq. (27). However, as \( T \) is lowered until \( \theta \) becomes less than \(-\theta_1 \), Eq. (27) changes sign, indicating a relative maximum at \( \sigma = 0 \). At this point \((-\theta_1/\theta = 1) \) another

\[
S(0) = Nk\left[\log(1+2\theta_1+\theta) + \frac{\varepsilon}{kT} \frac{\theta_0 + 2\theta_1 w/\varepsilon + w_1/2\varepsilon^2}{1 + 2\theta_1 + \theta}\right] \tag{26}
\]

\[
\frac{\partial^2 G}{\partial \sigma^2}(0) = 2NkT\left(\frac{\theta + \theta_1}{1 + \theta_1} - \frac{kT}{kT}\right) \tag{27}
\]
Fig. 10. Schematic behavior of Gibbs potential $G$ and fractional polarization $\sigma$. The letters (a), (b), (c), and (d) correspond to the cases treated in this section.
solution becomes possible, viz. \( \text{sech} \lambda = -\Theta_1/\Theta \), corresponding to a minimum in \( G \) which first appears at \( \sigma = \tanh(\text{sech}^{-1} 1) = 0 \) and moves to larger \( \sigma \) as \( T \) is further reduced. This is thus a second order transition as illustrated in Fig. 10(c).

(d) In the general case two qualitatively different behaviors are possible. There can be a second order transition when Eq. (27) changes sign, i.e., when

\[
\frac{\gamma}{kT_0} = \left[ \Theta(T_0) + \Theta_1(T_0) \right] / \left[ 1 + \Theta_1(T_0) \right].
\]

The second possibility is that there are two solutions of Eqs. (20) and (24) in the region \( 0 < \sigma < 1 \) while there is still a local minimum at \( \sigma = 0 \). There will then be a first-order transition at a temperature \( T_c > T_0 \), where \( T_0 \) is the root of Eq. (28); this transition occurs when the outer minimum falls below the level of \( G(0) \). This situation is illustrated in Fig. 10(d). It should be noted that if \( \gamma \) is allowed to be negative, corresponding to antipolar long-range coupling, the same two types of behavior are possible on the \( \gamma < 0 \) side as well, the first order transitions occurring for larger absolute values of \( \gamma \).

The susceptibility above \( T_c \) is

\[
\chi = \frac{(N/V)kM_\gamma M}{\partial^2 G / \partial \sigma^2} + \chi_0 \gamma
\]

where the denominator is given by Eq. (27) and vanishes at \( T_0 \), the root of Eq. (28).
One can obtain the Landau expansion coefficients in closed form for the SUS theory in a straightforward but tedious way\textsuperscript{29}. The first three of these are (for $\omega_1 = \infty$)

\begin{align*}
A_0 &= 2 \left( \frac{V}{N} \right) \frac{\mu}{\mu_i} \frac{k}{\mu} \left[ \frac{\Theta_0 + \Theta_1}{1 + \Theta_1} - \frac{\Theta_0}{(1 + \Theta_1)^2} \right] \\
B &= 4 \left( \frac{V}{N} \right)^2 \frac{\mu}{\mu_i} \frac{kT}{\mu^2} \left[ \frac{3a^2d^2 - 2bd^2 - a^4}{6a^4} \right] \\
C &= 6 \left( \frac{V}{N} \right)^3 \frac{\mu}{\mu_i} \frac{kT}{\mu^3} \left[ \frac{12a^4d^3 - 16a^2bd + 8b^2d^3 - 2b^3d^2 - 3a^7}{4a^7} \right]
\end{align*}

where $a = 1 + \Theta_1$, $b = 1 + \frac{\Theta_0}{\mu}$, $c = 1 + \Theta_1/16$, and $d = \Theta_1 + 2\Theta_0 + \Theta$.

Note that each of the Landau coefficients is multiplied by a single factor of $\mu/\mu_i = (1 + 2\chi_0)^{-1}$. The need for this is readily seen by comparison of the Landau equation of state (Eq. (5)) with the SUS expression obtained by setting Eq. (22) equal to zero.

For fitting the parameters of the SUS theory to the data for the deuterated crystal, the reader is referred to III.B.3., where it is shown that the theory is in excellent agreement with the best experimental evidence for DKDP for the $\gamma < 0$ case.

2. Tunneling Model.

a. Transverse Ising Model\textsuperscript{1}. The ferroelectric transition in KDP can be considered to be an order-disorder transition with respect to the two equilibrium sites for each proton in its hydrogen bond; therefore, as for any two-level system, the problem can be expressed in
terms of spin-$\frac{1}{2}$ operators, e.g., the three Pauli spin-$\frac{1}{2}$ matrices
\[ S^x = \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}, \quad S^y = \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix}, \quad S^z = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} \]
which, together with the unit matrix form a complete set of Hermitian $2 \times 2$ matrices. Such a pseudo-spin representation is useful because the large anharmonicity of the problem has been transformed out, and the analogy with magnetic systems such as the Heisenberg and Ising models permits the application of the more sophisticated computational techniques which have been worked out for these magnetic models; the theory of anharmonic phonons is rather primitive in comparison.

The Hamiltonian $\mathcal{H}_0$ consists of a single-particle part $\mathcal{H}_1(i)$ and an interaction part $\mathcal{H}_2(i,j)$:
\[
\mathcal{H} = \sum_i \mathcal{H}_1(i) + \sum_{i<j} \mathcal{H}_2(i,j). \tag{34}
\]
In the representation in which $\mathcal{H}_1(i)$ is diagonal we get:
\[
\mathcal{H}_1(i) = \sum_\alpha E_\alpha a_\alpha^i + a_\alpha^i, \tag{35}
\]
\[
\mathcal{H}_2(i,j) = \sum_{\alpha, \beta, \gamma, \delta} V_{\alpha\beta\gamma\delta} a_\alpha^i + a_\alpha^i a_\beta^j + a_\beta^j a_\gamma^i + a_\gamma^i a_\delta^j \tag{36}
\]
where the operators $a_\alpha^i$ and $a_\alpha^i$ are Fermi or Bose creation and annihilation operators for a proton or a deuteron at site $i$ in the single particle quantum state $\alpha$ (since there is always only one particle in
each H-bond, the results are independent of the statistics). The matrix element $v_{ij}$ represents a general interaction between the $i$-th $j$-th hydrogen bond which depends on the distance between the positions of $i$ and $j$ and also on their quantum states. Since the ground state of a single particle in a double well is a doublet, if we neglect higher excited states the single particle quantum numbers $\alpha$, $\beta$, $\gamma$, and $\delta$ can take on only two values, which we label $+$ and $-$. The corresponding eigenfunctions
\begin{equation}
\psi_+ = \frac{1}{\sqrt{2}} (\phi_L + \phi_R) \tag{37}
\end{equation}
\begin{equation}
\psi_- = \frac{1}{\sqrt{2}} (\phi_L - \phi_R) \tag{38}
\end{equation}
are the symmetric and antisymmetric linear combinations of wave functions localized in the left ($\phi_L$) and right ($\phi_R$) equilibrium sites. These functions are shown in Fig. 11.

Expressing the condition that there is just one hydrogen in each bond as
\begin{equation}
a_i^+ a_i^+ + a_i^- a_i^- = 1 \tag{39}
\end{equation}
we can now express the products of the creation and annihilation operators for a hydrogen in a given bond with the fictitious spin-$\frac{1}{2}$ operators:
\begin{equation}
S_i^x = \frac{1}{2} (a_i^+ a_i^+ - a_i^- a_i^-) \tag{40a}
\end{equation}
Fig. 11. Energy ground state and eigenfunctions for a single particle in a double-well potential \( v(x) \).
These obey the commutation relations for angular momentum operators:

\[ [S_i^x, S_j^y] = i \delta_{ij} S_i^z \]
\[ [S_i^y, S_j^z] = i \delta_{ij} S_i^x \]
\[ [S_i^z, S_j^x] = i \delta_{ij} S_i^y \]  \hspace{1cm} (41)

The operators \( a_\alpha^+ \) and \( a_\alpha^- \) which create and annihilate a particle in the quantum state \( \alpha = +, - \) are the symmetric (+) and antisymmetric (−) linear combinations of the corresponding operators for the creation and annihilation of a particle in the left or right equilibrium site in the hydrogen bond:

\[ a_\alpha^+ = \frac{1}{\sqrt{2}} (a_\alpha^L + a_\alpha^R) \]
\[ a_\alpha^- = \frac{1}{\sqrt{2}} (a_\alpha^L - a_\alpha^R) \]  \hspace{1cm} (42)

Substituting these expressions into Eqs. (40) we find:

\[ S_i^x = \frac{i}{2} (a_i^L a_i^R + a_i^R a_i^L) \]
\[ S_i^y = \frac{i}{2} (a_i^L a_i^R - a_i^R a_i^L) \]
\[ S_i^z = \frac{1}{2} (a_i^L a_i^R + a_i^R a_i^L) \]  \hspace{1cm} (43)
Comparing Eqs. (40) with the above, we see that the $x$ component of the pseudo-spin, which measures the difference in the occupation of the symmetric and antisymmetric quantum states, describes the tunneling between the two sides of the hydrogen bond. The $z$ component of the pseudo-spin, on the other hand, measures the difference in the occupation of the right- and left-hand sites or, alternatively, the tendency of the particle to undergo a transition between the symmetric and antisymmetric states. The $y$ component of the pseudo-spin is a local current operator in either representation.

Introducing the spin operators into the Hamiltonian (34) we obtain

$$\mathcal{H} = -\Omega \sum_i S_i^x - \frac{1}{2} \sum_{i,j} T_{ij} S_i^x S_j^y - \frac{1}{2} \sum_{i,j} B_{ij} S_i^x S_j^z, \quad (44)$$

where

$$\Omega = E_- - E_+ + \sum_{\delta} (V^+_{\delta+} - V^-_{\delta-}) \approx E_- - E_+ \quad (45)$$

$$T_{ij} = -\frac{1}{4} V^+_{ij} \quad (46)$$

$$B_{ij} = 2 V^+_{ij} - V^-_{ij} - V^+_{ji} - V^-_{ji} \quad (47)$$

(It should be noted that terms like $S_i^x S_j^z$ vanish for symmetry reasons, since the Hamiltonian must be invariant under the interchange $S_i^z \leftrightarrow -S_i^z$.) In the case where $B_{ij}$ (which measures the effect of one proton on the tunneling integral of another) is negligible, the
Hamiltonian (44) is identical to an Ising Hamiltonian in a transverse field \( \Omega \), which is equal to twice the tunneling integral—the difference in energy between the symmetric and antisymmetric quantum states of the particle in the well due to the fact that there is a finite probability of finding the particle in the classically forbidden region in the center of the well. The field \( \Omega \) favors a nonzero \( <s^x> \), which is proportional to the difference in populations of the symmetric and antisymmetric states. This tendency is frustrated by the tendency of the exchange-like terms \( J_{ij} \) to favor ordering in one of the states which are localized in the right- or left-hand side of the well; these are linear combinations of the symmetric and antisymmetric states. We will see in section III.3 that the four-particle cluster approximation, which takes into account the correlations of the protons around a given PO\(_4\) group, will generate an effective \( B_{ij} <s_i^x s_j^x> \) term even in the absence of a bare term \( B_{ij} s_i^x s_j^x \).

We will now examine the Hamiltonian

\[
\mathcal{H} = -\sum_i s_i^x + \frac{1}{2} \sum_{ij} s_i^x s_j^x
\]

in the mean field approximation (MFA). In the MFA, the \( z \) component of a given spin will interact with the average value of the remaining spins; this average value is to be determined self-consistently. We therefore can write the above Hamiltonian in the MFA as
\[ \gamma_{i}^{\hat{M} \hat{F}A} = - \hat{H}_{i} \cdot \vec{s}_{i}, \]  \hspace{2cm} (49) \]

where the molecular field \( \hat{H}_{i} = (H_{x}^{i}, H_{y}^{i}, H_{z}^{i}) = (\Omega, 0, \Sigma J_{ij} <S_{j}^{z}> \) forms a vector in our pseudo-spin space which interacts with the pseudo-spin variables.

The expectation value of the pseudo-spin at site \( i \) is given by

\[ \langle \vec{s}_{i} \rangle = \frac{\text{Tr} \, \vec{s}_{i} \, e^{-\beta \gamma_{i}^{\hat{M} \hat{F}A}}}{\text{Tr} \, e^{-\beta \gamma_{i}^{\hat{M} \hat{F}A}}} = \frac{d \log Z_{i}}{d(\beta H_{i})} = \frac{1}{2} \frac{\Delta_{i}^{z}}{\hat{H}_{i}} \, \text{th} \, \frac{\beta \Delta_{i}^{z}}{2}, \]  \hspace{2cm} (50) \]

where \( \Delta_{i}^{z} = |\hat{H}_{i}| = [\Omega^{2} + \langle \sum_{j} J_{ij} <S_{j}^{z}> \] \hspace{2cm} (51) \]

The individual components of the expectation value \( \langle \vec{s}_{i} \rangle \) are thus

\[ \langle s_{i}^{x} \rangle = \frac{1}{2} \frac{\Delta_{i}^{x}}{\hat{H}_{i}} \, \text{th} \, \frac{1}{2} \beta \Delta_{i}^{z} ; \] \hspace{2cm} (52) \]

\[ \langle s_{i}^{y} \rangle = 0 ; \] \hspace{2cm} (53) \]

\[ \langle s_{i}^{z} \rangle = \frac{1}{2} \frac{\Delta_{i}^{z}}{\hat{H}_{i}} \, \text{th} \, \frac{1}{2} \beta \Delta_{i}^{z} . \] \hspace{2cm} (54) \]

The solutions of this system of 3N equations will be stable only if they minimize the free energy.

One of the solutions of the above system exists at all temperatures. This solution, which represents a paraelectric state, is given
by:
\[ \langle S_i^z \rangle = 0 = \langle S_i^y \rangle, \quad \langle S_i^x \rangle = \frac{1}{2} \tanh \left( \frac{1}{2} \beta \Omega \right). \] (55)

This will minimize the free energy above a temperature \( T_c \), which is determined by the equation
\[ 2 \frac{\Omega}{J_0} = \tanh \left( \frac{1}{2} \beta \Omega \right), \quad \beta_c = \frac{1}{kT_c}, \] (56)

where \( J_0 = \sum j_{ij} \).

Below this temperature there will be a solution with a nonzero polarization \( P = 2N \mu \langle S^2 \rangle \), where \( \mu \) is the electric dipole moment of the two-position dipole and \( N \) is the number of dipoles per unit volume. This solution satisfies the transcendental equation:
\[ 2H = J_0 + \tanh \left( \frac{1}{2} \beta \mu \right). \] (57)

There is a significant isotope effect in \( T_c \) predicted by Eq. (56). Writing \( T_c \) in terms of the inverse hyperbolic tangent of \( 2\Omega/J_0 \) and expanding to second order in \( \Omega/J_0 \), we find that
\[ T_c \approx \left( J_0/4K \right) \left( 1 - \frac{4}{3} \left( \Omega/J_0 \right)^2 \right). \] (58)

One would therefore expect that \( T_c \) would be shifted upward in the deuterated crystal since the tunneling integral \( \frac{1}{2} \Omega \) is strongly dependent on the mass of the particle in the well. Such a shift is observed in KDP, where \( T_c \) is nearly doubled upon deuteration. In the ferroelectric phase, \( T < T_c \), we see from Eqs. (52) and (57) that \( \langle S^x \rangle \) is independent of temperature.
It can also be seen from Eq. (56) that if the tunneling field is larger than $\frac{1}{2}J_0$, no ordering can occur since there is no real solution for $T_c$. In this case, the paraelectric solution is stable at all temperatures. This differs from the behavior of a classical order-disorder system, which always becomes ordered as $T \to 0$.

The solution of the transverse Ising model in the MFA displays many of the qualitative features of the transition in KDP; however, it is incapable of even approximately describing the shape of the spontaneous polarization vs. temperature curve. It can give a semiquantitative value for the Curie constant $C \propto (T-T_0)\chi$, where $\chi = \frac{\partial^2 F}{\partial E}$ is the dielectric susceptibility, provided that one takes one spin per unit cell rather than four; this is an indication of the importance of four-particle correlations, which will be treated in the next section. One great advantage of the MFA solution is its simplicity, particularly if one wishes to study the dynamics of the system. It should be noted that the transverse Ising model has intrinsic dynamics since, unlike the case for the regular Ising model, the pseudo-spins do not commute with the Hamiltonian.

The Heisenberg equations of motion for the pseudo-spins,
\[ \frac{d \langle \hat{S}_i \rangle_t}{dt} = -i \langle [\hat{S}_i, \mathcal{H}] \rangle_t, \quad \hbar = 1, \quad (59) \]

reduce in the random phase approximation (RPA), which is an extension of the MFA to time-dependent problems, to the Larmor precession of the pseudo-spins around the molecular field:

\[ \frac{d \langle \hat{S}_i \rangle_t}{dt} = \langle \hat{S}_i \rangle_t \times \mathbf{H}_i(t), \quad (60) \]

where we have made the RPA replacement of the average of the product of two spin operators by the product of the averages,

\[ \langle \hat{S}_i^\alpha \hat{S}_j^\beta \rangle_t = \langle \hat{S}_i^\alpha \rangle_t \langle \hat{S}_j^\beta \rangle_t, \quad i \neq j. \quad (61) \]

Linearizing the Heisenberg equation of motion and Fourier transforming the problem into reciprocal space, we find the following collective mode frequencies for small fluctuations of the pseudo-spins in the paraelectric phase:

\[ \omega_1(\vec{q}) = 0 \quad (62) \]

\[ \omega_{2,2}(\vec{q}) = \Omega \left[ \Delta \Omega - \mathbf{J}_{q}^{\mathbf{r}} \langle \mathbf{S}_x \rangle \right] = \Omega \left[ \Delta \Omega - \mathbf{J}_{q}^{\mathbf{r}} + 3 \hbar \left( \frac{\mathbf{R}_{q}^{\mathbf{r}}}{\mathbf{R}_{q}^{\mathbf{r}}} \right) \right], \quad (63) \]

where \( J_{q}^{\mathbf{r}} = \sum_{j} J_{i}^{\mathbf{r}} e^{-i\mathbf{q} \cdot (\mathbf{R}_{j}^{\mathbf{r}} - \mathbf{R}_{i}^{\mathbf{r}})} \).

The solution \( \omega_1(\vec{q}) = 0 \) corresponds to the motion of the pseudo-spin in the x direction, which is the direction of the molecular field above \( T_c \), and hence represents a longitudinal mode. The pair of
solutions $\omega_{2,3}(q)$ represent transverse excitations and describe the free precession of the pseudo-spins around the molecular field. Since the polarization is proportional to $<S^z>$, these excitations are associated with fluctuations of the polarization.

At very high temperatures the precession frequency approaches the tunneling frequency

$$\omega_{2,3} \rightarrow \Omega \quad \text{as} \quad T \rightarrow \infty,$$

while at lower temperatures the interactions between particles reduces the collective precession frequency until it approaches zero when

$$\frac{\hbar}{6} \Omega - \frac{J^2}{q^2_0} + \hbar(\frac{1}{2} \beta \Omega) = 0; \quad \beta \equiv \frac{1}{kT}.$$

This is the stability limit $T_c$, determined by the maximum value $J^2$ of the Fourier transform $J^2_q$ of the interaction constant. The mode characterized by $q^2_0$ will become "frozen in" when $\omega(q^2_0) \rightarrow 0$, and the mode displacements will become the equilibrium positions in the low temperature phase. This is the soft mode description of the phase transition, which connects the order parameter with the displacements of a normal mode whose frequency goes to zero at some temperature $T_c$. For ferroelectric ordering $q^2_0 = 0$, and Eq. (65) becomes identical with the earlier equation for $T_c$ for the MFA, Eq. (56).

For the ferroelectric phase the linearized equations of motion lead to the following equation for the eigenfrequencies $\lambda$: 
\( i\omega[\omega^2 + \Omega^2 - \Omega J_q \langle S^x \rangle + (J_0 \langle S^z \rangle)^2] = 0. \) (66)

One of the solutions, \( \omega_1 = 0 \), is the same as for the paraelectric state, and again represents a longitudinal mode, although since the molecular field is no longer in the \( x \) direction but rather in a general direction in the \( xz \) plane, this mode can contribute to polarization fluctuations below \( T_c \). The pair of frequencies representing the precession of the pseudo-spins around the molecular field can be written

\[
\omega^2_{2,3}(q) = (J_0 \langle S^z \rangle)^2 + \Omega^2 (1 - \frac{J_q}{J_0}),
\] (67)

where we have used the fact that \( \langle S^x \rangle = \Omega/J_0 = \text{const} \) below \( T_c \) (see Eq. (58)). In the long-wavelength limit, \( q \to 0 \), the pseudo-spin-wave mode frequency \( \omega_{2,3} \) is proportional to the spontaneous polarization:

\[
\omega_{2,3}(q = 0) = J_0 \langle S^z \rangle = J_0 P/2\mu N.
\] (68)

This is a characteristic feature of the soft-mode description.

One can easily include the effects of a finite relaxation time for the molecular field to describe damping near \( T_c \) and the coupling to optical and acoustic phonons. K. K. Kobayashi examined the coupling to the optical phonon which is responsible for the polarization in KDP (the motion of the protons from right to left in the bonds is...
perpendicular to the actual ferroelectric axis $z$, and so the pseudo-spins are not directly responsible for the polarization). Solving the coupled system in the RPA, Kobayashi found that the coupling simply renormalized the coupling constant $J_q$ by an amount which depends on the strength of the pseudo-spin-phonon coupling divided by the phonon frequency $\omega_q$. Due to the piezoelectric coupling in KDP, however, the ferroelectric soft mode can couple to the transverse acoustic phonon as well. Here one finds that one of the coupled frequencies is given by

$$\omega^2 \approx \left( \frac{\nu^2 - \alpha}{\omega_B^2} \right) q^2 \approx \nu'^2 q^2,$$

where $\omega_B$ is the frequency of the ferroelectric mode and $\alpha$ is proportional to the square of the coupling strength. In this case, as $\omega_B \to 0$ the velocity of the renormalized acoustic mode goes to zero first, thus inducing the phase transition. This accounts for the spontaneous shear which occurs below $T_c$ in KDP. The problem of coupling with phonons is, of course, an effect due to the lack of perfect rigidity of the lattice and not properly a topic for this section. Many of the predictions of this treatment are analogous to those which will be treated phenomenologically in section III.A and in the four-particle cluster approximation in section III.B.

b. Four-particle cluster approximation (FPCA). In this section we will review the four-particle cluster approximation to the tunneling
model, following the treatment of Blinc and Svetina\textsuperscript{6}. The FPCA is a high-temperature treatment which considers both short-range and long-range forces, the finite overlap of the protonic wave functions between the two sites in a given hydrogen bond, and a part of the proton-lattice coupling. The approximation is based on the cluster expansion of the partition function of an order-disorder type hydrogen-bonded ferroelectric crystal, derived for the general case by Blinc and Svetina\textsuperscript{31} using the cumulant expansion technique of Kubo\textsuperscript{32}. The interactions among the four protons surrounding a given PO\textsubscript{4} group are taken into account explicitly and the rest are replaced by a molecular field, which is determined self-consistently. An attempt is made to take into account the effect of one proton on the tunneling integral of another. In the classical limit, in which the tunneling integral is zero, this approximation reduces to the theory of Silsbee, Uehling, and Schmidt (SUS)\textsuperscript{5}, which was discussed in section II.B.1. The connection of this approach to that of the transverse Ising model will be elucidated in the next section, II.B.3.

The Hamiltonian of the problem can be broken up into a tunneling term $H_t$, which describes the motion of protons between the two equilibrium sites in a given hydrogen bond; a short-range term $H_{SR}$, which describes the energy of configurations of protons surrounding a given PO\textsubscript{4} group; and a long-range term $H_{LR}$, which describes the interactions not included in $H_{SR}$. In the representation of localized
particles these terms may be written:

\[ H_{el} = -\frac{1}{2} \sum_{i=1}^{N} \sum_{\lambda=1}^{4} (S_{ij}^+ + S_{ij}^-) \] (70)

\[ H_{SR} = \sum_{i=1}^{N} \sum_{k_1 \cdots k_4 \psi_1 \psi_2 \psi_3 \psi_4} \epsilon_{k_1 k_2 k_3 k_4} n_{i1k_1} n_{i2k_2} n_{i3k_3} n_{i4k_4} \] (71)

\[ H_{LR} = -\frac{1}{4} \sum_{\sum_{i \neq j}} (n_{ij\lambda} - n_{ij\lambda'})(n_{ij\lambda'} - n_{ij\lambda'}) \] (72)

where the summation extends over all \( N \) phosphate groups in the crystal as well as over all four hydrogen sites near a given phosphate group.

Here \( S_{ij}^+ \) and \( S_{ij}^- \) are the proton "jump" operators

\[ S_{ij}^+ = b_{ij\lambda}^+ b_{ij\lambda}, \quad S_{ij}^- = b_{ij\lambda}^+ b_{ij\lambda} \] (73)

the \( n_{ijk} \) are the proton "number" operators

\[ n_{ijk} = b_{ijk}^+ b_{ijk} \quad (k = \lambda, \lambda') \] (74)

and \( b_{ijk}^+ \) and \( b_{ijk} \) are proton creation and annihilation operators defined by \( \psi_{ijk} = b_{ijk}^+ |0\rangle \). The sign \( \lambda \) or \( \lambda' \) means that the proton is created or annihilated near the lower or upper oxygen atom, respectively, of a given \( P_4O_{10} \) group (with respect to the ferroelectric axis \( z \)). The \( \epsilon_{k_1 k_2 k_3 k_4} \) in \( H_{SR} \) are the Slater-Takagi energies of the different configurations of protons around a given \( P_4O_{10} \) ion, i.e., the matrix elements.
where $H_{PO_{4}, i}^*$ is the complete Hamiltonian of a given $PO_{4}$ group; the integration is over all internal coordinates of a given $PO_{4}$ ion. Higher vibrational states of the proton are not included, and only the leading term in the proton overlap integral is taken into account.

The short-range interaction term for a given $PO_{4}$ ion can be written as a sum of terms describing states with zero, one, two, three, or four protons close to a given $PO_{4}$ ion. Using the condition that there is just one proton in a given hydrogen bond,

$$n_{i j \uparrow} + n_{i j \downarrow} = 1,$$  \hspace{1cm} (76)

and summing over all $PO_{4}$ groups in the crystal, we can write $H_{SR}$ up to a constant term as

$$H_{SR} = \sum_{i=1}^{N} \left[ w_{1} N_{i0} + w_{2} (N_{i1} + N_{i2} + N_{i3}) + \epsilon N_{i2} + w_{2} N_{i4} \right],$$  \hspace{1cm} (77)

where

$$N_{i0} = N_{i0} \left( \square \right),$$

$$N_{i1} = N_{i1} \left( \square \right) + N_{i1} \left( \square \square \right) + N_{i1} \left( \square \square \square \right) + N_{i1} \left( \square \square \square \square \right),$$

$$N_{i2} = N_{i2} \left( : \square \right) + N_{i2} \left( : \square \square \right) + N_{i2} \left( : \square \square \square \right) + N_{i2} \left( : \square \square \square \square \right),$$

$$N_{i3} = N_{i3} \left( \square \square \right) + N_{i3} \left( \square \square \square \right) + N_{i3} \left( \square \square \square \square \right),$$

$$N_{i4} = N_{i4} \left( \square \square \square \right) + N_{i4} \left( \square \square \square \square \right).$$
The square indices $\begin{array}{c}1 \\ 3 \\ 4 \end{array}$ indicate which particular configuration of the four protons surrounding a PO$_4$ ion is occupied. For example, $N_i(\begin{array}{c}\circ \\ \circ \\ \circ \end{array})$ stands for the operator

$$N_i(\begin{array}{c}\circ \\ \circ \\ \circ \end{array}) = n_{i_1} n_{i_2} n_{i_3} n_{i_4}. \tag{78}$$

The energies in Eq. (77) are given in terms of the energies $\epsilon_n$ of the configurations $N_{in}$ of Eq. (78) as

$$W = \frac{1}{2}(\epsilon_1 + \epsilon_3) - \epsilon_2, \quad \epsilon = \epsilon'_2 - \epsilon_2, \quad W_1 = \epsilon_0 - \epsilon_1 + \epsilon_3 - \epsilon_2, \quad W_2 = \epsilon_4 + \epsilon_4 - \epsilon_3 - \epsilon_2. \tag{79}$$

We will be investigating the free energy of our crystal in a four-particle cluster approximation, as this is the lowest approximation in which the specific properties of KDP-type lattices can be taken into account. This will mean taking the short-range terms into account exactly, and the rest only on the average. Specifically, we will replace the long-range interaction term (Eq. (72)) with a molecular field term.

The final expression for our approximate Hamiltonian is thus, up
to constant terms\(^6\)

\[
H = \sum_{i=1}^{\mathbb{N}} \left\{ -\frac{1}{2} \mu \sum_{j=1}^{4} (S_{ij}^+ + S_{ij}^-) + \left[ \omega_i (N_{i\gamma} - N_{i\delta}) + \right. \right.
\]
\[\left. \left. + \mathcal{W}(N_{i1} + N_{i2}) + \epsilon N_{i2}^{-} \right] \right\} + \frac{1}{2} \sum_{j=1}^{4} \left[-\gamma \sigma(N_{ij}^+ - N_{ij}^-) + \frac{1}{2} \gamma \sigma^2 \right],
\]

where \(\sigma = \langle n_{ij}^+ - n_{ij}^- \rangle\). It should be remembered that the

\(N_{is}\) (s = 0, 1, ..., 4) are four-particle operators, and \(\gamma\) is a constant
describing all long-range effects (including proton-proton coupling
as well as coupling through the lattice) in a molecular-field
approximation.

In order to carry out the four-particle cluster approximation, we
write the Hamiltonians for a single-particle cluster and for a four-
particle cluster as follows\(^6\):

\[
H_{(4)} = -(\mathcal{N} - \mathcal{N}_{ij}(S_{ij}^+ + S_{ij}^-)) - (\gamma \sigma' + \Delta)(n_{ij}^+ - n_{ij}^-), \quad (81)
\]
\[
H_{(4)} = \sum_{j=1}^{4} \left[-(\mathcal{N} - \frac{1}{2} \mathcal{N}_{ij}(S_{ij}^+ + S_{ij}^-)) - (\gamma \sigma' + \frac{1}{2} \Delta)(n_{ij}^+ - n_{ij}^-) \right.
\]
\[\left. \left. + \mathcal{W}(N_{i0} + N_{i4}) + \mathcal{W}(N_{i1} + N_{i2}) + \epsilon N_{i2}^{-} \right] \right\} \quad (82)
\]

where \(\Delta\) is an effective field which makes the potential well in the
H-bond asymmetric, and \(\eta\) is a field which takes into account the
effects of other protons on the tunneling integral of a given pro-
ton, and thus represents the change in the effective tunneling inte-
gral due to proton correlations. It should be pointed out that \(\eta\) is
nonzero even above $T_c$ and, in fact, goes to zero only for $T > T_c$, when the protons are moving as independent particles. The factors of $\frac{1}{2}$ in front of $A$ and $\eta$ in $H_{(4)}$ are due to the fact that in the four-particle cluster Hamiltonian just half of the interactions of any given proton are being taken into account explicitly, and half through the effective fields $\Delta$ and $\eta$; in $H_{(1)}$ all the interactions of a proton with the neighboring protons are taken into account through the effective fields.

The total free energy in the EPCA is given by

$$F_{(4)} = -kT \left( \log \text{Tr} e^{-\beta H_{(4)}} - 2 \log \text{Tr} e^{\beta H_{(4)}} + N \delta \sigma^2 \right)$$

Both $\Delta$ and $\mu$ are obtained by a minimization of the approximately determined free energy:

$$\frac{\partial F_{(4)}}{\partial \Delta} = 0, \quad (84)$$
$$\frac{\partial F_{(4)}}{\partial \mu} = 0, \quad (85)$$

leading to the following equations:

$$\text{Tr} \left( n_{ij} - n_{ij}^e \right) \rho_{(4)} = \frac{1}{4} \text{Tr} \sum_{j=1}^{4} \left( n_{ij} - n_{ij}^e \right) \rho_{(4)} \quad (86)$$

$$\text{Tr} \left( S_{ij}^+ + S_{ij}^- \right) \rho_{(4)} = \frac{1}{4} \text{Tr} \sum_{j=1}^{4} \left( S_{ij}^+ + S_{ij}^- \right) \rho_{(4)} \quad (87)$$
Thus we see that the minimization of the free energy with respect to $\Delta$ and $\eta$ is equivalent to the requirement that the thermal expectation values of the reduced dipole moment operator $\sigma_{ij} = n_{ij} + n_{ij}^+$ and the proton jump operator $s_{ij} = s_{ij}^+ + s_{ij}^-$ be the same whether determined from the four- or single-particle density matrix. Once we know $\Delta$ and $\eta$ as functions of temperature, we also know the temperature dependence of the free energy in this approximation, so we can deduce all of the polarization properties of our system.

The explicit form of the four-particle cluster Hamiltonian $H^{(4)}$ can be similarity transformed to the following matrix:

$$U^{(4)} = A^{(3)} \times A^{(3)} \times B^{(3)} \times C^{(6)} \times D^{(1)}$$

where the matrices occurring in the above direct product are

$$A^{(3)} = \begin{pmatrix} w & 2b & -a \\ 2b & e & 0 \\ -a & 0 & w \end{pmatrix}, \quad B^{(3)} = \begin{pmatrix} w & 2b & -a \\ 2b & w_1 & 0 \\ -a & 0 & w \end{pmatrix},$$
There we have used the notation \( b = -\Gamma + \frac{1}{2} \eta \) and \( a = \Delta + 2 \gamma \sigma \). The consistency equations (86) and (87) can now be written explicitly as

\[
(\Gamma - \eta) - (\frac{a}{\sigma^2} - \gamma) \langle \mathbf{S} \rangle = 0
\]

and

\[
\left[ (\alpha - \gamma \sigma)^2 + (\Gamma - \eta)^2 \right]^{\frac{1}{2}} = (\frac{a}{\sigma^2} - \gamma) + \frac{\beta}{\sigma} \left( (\alpha - \gamma \sigma)^2 + (\Gamma - \eta)^2 \right)^{\frac{1}{2}}
\]

Landau expansion. We will now expand the FPCA free energy, which is given by Eq. (83) with Eqs. (91) and (92) (or (86) and (87)) taken into account, in a series in the dipole moment operator expectation value (or fractional polarization) \( \sigma \),

\[
F = F_0 + \frac{1}{2} \alpha \sigma_0 (T - T_0) \sigma^2 + \frac{1}{4} b \sigma^4 + \frac{1}{6} c \sigma^6 + \ldots
\]

This can be done in the following way. First, \( \Delta \) is eliminated in favor of \( \sigma \) using Eq. (92). Next, the free energy is explicitly minimized with respect to \( \eta \) at constant \( \sigma \), which assures that the other consistency condition (Eq. (85), (87), or (91)) is also satisfied. The fact that the minimization with respect to \( \eta \) is to be carried out at constant \( \sigma \) rather than at constant \( \Delta \) requires that the
input value of $\Delta$ be continually adjusted for different trial values of $\eta$ in such a way that $\sigma$ remains constant. One then computes the FPCA free energy (per particle) for various fixed values of $\sigma$ and constant values of the physical variables and FPCA parameters $w, \varepsilon, \gamma$, and $\Gamma$. The Landau expansion (93) can be obtained from this set of free energies at fixed values of $\sigma$ by an iteration procedure of the author's device. Finally, the Landau expansion of the free energy per unit volume in powers of the polarization $P$

$$F = F_0 + \frac{1}{2}A_0(T-T_0)P^2 + \frac{1}{4}BP^4 + \frac{1}{6}CP^6 + \ldots$$  \hspace{1cm} (94)

is obtained by multiplying by $N/V$ and making the substitution $P = (N\mu/V)\sigma$. The coefficients of the Landau expansions in $\sigma$ and $P$ are thus related by

$$A_0 = (V/N\mu^2)(\mu/\mu_1)A_0,$$

$$B = (V^3/N^3\mu^4)(\mu/\mu_1)b,$$

$$C = (V^5/N^5\mu^6)(\mu/\mu_1)c,$$  \hspace{1cm} (95)

where the factor $\mu_1$ takes into account the coupling of $\gamma$ to the polarizability of the lattice (see Eq. (16)). Thus when we examine the pressure dependence of the Landau coefficients in part III we will have to take into account the pressure dependence of $N/V$ and $\mu$ as well as that of the microscopic coefficients $a_0, b$, and $c$. 

3. Relations Among the Microscopic Theories. In this section we will explore the formal connections between the different microscopic models discussed in parts 1 and 2 of this section. We will first examine the classical limit $\Gamma = 0$ of the FPCA and show how the self-consistency condition for the molecular field reduces to that of the SUS theory. Next, we will show how the Slater-Takagi (four-body) energies can in practice be obtained from the two-body interactions assumed in the transverse Ising model if both polar and antipolar nearest-neighbor interactions are assumed. Finally, we will examine the effective renormalization of the interaction constants of the transverse Ising Hamiltonian in the mean field approximation (MFA) due to four-body correlations, as determined by the FPCA.

In the case that the tunneling integral $\Gamma$ is identically zero, the energy matrix corresponding to the four-particle cluster Hamiltonian (Eq. (82)) is already in diagonal form. Eliminating $\Lambda$ by Eq. (92) and using $\sigma = \text{Tr}(n_{1\uparrow} - n_{1\downarrow})$, we obtain a consistency equation:

$$\sigma' = \frac{2e^{-\beta w} \sinh \lambda + \sinh 2\lambda}{e^{-\beta w_1} + 4e^{-\beta w} \cosh \lambda + \cosh 2\lambda + 2e^{-\beta e}}$$  \hspace{1cm} (96)

where

$$\lambda = \tanh^{-1} \sigma + \beta \sigma' \sigma \sigma$$  \hspace{1cm} (97)
These expressions are equivalent to Eqs. (20) and (24) from the SUS theory.

We will now turn our attention to the second of the problems mentioned above, namely, the connection of the Slater-Takagi energies to the spin-spin interaction term of the transverse Ising model. If the tunneling field \( \Omega \) is zero, the Hamiltonian (48) reduces to

\[
\mathcal{H}_0 = - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z.
\]  

(98)

From the symmetry properties of the crystal it is clear that the interaction between protons having the same \( z \) coordinate is not the same as the interaction between protons at different levels, i.e., the interaction across the top or bottom of a \( \text{PO}_4 \) group is not the same as the interaction between a proton at the top of a given group and one at the bottom of the same group. Using again the square indices \((1 \ 2 \ 3 \ 4)\) (Eq. (78) ff.), we can write for the interaction constants in Eq. (98)

\[
J_{12} = J_{34} = \mathcal{U}
\]

\[
J_{13} = J_{24} = J_{23} = J_{14} = \mathcal{V}
\]  

(99)

The Ising Hamiltonian of a cluster of hydrogens around a given group now becomes

\[
\mathcal{H}_0^{(4)} = - \mathcal{U}(S_1^z S_2^z + S_3^z S_4^z) - \mathcal{V}(S_1^z S_3^z + S_2^z S_4^z + S_2^z S_3^z + S_1^z S_4^z).
\]  

(100)
Solving for the Slater-Takagi energies in terms of $U$ and $V$ as shown in Fig. 12, we obtain

$$U = -2w + 2\epsilon$$

$$V = 4w - \epsilon.$$  \hspace{1cm} (101)

For consistency, we must also have

$$w_1 = 4w - 2\epsilon.$$ \hspace{1cm} (102)

This is because there are three Slater-Takagi parameters, $\epsilon$, $w$, and $w_1$, but only two different Ising model parameters, $U$ and $V$. However, since $w >> \epsilon$ one has $w_1 >> w$ as well, and the difference in taking $w_1 = 4w - 2\epsilon$ instead of $w_1 = \infty$ as is usually done is small. (for DKDP the Boltzmann factors $\Theta_0$, $\Theta_1$, and $\Theta_2$ (see Eq. (19) at $T_c$ will turn out to be 0.43, 0.01, and $10^{-7}$ respectively). It is noteworthy that the MFA interaction parameter $J_0 = \Sigma J_{ij} = 4w$ and, hence, the thermodynamic properties in the MFA are determined by the Takagi energy $w$ while in the FPCA the most important factor is the Slater energy $\epsilon$.

With this result the FPCA treatment of the tunneling model can be considered to be the solution of the transverse Ising model up to the four-link terms in the cumulant expansion of Kubo, the non-nearest neighbor interaction terms $J_{ij}$ being subsumed in the parameter $\gamma$.

Now we can examine the third of the problems mentioned above--the renormalization of the MFA interaction constants by four-particle correlations. The self-consistency conditions (86) and (87) which
<table>
<thead>
<tr>
<th>Configuration</th>
<th>Pseudo-spin Configuration</th>
<th>Ising Energy = $\frac{1}{4}[-2U+4V] = c-w$</th>
<th>Slater-Takagi Energy = $w$</th>
<th>Net Dipole Moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Box$</td>
<td>$\uparrow \Box \uparrow$</td>
<td>$\frac{1}{4}[-2U-4V] = c-w$</td>
<td>$\mu$</td>
<td></td>
</tr>
<tr>
<td>$\Box$</td>
<td>$\uparrow \Box \downarrow$</td>
<td>$\frac{1}{4}[-2U-4V] = c-w$</td>
<td>$-\mu$</td>
<td></td>
</tr>
<tr>
<td>$\Box$ etc.</td>
<td>$\uparrow \Box \downarrow$</td>
<td>$2U/4 = 0-w$</td>
<td>$0$</td>
<td></td>
</tr>
<tr>
<td>$\Box$ etc.</td>
<td>$\uparrow \Box \uparrow$</td>
<td>$0 = w-w$</td>
<td>$\frac{1}{2} \mu$</td>
<td></td>
</tr>
<tr>
<td>$\Box$</td>
<td>$\uparrow \Box \downarrow$</td>
<td>$0 = w-w$</td>
<td>$-\frac{1}{2} \mu$</td>
<td></td>
</tr>
<tr>
<td>$\Box$</td>
<td>$\uparrow \Box \uparrow$</td>
<td>$\frac{1}{4}[-2U+4V] = w_1-w$</td>
<td>$0$</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 12. The relationship of the Slater-Takagi parameters to those of the Ising-like pseudo-spin model.
result from the minimization of the free energy with respect to Δ and η are that $σ = <n_{ij}^+ - n_{ij}^->$ and $<s> = <s_{ij}^+ + s_{ij}^->$ be the same whether determined from the one- or four-article density matrix. Thus at the appropriate values of Δ and η one obtains the same results using the single-particle Hamiltonian

$$H_{(1)} = -(\Gamma - \eta)(s_i^+ + s_i^-) - (\gamma <s> + \Delta)(n_i^+ - n_i^-)$$ (81)

as from the four-particle Hamiltonian; the FPCA is used only to determine Δ and η. In terms of the pseudo-spin representation $\vec{H}_{(1)}$ can be written

$$\vec{H}_{(1)} = -\vec{H} \cdot \vec{S}_i$$

where $\vec{H} = (2(\Gamma - \eta), 0, 2(2\gamma <s^2> + \Delta))$. Comparison with the MFA expression for the Transverse Ising model (cf. Eq. (49))

$$\vec{H}_i = (\Omega, 0, \Sigma_j J_{ij} <s_j^z>)$$ (103)

implies that $\Omega = 2(\Gamma - \eta)$ and $\Sigma_j J_{ij} <s_j^z>^2 = J_0 <s^2> = 2(2\gamma <s^2> + \Delta)$. Thus one sees that the effective values of $\Omega$ and $J_0$ are temperature dependent, since the fields Δ and μ which minimize the free energy are temperature-dependent. Taking in the low temperature phase Δ = $Δ_0 <s^2>$ where $Δ_0 \approx \text{const}$, the consistency condition (91) implies that $\Gamma - \eta = (\gamma + Δ_0) <s>$, or using the above relations between Ω and $J_0$ and the FPCA parameters,

$$<s^x> = \Omega / J_0.$$
which is identical with Eq. (58).

Rewriting the Hamiltonian (44) in the form

\[ \mathcal{H}_0 = -\sum_i \left[ (\Omega + \frac{1}{2} \sum_j B_{ij} S_j^x) S_i^x + \frac{1}{2} \sum_j J_{ij} S_j^y S_i^z \right] \]

and making the MFA, we find that the effective H field is

\[ \mathbf{H} = \left( \Omega + B_0 \langle S^x \rangle, 0, J_0 \langle S^y \rangle \right). \]  \tag{104}

Thus the \( \Omega \) that one obtains from an MFA fit, viz. \( \bar{\Omega} = \Omega - 2\eta \) can be given in terms of \( B \) and \( \langle S^x \rangle \) as

\[ \bar{\Omega} = \Omega + B_0 \langle S^x \rangle, \]  \tag{105}

which would imply that \( \eta = -\frac{1}{2} B_0 \langle S^x \rangle \). The value of \( \eta \) which minimizes the free energy in the PPCA does indeed behave much like \( \langle S^x \rangle \) in the mean field approximation, being sensibly constant below \( T_c \) and falling gradually to zero as \( T \to \infty \) (cf. Eq. (55)).
III. STRAIN AND DEUTERATION DEPENDENCE

A. Phenomenological Theory

In this section we will examine phenomenologically the terms which can arise in the free energy of a crystal with the symmetry \((42m)\) of KDP due to the fact that the lattice is not perfectly rigid. This will ensure that the microscopic theory to be developed in the next section is internally consistent, and will permit the use of experimental data on phenomena which are not obviously connected with

the pressure dependence of the ferroelectricity in establishing the pressure dependence of the parameters of the microscopic theory. In particular, we will find that applied hydrostatic pressure is coupled to the free energy of the crystal through the electrostriction effect, which is also responsible for the expansion of the volume of the crystal on passing to the ferroelectrically ordered state.

The free energy of the clamped crystal \(F_0(\{x^\perp\} = 0, T, P_3 = P)\), the microscopic counterpart of which is given by the FPCA with constant \(w, \varepsilon, \gamma, \) and \(\Gamma\), must be modified to include terms which depend on the strains \(x^\perp\) in low order\(^33,34\):

\[
F(\{x^\perp\}, T, P) = F_0 - \sum_{i=1}^6 a_{3i} x^i P - \sum_{i=1}^6 q_{13} x^i P^2 - \sum_{i=1}^6 r_{13} P^4 + \frac{1}{2} \sum_{i,j=1}^6 c_{ij} x^i x^j , \tag{106}
\]

where \(a_{3i}, q_{13}, r_{13}\) and \(c_{ij}\) are elements of the matrices representing the piezoelectric, electrostriction, "quadratic electrostriction," and
elastic stiffness tensors, respectively. For a crystal with the
symmetry (42m) of the high-temperature phase of KDP, one derives the
applied stresses $X_i$:

$$X_i = \frac{\partial F}{\partial x_i} = -q_{i3} P^2 - r_{i3} P^4 + \sum_{j=1}^{3} C_{ij} x_j, \quad i=1, 2, 3; \quad (107)$$

$$X_6 = \frac{\partial F}{\partial x_6} = -A_{36} P + C_{66} x_6. \quad (108)$$

For the case of hydrostatic pressure, $X_i = -p(\delta_{i1} + \delta_{i2} + \delta_{i3})$,
one obtains the equilibrium strains

$$\tilde{x}_i = \frac{3}{2} E_s [q_{i3} P^2 + r_{i3} P^4 - \rho \delta_{i1} + \delta_{i2} + \delta_{i3}]$$

$$= Q_{3i} P^2 + R_{3i} P^4 - \rho \delta_s \delta_i, \quad i=1, 2, 3; \quad (109)$$

$$\tilde{x}_6 = S_{66} A_{36} P = b_{36} P, \quad (110)$$

where $s_{ij} = (c^{-1})_{ij}$, $S_i = \Sigma_j s_{ij}$, and $Q_{3i} = \Sigma_j s_{ij} q_{ij}$. The coefficients $b_{36}$, $Q_{3i}$, and $R_{3i}$ can be determined by examination of the spontaneous strains as functions of the polarization.

The free energy as a function of pressure $F(p, T, P) =$

$$F(x, T, P) - E_{1X_1X_1} \text{ is now}$$

$$F(p, T, P) = \frac{1}{2} A_0 \left[ T - (T_0 + \frac{C_{66} b_{36}^2}{A_0} - \rho \frac{2 Q_0}{A_0}) P^2 + \frac{1}{4} \left[ B(T) - 4 q_{6s} + 4 \rho R_h \right] P^4 + \cdots \right], \quad (111)$$

where $Q_0 = \Sigma_i Q_{3i}$ is the volume electrostriction coefficient,
\[ A_h = \Sigma_i R_{3i}, \text{ and } A_s = \frac{1}{2} \Sigma_{i,j} c_{i,j} A_{3i} A_{3j}. \]

It is seen that the piezoelectric effect causes the Curie-Weiss temperature \( T_0 \) to be shifted upward in the free crystal by an amount \( c_{60} b_{36}^2 / A_0 \), which is about 4 degrees in KDP. This shift is observed experimentally at high frequencies, where the crystal is inertially clamped. However, this term can be considered to be included in the parameter \( \gamma \) and will be of no further interest here. The electrostriction effect is seen to cause a change in \( T_0 \) under applied pressure through \( A_h \) as well as a shift in the Landau coefficient \( B \) through \( A_s \) (see Fig. 13). The quadratic electrostriction effect causes the Landau coefficient \( B \) to be pressure dependent through \( A_h \).

We will now use the experimental results of several authors to calculate values of the electrostriction coefficients for KDP and DKDP.

The electrostriction coefficient \( A_{33}^H \) has been measured to be about \( 2.8 \times 10^{-12} \) esu once \(^37\) and \( 3.2 \times 10^{-12} \) esu twice \(^38, 18\). We will therefore adopt the value \( A_{33}^H = (3.1 \pm 0.2) \times 10^{-12} \) esu. The value \( A_{31}^H = 3.8 \times 10^{-12} \) esu was reported by von Arx and Bantle \(^39\) and by Kobayashi et al. \(^38\). However, both of these experiments revealed a "temperature dependence" in \( A_{31}^H \) which can be considered to arise from the quartic term \( R_{31}^H P_4 \) of Eq. (108), as a plot of \( x_1 \) vs. \( P^2 \) will readily show. A least squares fit using the strain vs. temperature data of von Arx and the spontaneous polarization vs. temperature curve of Samara \(^30\) gives the values
Fig. 13. Schematic representation of the free energy $F$ as a function of a dilatation strain $x$ and the polarization $P$, showing the behavior which results from inclusion of electrostriction term:

$$F = F_0 - qxP^2 + \frac{1}{2}cx^2.$$ Here $x = c^{-1}qP^2$ is the equilibrium value of $x$ at fixed $P$, shown by dashed curve in (d); (c) shows effective $-\frac{1}{2}c^{-1}q^2P^4$ term.
\[ Q_{31}^H = (2.8 \pm 0.1) \times 10^{-12} \text{ esu}, \]
\[ R_{31}^H = (3.2 \pm 0.6) \times 10^{-21} \text{ esu}. \]  
(112)

Since \( Q_{33}^H \) is reported to lack such temperature dependence\(^{38,18} \), one can infer that \( R_{33}^H = (0 \pm 1.0) \times 10^{-21} \text{ esu} \). With the above values of the \( Q_{31}^H \) and the elastic constant data of Haussuhl\(^{40} \), the relations
\[ q_{13} = \Sigma_{j} c_{ij} Q_{3j}, \quad q_{s} = \Sigma_{j} c_{ij} Q_{31} Q_{3j} \]
give (in cgs esu)
\[ q_{13}^H = 2.8 \pm 0.1, \quad q_{33}^H = 2.6 \pm 0.1, \quad q_{s}^H = (1.04 \pm 0.10) \times 10^{-12}. \]
(113)

Using the relation \( dT_o^H/dp = -2Q_{3j}/A_0 \), which follows from Eq. (111), and the value \( A_0^H = (4.0 \pm 0.2) \times 10^{-3} \text{ esu/K} \) (see Table II), one can calculate the value
\[ \frac{dT_o^H}{dp} = -4.35 \pm 0.4 \text{ K/kbar}, \]
which is in satisfactory agreement with the experimental\(^{41,17} \) value
\(-4.6 \pm 0.1 \text{ K/kbar} \).

For the deuterated case we will use the observation of Zeyen et al.\(^{42} \) that the fractional jump in the lattice constant \( a_3 \) on entering the ferroelectric phase is \( 6.5 \times 10^{-4} \) for a crystal with \( T_c \approx 212 \text{ K} \). For a similarly deuterated crystal \( (T_c = 211 \text{ K}) \), Uesu et al.\(^{43} \) found a jump in the strain \( x_1 + x_2 \) of \( 3.5 \times 10^{-4} \). The jump in the spontaneous polarization for a crystal with this deuteration
(82%) is about $4.2 \mu C/cm^2 = 1.26 \times 10^4 \text{esu}^{30}$. This value of $\Delta P$ would then give

$$
\begin{align*}
Q_{31} &= 1.1 \times 10^{-12} \text{ esu}, \\
Q_{33} &= 4.1 \times 10^{-12} \text{ esu}, \\
Q_h &= 6.3 \times 10^{-12} \text{ esu},
\end{align*}
$$

(114)

which would lead to the value

$$
d\sigma_0 / d\rho = -2Q_h / A_0 = -4.1 \text{ K/kbar},
$$

where we have used the experimental value $A_0 = 3.1 \times 10^{-3} \text{ esu/k}$ obtained by Samara$^{44}$ for a crystal with $T_c = 208 \text{ K}$. This value is in fair agreement with the value $-3.9 \pm 0.1 \text{ K/kbar}$ obtained for the same crystal in an experiment performed over the 0--3 kbar range, using a low viscosity silicone oil as a pressure medium. However, with the preponderance of evidence$^{41}$ now supporting values in the neighborhood of $-2.7 \text{ K/kbar}$ for crystals with this degree of deuteration, it is now thought that the oil used in this experiment may have become rather viscous at the pressures and temperatures which were used, possibly imparting non-hydrostatic stresses to the crystals$^{45}$. There is also reason to believe that the value of $Q_h$ obtained above is somewhat too large. Examination of the fractional jump in the strain $x_6 = b_{36} \Delta P$ (See Eq. (110) in the Uesu$^{43}$ experiment reveals that the jump in the polarization was about $\Delta P = 4.9 \mu C/cm^2$ (this also explains the flatness of their dilation strain $x_1 + x_2$ vs. temperature curve). Using this
value of $\Delta P$ and also making a correction for higher order terms in $P$
using our theoretical model for the negative $\gamma$ case, one finds

$$Q_{31}^D = 0.2 \times 10^{-12} \text{ esu},$$

which corresponds to the acceptable value $dT_0/dp = -2.8$ K/kbar for this

crystal. Linear extrapolation to our standard deuterated crystal with

$T_c = 220$ K gives

$$Q_{31}^D = 0.1 \times 10^{-12} \text{ esu}$$

$$Q_{33}^D = 4.2 \times 10^{-12} \text{ esu}. \quad (115)$$

This model then predicts the value

$$dT_0^D/dp = -2.9 \pm 0.4 \text{ K/kbar},$$

where the indicated uncertainty is a rough estimate for the whole

procedure. This is to be compared with the experimentally mea-

sured\(^{41,45}\) value of

$$dT_0^D/dp = -2.5 \pm 0.1 \text{ K/kbar}.$$ 

Using the elastic constant data of Shuvalov and Mnatskanyan\(^{46}\) for

DKDP ($T_c = 211$K), one obtains (in cgs esu)

$$Q_{31}^D = 0.6 \pm 0.2, \quad Q_{33}^D = 2.3 \pm 0.2, \quad Q_6 = (0.5 \pm 0.3) \times 10^{-11}. \quad (116)$$

To facilitate comparison, we will collect the results given in

Eqs. (112), (113), and (116) in the following table (all values are in

cgs esu):
It is seen that $q_{13}$ decreased markedly on deuteration, while $q_{33}$ remains nearly the same. This behavior suggests the interpretation that $q_{33}$ is due to the dependence of the long-range interaction parameter $\gamma$ on the lattice constant $a_3$; also, it would seem that $q_{13}$ is affected by the presence of tunneling in KDP. With the above values for the $R_{31}$ one can calculate the pressure derivative of the Landau coefficient $B$ as (cf. Eq. (111))

$$\frac{\partial B}{\partial \rho} \bigg|_{T=\text{const}} = 4 R_h = 4(2R_{31} + R_{33}) = (2.6 \pm 0.5) \times 10^{-11} \text{ esu/kebar} \tag{118}$$

The experiments of Schmidt et al.\textsuperscript{17} on the pressure dependence of the order of the ferroelectric transition provide the value

$$\frac{d B}{d \rho} \bigg|_{T=T_0(\rho)} = (0.6 \pm 0.2) \times 10^{-11} \text{ esu/kebar}. \tag{119}$$

The relation

$$\frac{d B}{d \rho} \bigg|_{T=0(\rho)} = \frac{\partial B}{\partial \rho} \bigg|_{T=\text{const}} + \left( \frac{d T_0}{d \rho} \frac{\partial B}{\partial T} \right)_{p=\text{const}} \tag{120}$$
then implies that

\[ \frac{\partial B}{\partial T} \bigg|_{p=\text{const}} = (0.4 \pm 0.1) \times 10^{-11} \text{ esu}/K. \]  

(121)

The values of the $q_{13}$ obtained in this section will be applied in the following section to the construction of a microscopic theory of strain dependence, while the values of the temperature and pressure derivatives of the Landau coefficient $B$ will be compared to the predictions of the microscopic models. It will be seen that the fact that $\partial B/\partial T|_p$ is unambiguously positive supports the choice of a negative value of the FPCA parameter $\gamma$. This conclusion is of course independent of the microscopic model of pressure dependence, since it refers to a derivative at constant pressure.
B'. Microscopic Theory

1. Introduction. We will now attempt to construct a microscopic theory which is quantitatively consistent with the body of experimental evidence on the pressure (and strain) dependence of the ferroelectric properties of KDP and its deuterated isomorph DKDP. The electrostriction constants $q_{13}$ and $q_{33}$, which together determine the pressure derivative of the Curie-Weiss temperature $T_0$, and the quadratic electrostriction constants $R_{31}$ and $R_{33}$, which determine the pressure derivative of the Landau coefficient $B$ (and, hence, the order of the ferroelectric transition), were discussed in the preceding section. There are experimental data on all these quantities and on the pressure derivatives of the inverse Curie constant $A_0$ and the saturation polarization $P_s$ for both KDP and DKDP. These data, along with the ambient-pressure values for the Landau expansion coefficients $A_0$, $T_0$, $B$, and $C$ for both crystals (for the deuterated case, as reflected by the shape of the spontaneous polarization vs. temperature curve) and the transition entropy (which is also related to the Landau coefficients), are the experimental results to which the theoretical predictions must conform.

There have been several previous attempts at modeling the pressure dependence of ferroelectricity in KDP. Lage and Stinchcombe have examined the pressure dependence of the parameters which occur in the Kobayashi model, and Blinc and Zeks have constructed a model...
for the pressure dependence of the parameters of the four-particle cluster approximation which is basically similar to the one which will be used here. Neither of these models was compared systematically with all the relevant experimental data, however, and they cannot be considered quantitatively correct. Furthermore, since the date of the paper by Blinc and Zeks (1968) there has been much experimental activity in the area of pressure dependence, so that much of the experimental data employed here was not available to these authors. Thus the theoretical effort reported here is essentially a systematic re-examination of the model of Blinc and Zeks in the light of new evidence; only those changes which are necessary to provide overall consistency have been made.

2. Pressure and Deuteration Dependence in the FPCA.

a. General remarks. We recall that in the four-particle cluster approximation the interactions of protons surrounding a given phosphate group are treated explicitly, while the remaining interactions are treated as self-consistent fields. The theory is specified by the parameters \( w, e, \gamma, \text{ and } \Gamma \), where \( w \) is the energy associated with a singly ionized (Takagi^{27}) \( \text{HPO}_4 \) or \( \text{H}_3\text{PO}_4 \) group, \( \gamma \) is the energy of a non-polar non-ionized (Slater^{4}) \( \text{H}_2\text{PO}_4 \) group (See Figs. 9 and 14), \( \gamma \) is the parameter introduced by Senko^{28} to describe long-range dipolar interactions (contributing a term proportional to \(-\gamma \vec{p}^2\) to the free
Fig. 14. Schematic projection of crystal structure on the xy plane, perpendicular to the ferroelectric axis z. The squares represent PO₄ tetrahedra with upper edges along the indicated diagonals; the z coordinate of the P ion is given above the diagonal. The H bonds, which connect an oxygen at the top of one PO₄ group with one at the bottom of another, are represented by dashed lines; the location along the bond of the proton (or deuteron) is shown by a dot. Where the dashed lines are broken the H bond connects with a PO₄ group one lattice spacing removed. The configuration of the protons around a given PO₄ group is associated with an energy and z axis dipole moment; these are given in parentheses below the diagonal. The dimensions a, R, and δ are those referred to in Table II.
energy) and $\Gamma$ is the proton tunneling integral for the H-bond double well. In the case $\Gamma = 0$, the theory is identical to the Slater-takagi-Senko-SUS model, which can be used to describe the deuterated crystal (the tunneling integral $\Gamma$ enters the statistics through the combination $\Gamma^2/wc$, which is probably several orders of magnitude smaller in DKDP\textsuperscript{49}). In this paper pressure and deuteration effects are taken into account in a consistent way, so that within the framework of an extended model the ferroelectric properties (including their pressure dependence) of both KDP and DKDP can be described. One may thus use experimental data from both crystals to restrict the freedom of the various parameters which occur in the theory.

b. The parameter $d$. We will assume as usual\textsuperscript{50} that the FPCA parameters $w$ and $\varepsilon$ are in lowest order proportional to the square of the distance $\delta$ between proton (or deuteron) sites in the hydrogen bond. This is the case for a simple electrostatic model of these energies; moreover, it is suggested by the fact that they represent the relative energies of configurations which would be identical if the particles were centered on the bonds.

The long-range interaction parameter $\gamma$ contributes to the free energy per unit volume a term

$$-(N/V)\delta \sigma^2 = -(\delta V/N\mu^2)P^2 = -\gamma P^2, \quad (122)$$
where $\sigma = (V/N\mu)P$ is the fractional polarization (the order parameter),
$\mu$ is the dipole moment associated with a polar Slater group (See Figs. 9 and 14), and $N$ is the number of PO$_4$ groups in volume $V$. If the contributions to $\text{\gamma}$ of different powers in the lattice constants $a_i$ are of nearly the same magnitude but of opposite sign, $\text{\gamma}$ can depend rather strongly on the lattice constants. The FPCA parameter $\gamma = (N\mu^2/V)\text{\gamma}$ depends on $\mu$ as well. Elementary considerations suggest that $\mu \propto \delta$; this relation will be seen in fact to be supported by experimental evidence. Thus $\gamma$ depends both on the intersite distance $\delta$ and on the set of lattice constants $\{a_i\}$.

Since elongation of $\delta$ is rather the most important crystallographic effect of deuteration 51, one can estimate the parameters $w_H$, $v_H$, and $\gamma_H$ for KDP from those of DKDP (denoted by $w_D$, $v_D$, and $\gamma_D$) by the relation:

$$d^2 = \frac{c_H}{c_D} = \frac{w_H}{w_D} \simeq \frac{\gamma_H}{\gamma_D}$$

One can estimate the parameter $d$ from the ratio of saturation
<table>
<thead>
<tr>
<th>Crystal</th>
<th>Dimension (in Å)</th>
<th>Room Temperature</th>
<th>Just Above $T_C$</th>
<th>Well Below $T_C$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>KDP</td>
<td>$H - H$ ($6_H$)</td>
<td>0.381(6)</td>
<td>0.350(3)</td>
<td></td>
<td>Nelmes$^{51}$</td>
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<td></td>
<td></td>
<td>0.35(1)</td>
<td>0.34(1)</td>
<td>0.38(2)</td>
<td>Bacon$^{52}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.400(25)</td>
<td></td>
<td></td>
<td>Plesser$^{53}$</td>
</tr>
<tr>
<td></td>
<td>$O - 0$ ($R_H$)</td>
<td>2.494(2)</td>
<td>2.481(2)</td>
<td></td>
<td>Nelmes$^{51}$</td>
</tr>
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<td></td>
<td></td>
<td>2.492(5)</td>
<td>2.480(4)</td>
<td>2.491(4)</td>
<td>Bacon$^{52}$</td>
</tr>
<tr>
<td></td>
<td>$P - P$ ($\frac{1}{2}a_H^{av}$)</td>
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<td>3.713</td>
<td>3.714</td>
<td>Kobayashi$^{38}$</td>
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<td>DKDP</td>
<td>$D - D$ ($6_D$)</td>
<td>0.448(3)</td>
<td>0.448(6)</td>
<td></td>
<td>Nelmes$^{51}$</td>
</tr>
<tr>
<td></td>
<td>$O - 0$ ($R_D$)</td>
<td>2.523(2)</td>
<td>2.520(4)</td>
<td></td>
<td>Nelmes$^{51}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.519(1)</td>
<td>2.521(2)</td>
<td>2.530(2)</td>
<td>Nakano$^{54}$</td>
</tr>
<tr>
<td></td>
<td>$P - P$ ($\frac{1}{2}a_D^{av}$)</td>
<td>3.732</td>
<td>3.730</td>
<td>3.730</td>
<td>Nakano$^{34}$</td>
</tr>
</tbody>
</table>
polarizations for the two crystals
\[
\frac{P_{s,H}}{P_{s,D}} = \frac{(N/V)_H \mu_H \sigma_{s,H}}{(N/V)_D \mu_D \sigma_{s,D}},
\]
where \( \sigma_s \) is the value of the order parameter at the temperature at which the "saturation" polarization is measured. Because of the appreciable tunneling in KDP, \( \sigma_H \) will differ from unity even at \( T = 0 \), although the difference is expected to be small. Samara measured \( P_H = 4.95 \pm 0.07 \) and \( 5.00 \pm 0.07 \mu \text{C/cm}^2 \) in two samples of KDP at 35 to 40 degrees below the transition, but noted that \( P \) was still increasing somewhat with decreasing temperature, which led him to adopt \( P_{s,H} = 5.10 \mu \text{C/cm}^2 \) as the true saturation value. (In fact, one of our results will be that \( \sigma_H \approx 0.981 \) at \( T = 81 \text{ K} \) (cf. Table III.A), which would yield \( N_{H} / V = 5.00/0.981 = 5.10 \mu \text{C/cm}^2 \). For a heavily deuterated sample with \( T_c \approx 220 \text{ K} \), which we adopt as our standard DKDP crystal, the value \( P_{s,D} = 6.21 \pm 0.07 \mu \text{C/cm}^2 \) was measured \(^3^0\), so
\[
\delta \approx \frac{\mu_H}{\mu_D} \approx \frac{(N/V)_D (5.10 \pm 0.07)}{(N/V)_H (6.21 \pm 0.07)} = 0.81 \pm 0.02. \tag{125}
\]
The ratio \( \mu_H / \mu_D \) calculated above from the ratio of saturation polarizations should agree with the ratio of intersite distances \( \delta_H / \delta_D \) at temperatures well below the transition, where information on \( \delta_D \) is lacking (see Table II). However, the increase in the total bond length \( R \) (the 0...0 distance) which occurs in passing to the low temperature phase has been measured for both crystals\(^5^2,5^4\). One
can see that $\delta$ increases about $2\frac{1}{2}$ times as much as $R$ increases between $T_c + 5$ K and room temperature in KDP, and that the same ratio of changes in consistent with the data between $T_c + 5$ K and $T_c - 40$ K. Furthermore, $\delta$ increases about $2\frac{1}{2}$ times as much as $R$ increases upon deuteration at room temperature, so it seems reasonable to assume that

$$\frac{\Delta \delta}{\Delta R} \approx 2.5$$

for either crystal. This agrees with our estimate of about $2\frac{1}{2}$ for bonds of approximately $2.5 \AA$ in length from the graph of $0\ldots H$ versus $0\ldots 0$ distances in various compounds. (We will make use of Eq. (126) several times in this paper, although only in a secondary role.)

Then if $R$ increases by $0.011 \AA$ and $0.009 \AA$ for KDP and DKDP respectively in passing to the polar state, the calculated ratio $\delta_H/\delta_D$ would increase from its value of $0.78 \pm 0.02$ just above $T_c$ to the value $0.80 \pm 0.02$ well below $T_c$. This estimate is thus in good agreement with that from the ratio of saturation polarizations (Eq. (125)), and one may say that $d = 0.81 \pm 0.02$. The equivalence of $\mu_H/\mu_D$ and $\delta_H/\delta_D$ supports the assumption that $\mu \approx \delta$.

c. Pressure dependence. At the same time, the assumption (123) that $w$ and $\varepsilon$ are proportional to $\delta^2$ gives the logarithmic pressure derivatives (denoted throughout by primes)

$$w' = d \log w/d\rho = \varepsilon' = 2\delta'$$

since these parameters are assumed to depend on the intersite
distance only.

The dependence of the tunneling integral on $\delta$ will be compared to that determined from the expression calculated by Blinc and Hadži\textsuperscript{56,48} for a potential composed of two harmonic oscillator potentials placed a distance $\delta$ apart:

$$\Gamma = A \Gamma_0 \propto A E_0 \frac{2}{\hbar} \sqrt{\frac{\hbar}{\Delta \omega}} \delta e^{-\frac{\hbar}{\Delta \omega}},$$  \hfill (128)

where $A$ is a factor (assumed roughly independent of pressure) due to renormalization by proton-lattice coupling\textsuperscript{48}, $q^2 = \hbar m E_0 \delta^2 / \Delta \omega^2$, and $E_0$ is the zero-point energy of the particle in the well; the approximation is valid for $q^2 \gg 1$. One can take $E_0$ as one half the infrared or Raman frequencies\textsuperscript{56}, giving $E_{0,H} = 1250$ or $1200 \text{ cm}^{-1}$ respectively; these values compare rather well with the value of the zero-point energy $E_{0,H} = 0.079 \text{ eV} = 1300 \text{ cm}^{-1}$ which Bacon and Pease\textsuperscript{52} estimated directly by examining the temperature dependence of the mean-square hydrogen amplitude. We therefore adopt the value $E_{0,H} = 1250 \text{ cm}^{-1}$, which gives $q_H^2 = 2.29$ for $\delta_H = 0.350 \text{ Å}$, as was measured recently by Nelmes et al.\textsuperscript{51} (see Table II). This value of $q_H$ gives $\Gamma_0 = 310$ degrees, which, when compared with $\Gamma = 100$ degrees obtained from fitting the ferroelectric data, indicates that $A$ is about 0.3. This model gives for the logarithmic pressure derivative

$$\Gamma' = \kappa \frac{\Gamma_0'}{\Gamma_0} = \kappa (1 - 2q_H^2) \delta_H' = -3.6 \kappa \delta_H', \hfill (129)$$
where \( r \) is a parameter introduced here to accommodate possible deviations from the rather simple model outlined above. Values of \( r \neq 1 \) could be ascribed to pressure dependence in the factor \( A \), to use of the wrong value for \( \delta_H \) or \( E_0, H' \), or perhaps to more fundamental inadequacies in the model. For the purposes of this paper, specifying \( r \) is equivalent to specifying \( \Gamma_H' \) once \( \delta_H' \) is given.

For the logarithmic pressure derivative of \( \chi = (N\mu^2/V)\chi \) one has

\[
\chi' = 2\delta' - V' + \bar{\chi}',
\]

(130)

where we have used the relation \( \mu \propto \delta \). The terms \( \bar{\chi}' \) and \( V' \), which arise from the pressure dependence of the lattice constants, are the only contributions to the pressure dependence of the microscopic model which do not depend directly on the pressure derivative \( \delta' \). In the next section we will make the identification \( d\bar{\chi}/dp = -Q_h^L \), where \( Q_h^L \) is the contribution to the volume electrostriction \( Q_h \) which is due to explicit dependence of the free energy on the lattice constants.

The pressure dependence of the model is now completely specified by the parameters \( \delta' \), \( r \), and \( Q_h^L \).

d. Connection with the phenomenological theory. It was shown in part A of this section that pressure is coupled to the free energy through the electrostriction effect; hence, there must be a connection between the pressure dependence of the FPCA parameters given above and the electrostriction coefficients \( q_{13} \). This connection may be elucidated in the following way. Since the FPCA free energy is
assumed to depend on the strains through the parameters \( w, \varepsilon, \gamma, \) and \( \Gamma \) through the intersite distance \( \delta \) (and also directly in the case of \( \gamma \)), we expand the theoretical free energy in the dilatation strains \( x_1, x_2, \) and \( x_3 \) as

\[
F(x_i, T, P) = F_0(\delta = \delta_0, \{a_i\} = \{a_i\}_0, T, P) +
\]

\[
+ \sum_{i=1}^{3} x_i \frac{\partial}{\partial x_i} F_0(\delta, \{a_i\}, T, P) + \cdots ,
\]

where the \( a_i \) are the lattice constants and \( F_0(\delta, \{a_i\}, T, P) \) is the FP model expression for the free energy, which has the Landau expansion

\[
F_0 = \frac{1}{2} A_0(T - T_0) P^2 + \frac{1}{4} B P^4 + \frac{1}{6} C P^6 + \cdots .
\]

Comparison with Eq. (106) shows that

\[
q_i = \frac{3}{\delta} [\frac{1}{2} A_0(\delta)(T - T_0) - \bar{\delta}(\{a_i\})], \tag{132}
\]

where \( T_{00}(\delta) \) is the Curie-Weiss temperature which would obtain if \( \gamma \) were zero. With \( \frac{a}{a_j} = \frac{3}{\delta} \frac{\delta}{\delta a} a_j + a_j \frac{\partial}{\partial a} \) and \( \delta = -pS \), one finds

\[
Q_h = \sum_{i=1}^{3} q_i = \sum_{i,j=1}^{3} \bar{S}_i \epsilon_j q_i = \sum_{i=1}^{3} \bar{S}_i q_i = Q_h^L + \delta [\frac{3}{\delta} A_0(T - T_0)] \tag{133}
\]

where

\[
Q_h^L = \sum_{j=1}^{3} \bar{S}_j q_j^L = \sum_{j=1}^{3} \bar{S}_j a_j \frac{\partial}{\partial a_j} \bar{\delta} = -\frac{d\bar{\delta}}{dp}. \tag{134}
\]

3. Fitting Procedure.

a. Ambient pressure. A set of parameters \( w_D, \varepsilon_D, \) and \( \gamma_D > 0 \)
(with $\Gamma_D = 0$) is readily found such that $T_{0,D}$ has its experimental value of 218.3 K and a good fit to the spontaneous polarization curve of the nominally 98% deuterated sample of Samara is obtained (see Fig. 15). Since the shape of the polarization curve involves the Landau coefficients only in certain ratios, however, their actual magnitude may not agree with experiment. This is most clearly manifested in the fact that the theoretical inverse Curie constant $A_{0,D}$ is somewhat too large, even when a reasonable correction is made for the polarizability of the lattice (the theoretical Landau coefficients are divided by the factor $\frac{1}{1 + 2\gamma X_0}$, where $X_0 \approx 0.5$ is the polarizability of the lattice $^5, ^{57}$ (see Eqs. (29-32). Extension of the parameter space to the region of negative $\gamma$ improves the situation, although one finds that for a similar fit to the curve (Fig. 15) the value of $A_{0,D}$ is now slightly too small. Finally, inclusion of the electrostriction correction $q_s$ of Eq. (III) decreases the absolute value of $\gamma$ which is needed for a similar fit and thus tends to merge the solutions, causing the value of $A_{0,D}$ to agree very well with experiment for the negative $\gamma$ case (see Table III. A)

For a particular set of parameters $\{w_D, \epsilon_D, \gamma_D\}$ obtained in this way, we generate a set of parameters for the undeuterated crystal $\{w_H, \epsilon_H, \gamma_H\}$ by multiplying by $d^2$ (we also include a small correction in $\gamma_H$ due to the difference in the lattice constants of the two crystals (see the Appendix)). Next $\Gamma$ is adjusted such that $T_{0,H}$ falls
Fig. 15. The spontaneous polarization vs. reduced temperature for DKDP and KDP, comparing the experimental points of Samara\textsuperscript{30} with those calculated in the FPCA. The DKDP curves are calculated for $\Gamma_D = 0$ and $q_s^D = 0$, with $\{w_D, \varepsilon_D, \gamma_D\} = \{1000, 114, 22.4\}$ and $\{1000, 200, -19.4\}$ Kelvin for the two cases. An essentially similar fit to the DKDP curve was found for the other sets of parameters in Table III (with $q_s^D = 0.5 \times 10^{-11}$ cgs esu). The KDP curves are for the negative $\gamma$ case with $q_s^H$ set equal to its experimental value of $1.04 \times 10^{-11}$ cgs esu. The FPCA parameters were $\{w_H, \varepsilon_H, \gamma_H\} = d^2 \{1000, 187, -14.1 + (0.6/d^2)\}$ Kelvin, with $\Gamma_H = 105$ Kelvin for $d = 0.81$ and $\Gamma_H = 130$ Kelvin for $d = 0.84$; in each case $\mu_H$ was taken to be $d$ times $\mu_D$. 
Fig. 15

Polarization (μC/cm²)

DKDP (T_c ≈ 220K)
- Experiment
- FPCA Positive γ
- FPCA Negative γ

KDP (T_c ≈ 122K)
- Experiment
- FPCA d = 0.81
- FPCA d = 0.84

Reduced Temperature T/T_c
TABLE III. Results for TPCA models for zero pressure (A) and applied pressure (B). All models shown agree quantitatively with experiment for $T_0^D$ and the shape of the $P'_D$ vs. $T$ curve, $A_0^D$, $P_0^D$, and $T_0^H$, as well as $q_1^D$, $q_3^D$, $q_1^H$, and $q_3^H$ (and, hence, with $dT_0^D/dp$ and $dT_0^H/dp$).

The model parameters $w^D$, $\varepsilon^D$, $\gamma^D$, $\Gamma^H$, $\delta^H$, and $r$ are inputs; the Landau coefficients $A^0_D$, $A^0_H$, $E^H$, and $C^H$ and their derivatives, as well as $\sigma^H(81\text{ K})$ and $P'_H(81\text{ K})$, are predictions of the models. It is seen that when the $q_s$ correction is included (as it must be for consistency), the model with the experimental value $d = 0.81$ is in good agreement with the experimental data. The reader can gauge the effects of small changes in $d$ and $\delta^H$. Note that the models with positive $\gamma$ predict the wrong sign of $\Delta B/\Delta T|_{T_0}$ and quantitatively incorrect values of $A_0$ and $\Delta B/\Delta P|_{T_0}$.

The references for the experimental values listed in Table III are: $^a$Eq. (117); $^b$Ref. 30, also R. M. Hill and S. K. Ichiki, Phys. Rev. 132, 1603 (1963); $^c$Eq. (125); $^d$See Table I.; $^e$Eq. (121); $^f$Eq. (129); $^g$Eq. (118); $^h$Ref. 17; $^i$C. A. Samara, Ferroelectrics 20, 87 (1978).
| $q_s$ | $\gamma_D$, $\varepsilon_D$, $\omega_D$ | $A_{0,D}$ | $d$ | $\Gamma_H$ | $\sigma_H$ | $A_{0,H}$ | $B_H$ | $C_H$ | $\Delta B/\Delta T|_p$ |
|-------|-----------------|---------|-----|----------|----------|--------|------|-----|---------------------|
| $10^{-11}$ esu | Kelvin | $10^{-3}$ esu/K | Kelvin | $10^{-3}$ esu/K | $10^{-11}$ esu | $10^{-19}$ esu | $10^{-11}$ esu/kbar |
| 0     | 22.4, 114, 1000 | 3.37    | 0.81 | 109     | 0.981   | 5.10   | -1.7 | 4.3 | -0.42 |
| -19.4, 200, 1000 | 2.87    | 0.81   | 104 | 0.981   | 3.96    | -1.2  | 2.8  | 0.45 |
| $q_s^D=0.5$ | 17.2, 123, 1000 | 3.34    | 0.81 | 109     | 0.981   | 5.03    | -2.3 | 3.7 | -0.31 |
| $q_s^H=1.04$ | -14.1, 187, 1000 | 2.98    | 0.78 | 76      | 0.991   | 4.39    | -2.5 | 2.2 | 0.34 |
|          |          |        | 0.81 | 105     | 0.981   | 4.20    | -1.9 | 3.4 | 0.30 |
|          |          |        | 0.82 | 114     | 0.978   | 4.12    | -1.5 | 3.4 | 0.33 |
|          |          |        | 0.83 | 122     | 0.974   | 4.05    | -1.2 | 3.6 | 0.34 |
|          |          |        | 0.84 | 130     | 0.969   | 3.99    | -0.9 | 3.6 | 0.35 |
| $q_s^D=0.5$ | Experimental | 3.06    | 0.81 |        |         | 4.0    | -2.0 | 4.8 | 0.4 |
| $q_s^H=1.04$ | ± 0.10 | ± 0.09 | ± 0.02 |         |         | 4.2    | ±0.5 | ±0.1 | ±0.1 |
| $q_s$ | $\gamma_D', \varepsilon_D', \omega_D$ | d | $\delta^I_{H}=\mu^I_{H}$ | r | $T_H'$ | $\Delta B/\Delta p|_{T}$ | $\Delta B/\Delta p|_{T_0(p)}$ | $P_H'$ | $A_0'$ |
|-------|----------------|----|----------------|----|---------|----------------|-----------------|--------|--------|
| $10^{-11}$ esu | Kelvin | %/kbar | %/kbar | $10^{-11}$ esu/kbar | $10^{-11}$ esu/kbar | %/kbar | %/kbar |
| 0 | 22.4, 114, 1000 | 0.81 | -0.95 | 1.2 | 4.1 | -1.1 | 0.01 | -1.5 | 1.4 |
| | -19.4, 200, 1000 | 0.81 | -0.95 | 1.1 | 3.8 | 3.2 | 0.49 | -1.4 | 0.1 |
| $q_s^D=0.5$ | 17.2, 123, 1000 | 0.81 | -0.95 | 1.2 | 4.1 | -0.8 | 0.21 | -1.6 | 1.3 |
| $q_s^H=1.04$ | -14.1, 187, 1000 | 0.78 | -0.95 | 2.5 | 8.6 | 2.7 | 0.48 | -1.2 | 0.4 |
| | 0.81 | -0.95 | 1.1 | 3.8 | 2.6 | 0.59 | -1.4 | 0.3 |
| | -1.05 | 0.82 | 3.1 | 2.6 | 0.58 | -1.4 | 0.6 |
| | -1.15 | 0.58 | 2.4 | 2.4 | 0.60 | -1.5 | 0.9 |
| | 0.82 | -0.95 | 0.84 | 2.9 | 2.5 | 0.60 | -1.5 | 0.3 |
| | 0.83 | -0.95 | 0.67 | 2.3 | 2.5 | 0.59 | -1.6 | 0.1 |
| | 0.84 | -0.95 | 0.50 | 1.7 | 2.4 | 0.62 | -1.7 | -0.3 |
| $q_s^D=0.5$ | Experimental | 0.81 | nom. | 2.6 | 0.6 | -1.6 | 0.7 |
| $q_s^H=1.04$ | $\pm 0.02$ | $c$ | $[f]$ | $[g]$ | $[h]$ | $[i]$ | $[j]$ |
| $\pm 0.10$ | $[a]$ |
between 122 and 122.5 K. This leaves the Landau coefficients $A_0, B_H, C_H$ for the undeuterated crystal as predictions of the theory. Comparison of the values from the theory given in Table III, A with the experimental values from Table I shows that models with negative $\gamma$ agree fairly well with experiment (the "experimental" values in this part of Table III, A are averages over the experimental values in Table I, excluding those which fall outside of one standard deviation).

As a further check on the model, we have plotted in Fig. 15 the polarization vs. temperature curve for KDP from the FPCA, with parameters determined by the above procedure, along with the experimental data of Samara. The polarization is $P = (N/V) \mu_H \sigma_H$, where $\mu_H$ is taken to be $d$ times $\mu_D$; the curves are thus specified by the single parameter $d$ (indeed, inasmuch as our earlier estimate of $d$ from the neutron diffraction data was $\delta_H/\delta_D = 0.80 \pm 0.02$, the $d = 0.81$ curve can be considered to be essentially a zero-parameter fit). It is seen that the shape of the curve for $d = 0.84$ is in somewhat better agreement than that for the $d = 0.81$ case, although the polarization in the former case is about 3% higher than the experimental values over most of the range. The best value $d = 0.84$ from the relation $\{w_H, \epsilon_H, \gamma_H\} = d^2 \{w_D, \epsilon_D, \gamma_D\}$ is thus slightly higher than the value $d = \mu_H/\mu_D = 0.81 \pm 0.02$, although the difference is hardly remarkable in view of the uncertainties involved. Furthermore, since $\delta_H$ (and, hence, $\mu_H$)
depends on both temperature (see Table II) and polarization (through the electrostriction effect), it is doubtful that $\mu_H$ can be considered constant to within a few per cent over the entire range of data shown in Fig. 15. In any case, the fairly close agreement would seem to indicate that effects of higher order in $d$ are not very important.

b. Applied pressure. As in the ambient pressure case, we will begin with the deuterated crystal, since its pressure dependence is governed by only two parameters $\delta_D^s$ and $Q^L_n$ (the tunneling integral derivative parameter $r$ is irrelevant in DKDP). The theory should agree with the experimental values for the logarithmic pressure derivatives of the saturation polarization and the Curie constant, and with the values calculated from experiment for $q_{13}^D$ and $q_{33}^D$ (and, hence, with $dT_0^D/dp$).

In an experiment performed over a 3 kbar range on an 82% deuterated sample ($T_c = 208$ K) Samara measured $P'_s = -0.6\%$/kbar, $A'_0 = 1.5 \pm 0.3\%$/kbar, and $dT_0^D/dp = -3.9 \pm 0.2$ K/kbar. With $P_s = (N/V)\mu s_s$ one has $\mu' = P'_s + V'_s - \sigma'_s$. Since $\sigma'_s$ can be taken to be zero in DKDP and $V'_D = -0.4$/kbar, one obtains $\mu' = -1.0\%$/kbar. The logarithmic derivative of the inverse Curie constant $A'_0$ is given by $A'_0 = V' - 2\mu' + a'_0$, where $a'_0$ is the value calculated from the microscopic theory (see Eq. 95).

In SUS theory, the logarithmic derivative $a'_0$ is positive for $T'_0 - \epsilon' > 0$, negative for $T'_0 - \epsilon' < 0$, and zero if $T'_0 = \epsilon'$. For the above value of $dT_0^D/dp$ one has $T'_0 = 1.9 \pm 0.1$/kbar, and with $\epsilon' = 2\mu' = -2.0$/kbar one finds $a'_0 = 0.1$/kbar, which leads to the value
$A_0' = 1.7\% / \text{kbar}$ for the 82% deuterated crystal, in satisfactory agreement with the measured value. A subsequent extension\textsuperscript{58} of the pressure range to 25 kbar with a similarly deuterated sample, however, showed a linear $T_c$ vs. $p$ curve with a slope which we estimate to be about -2.9 K/kbar. The average logarithmic derivative over the 25 kbar range is then $T_0' = -1.7\% / \text{kbar}$. With this value of $T_0'$ and with $\varepsilon_0 = 2\mu' = -1.9\% / \text{kbar}$, one calculates the values $P_8' = -0.6\% / \text{kbar}$ and $A_0' = 1.8\% / \text{kbar}$, still in satisfactory agreement with experiment\textsuperscript{59}.

With this value of $\mu_D' = \delta_D'$ one calculates for the contribution to the electrostriction coefficient $q_{13}$ from the dependence on the bond length the value $q_{13}^{D,B} = 2.3 \pm 0.1 \text{ cgs esu}$. When this is compared with the estimate made in the Appendix of $q_{13}^{D} = 0.6 \pm 0.2 \text{ cgs esu}$, one is able to calculate the contribution to $q_{13}^{D}$ from the explicit dependence on the lattice constants themselves as

$$q_{13}^{D,L} = q_{13}^{D} - q_{13}^{D,B} = 1.7 \pm 0.2 \text{ cgs esu}.$$  

If it is assumed that the length of the hydrogen bond is not affected by changes in the lattice constant $a_3$, it follows that $q_{33}$ arises solely from the dependence of $\gamma$ on $a_3$, that is, $q_{33} = q_{33}^{L}$. Then

$$q_{33}^{D,L} = q_{33}^{D} = 2.3 \pm 0.2 \text{ cgs esu},$$

which yields the value $q_{33}^{D,L} = \sum_j S_{j}^{D} q_{j3}^{L} = 1.9 \pm 0.4 \times 10^{-12} \text{ cgs esu}$, where we have used the elastic constant data of Shuvalov and Mnatskanyan\textsuperscript{46} for DKDP.
We will now turn our attention to the undeuterated crystal. For this case, one can no longer assume that $\sigma_s'$ is zero. The FPCA value for $\sigma_s'$ in the neighborhood of $T_c - 40$ K will depend on the model parameters, including $\delta_H' = \eta_H'$, so that knowledge of $\eta_{s,H}' = -\psi_H' + \mu_H' + \sigma_s',H$ cannot immediately be used to determine $\delta_H';$ therefore, we begin by assuming a value for $\delta_H'.$ The simplest assumption would be $\delta_H' = \delta_D' = -0.95\% / \text{kbar}$. This assumption is quite reasonable since the ratio of axial compressibilities $S_{1H}/S_{1D}$ at room temperature is about the same as the ratio of intersite distances $\delta_H/\delta_D'(\text{see Table II}).$ We have examined the effects of small changes from this value in Table III. B.

The lattice contribution to the volume electrostriction $q_{H,L}^{H}$ is found by assuming that

$$q_{013}^{H,L} = q_{013}^{D,L} = -1.7 \pm 0.2 \ \text{cgs esu}$$

(see Eq. (26)), and, as in the deuterated case,

$$q_{033}^{H,L} = q_{033}^{H} = 2.6 \pm 0.1 \ \text{cgs esu}.$$  

Using the elastic constant data of Haussühl for KDP, one then finds

$$q_{H,L}^{H} = -(1.6 \pm 0.4) \times 10^{-12} \ \text{esu}.$$ 

The tunneling integral parameter $r$ is then adjusted to give $q_{13}^{H,B} = q_{13}^{H} - q_{13}^{H,L} = 4.0 \pm 0.2 \ \text{cgs esu},$ whereupon the pressure dependence of the microscopic model is completely specified.
4. Results.

The results are presented in Table III. It is seen that the models with positive $\gamma$ predict the wrong sign of the pressure and temperature derivatives of the Landau coefficient $B$, as well as predicting values of $A_0^D$ and $A_0^H$ which are too high. For models with negative $\gamma$ the values of $\Delta B/\Delta T|_P$ are in satisfactory numerical agreement with the value calculated using Eq. (120). This result is independent of the model presented here for the pressure dependence of the FPCA parameters.

A negative value for $\gamma$ corresponds to the circumstance that the long-range dipolar interactions in the crystal tend to favor the nonpolar state. This tendency is offset in our model by an increase in the value of $\varepsilon$, the relative energy of a nonpolar (Slater) $\text{H}_2\text{PO}_4$ group, which is a measure of the tendency of the short-range forces to cause ordering of the crystal. It should be noted that the value $w_D = 1000 \pm 20$ deg K is the one for which the model reproduces the spontaneous polarization curve of Fig. 2 independent of the sign of $\gamma$ and of the inclusion of the $q_s$ correction. It is this parameter which regulates the steepness of the rise in spontaneous polarization as the temperature is lowered through $T_C$ (in the pure-Slater model, for which $w = \infty$, the rise is infinitely rapid)\textsuperscript{4,5}. The value for $w_D$ found here is in good agreement with the estimate of $900 \pm 200$ deg K from the measured activation energy for deuteron intrabond hopping\textsuperscript{5}. 
It is noteworthy that the tunneling integral derivative parameter $r$ is close to its nominal value of unity when $d$ is at its experimentally determined value 0.81. This reflects favorably on the model of Bllin and Hadzi for the tunneling integral (Eq. (128)). The logarithmic pressure derivative of $\Gamma$ is rather sensitive to the values of $d$ and $d'$; however, one can say that it is probably in the range $1.5 < \Gamma' < 4.0\% / \text{kbar}$. The value of $\Delta B / \Delta P_{T_0}(p)$, which measures the effect of pressure on the order of the ferroelectric transition, is in excellent agreement with the experimentally determined value$^{17}$ for the negative $\gamma$ case at $d \approx 0.81$, whereas for the positive $\gamma$ case there is disagreement here also.

Finally, the value $\delta_h' \approx -1\% / \text{kbar}$ might at first seem incompatible with the recent finding of Nelmes et al.$^{51}$ that the $0...0$ distance $R_h$ is practically unchanged in going from 1 bar to 20 kbar at room temperature. However, if $\Delta \delta / \Delta R$ is about 2.5 as given by Eq. (6), this value of $\delta_h'$ would require a change in $R_h$ over the 20 kbar range of only 0.03 Å, which may not be significant in this experiment. Also, the room-temperature volume compressibility measurements of Morosin and Samara$^{60}$ over a 22 kbar range show a marked decrease in the compressibility at high pressure, which would further decrease the expected change in $R_h$ (by a factor of $\approx 1.4$).
IV. CLOSING REMARKS

1. Conclusion. We have found that the four-particle cluster approximation describes in an unstrained and natural way the static ferroelectric properties of KDP, including their pressure and deuteration dependence, while using only a minimal number of free parameters. Specifying for the deuterated case the three parameters $\omega_D$, $\varepsilon_D$, and $\gamma_D$ provides good agreement with experiment for at least four quantities: $T_0^D$, $A_{0,D}$, and the jump rate of rise of the spontaneous polarization vs. temperature curve (see Fig. 15); the value of $\omega_D$ obtained for this fit is also in agreement with an independent experimental estimate. The pressure dependence of the DKDP model is given by two parameters, $\delta'$ and $Q_{h}^{D,L}$. Specifying these two parameters gives acceptable agreement for three quantities: $dT_0^D/dp$, $P'_{s,D}$, and $A_{0,D}'$. Only one more parameter ($\Gamma_H$) is needed to give $T_0^H$, $A_{0,H}$, $B_{H}$, and $C_H$. Finally, specifying just one additional parameter ($T_H'$ or $r$) provides acceptable to very good agreement with experiment for five quantities: $dT_0^H/dp$, $A_{0,H}'$, $dB/dp|_T$, $dB/dp|_{T_0(p)}$, and $P'_{s,H}$. Furthermore, this last parameter ($\Gamma_H'$) is predicted rather well by a theoretical model (Eq. (8)). The number of free parameters used is therefore quite conservative.

2. Recommendations for Further Study. The success of the description of pressure and deuteration effects on the microscopic parameters of
the FPCA for KDP encourages one to look for further application of the methods that were employed in this study. As was mentioned in the Introduction, KDP is a member of a large family of crystals which display ferroelectricity or antiferroelectricity. These include \( \text{KH}_2\text{AsO}_4 \), \( \text{RbH}_2\text{PO}_4 \), \( \text{RbH}_2\text{AsO}_4 \), \( \text{CsH}_2\text{PO}_4 \), \( \text{CsH}_2\text{PO}_4 \), \( \text{CsH}_2\text{AsO}_4 \) and their deuterated isomorphs in the ferroelectric category; and \( \text{NH}_4\text{H}_2\text{PO}_4 \) and \( \text{NH}_4\text{H}_2\text{AsO}_4 \) and their deuterated isomorphs of the antiferroelectric type. Although the experimental data on these crystals is somewhat sketchy compared with that for KDP, enough is known that there have been several attempts to determine the FPCA parameters for these crystals. However, neither of these attempts was entirely successful, perhaps because they failed to examine the negative \( \gamma \) half of the parameter space. What we have learned here about how \( \gamma \) changes with the lattice constants and how \( \Gamma \) and the Slater-Takagi energies change with the intersite distance \( \delta \) may be at least in part applicable to these other crystals.

Another topic of further interest is the possibility of using the results of the FPCA analysis to study how the MFA interaction parameters \( \Omega \) and \( J_0 \) depend on pressure and temperature (see Eq. (103) ff). This might be useful in examining the dynamics in the RPA; one could attempt to use the FPCA four-particle-correlation corrections to the mean field about which the RPA dynamics take place without including four-particle dynamical correlations. Recently the study of
dynamical effects has been the principal focus of theoretical and experimental research on KDP and other ferroelectrics (see, e.g., Ref. [1]).

Finally, the experiments of Uesu, et al. on the electrostriction effect under applied field show an anomalous behavior for KDP and DKDP. The electrostriction constant $Q_{31}$ appears to be negative in the high temperature phase under a constant applied $E$ field, but in the low temperature phase it takes on its normal (zero-field) positive value, as calculated in Eqs. (112) and (114). It would appear that the ratio of coefficients $Q_{31}$ in the deuterated case is about $Q_{31}(T_c(E)^+) / Q_{31}(T_c(E)^-) \approx -12$, while the ratio $Q_{31}^L / Q_{31}^0$ for this same crystal is about $-15$. A similar agreement of ratios of these coefficients is found for the undeuterated crystal as well ($-1.1$ and $-1.2$ respectively). This numerical agreement seems rather suggestive.

It is known from X-ray data that the onset of the ferroelectric phase is accompanied by the lengthening of the hydrogen bonds and a rotation of the PO$_4$ tetrahedra in such a way as to tend to keep the lattice constant the same (see Table II). This can be understood from our results on the signs of $q_{13}^B$ and $q_{13}^L$. The lattice contribution $q_{13}^L$ to the electrostriction constant $q_{13}$, being negative, tends to decrease the lattice constant $a_1$, while the bond length contribution $q_{13}^B$, which is positive, tends to increase the lattice constant by increasing the length of the bonds. Of course, if the PO$_4$ groups are
free to rotate both tendencies can be accommodated. As yet, however, we have no explanation for the anomalous effect. Again, there have been several theoretical attempts to explain the anomaly, but neither of them is more than barely qualitative.


29. V. H. Schmidt, unpublished.


45. G. A. Samara, private communication.


50. See, for example, Refs. [5], [6], [48], and [49].


57. G. Busch, Helv. Phys. Acta 11, 269 (1938); see also Ref. [36].


59. More recent measurements in Ref. [58] suggest the values $A'_{0,D} = 1.8\%$/kbar and $P'_{s,D} = -0.8\%$/kbar for crystals with $T_c \approx 220$ K.

60. B. Morosin and G. A. Samara, Ferroelectrics 3, 49 (1971).


We will calculate in this appendix the change in $\gamma$ due to the change in lattice constants in going from the deuterated to the undeuterated crystal, using the relation

$$\overline{\delta}_H = \overline{\delta}_D + \sum_{i=1}^{3} q_i \frac{(a_i^H - a_i^D)}{a_i^D}$$

which follows from Eq. (134). Using the lattice constants found by Nakano et al.\textsuperscript{54} for DKDP and by Kobayashi et al.\textsuperscript{38} for KDP at temperatures just above $T_c$ in either case, one finds the "strains"

$$\frac{(a_i^H - a_i^D)}{a_i^D} = -4.5 \times 10^{-3}$$

Using the values $q_{13}^L = -1.7$ cgs esu (Eq. (28)) and $q_{33}^L = \frac{1}{2}(q_{33}^D, L + q_{33}^L) = 2.4$ cgs esu, one obtains

$$\overline{\delta}_H = \overline{\delta}_D + 3.5 \times 10^{-3} \text{ esu}.$$  

Recalling that $\gamma = (N \mu^2 / V) \gamma$, one finds

$$\gamma_H = d^2 \gamma_D + 0.6 \text{ K}.$$