Tricritical point in KH2PO4
by Charles Robert Bacon

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Physics
Montana State University
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Abstract:
The presence of a tricritical point is shown to exist near 2.4 kbar by measuring the polarization as a function of electric field, temperature, and pressure. By applying a dc field across the KH2PO4 crystal and varying the temperature data points were obtained at preselected polarizations. The behavior of the electric field, polarization, and the temperature are excellently described by the Landau equation of state, \[ E = A_0(T - T_0)P + BP^3 + CP^5. \] In the T-E plane this equation gives straight lines for constant polarization. These lines of constant polarization are called isopols. The coefficients in the Landau equation of state are temperature and/or pressure dependent.

The nature of the B coefficient in particular was an indication of the order of the transition. By assuming a linear pressure dependence of B, and fitting a line to a graph of B vs. p, the pressure, a value for the tricritical pressure, pt, was found to be near 2.4 kbar. The isopol method of analysis also yeilded results that enabled a determination of the \( \delta \) exponent where \( \delta \) is defined by the relationship of the electric field to polarization. The measured values of the \( \delta \) exponent agree within experimental accuracy with the predicted mean-field value of 5 at the tricritical point.
TRICRITICAL POINT IN KH PO

by

CHARLES ROBERT BACON

A thesis submitted in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE
in
Physics

Approved:

V. Hugo Schmidt
Chairperson, Graduate Committee

Head, Major Department

Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana
December, 1977
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The presence of a tricritical point is shown to exist near 2.4 kbar by measuring the polarization as a function of electric field, temperature, and pressure. By applying a dc field across the KH₂PO₄ crystal and varying the temperature data points were obtained at pre-selected polarizations. The behavior of the electric field, polarization, and the temperature are excellently described by the Landau equation of state, \( E = A (T - T_c)P + B P^3 + CP^5 \). In the T-E plane this equation gives straight lines for constant polarization. These lines of constant polarization are called isopols. The coefficients in the Landau equation of state are temperature and/or pressure dependent. The nature of the B coefficient in particular was an indication of the order of the transition. By assuming a linear pressure dependence of B, and fitting a line to a graph of B vs. p, the pressure; a value for the tricritical pressure, \( p_t \), was found to be near 2.4 kbar. The isopol method of analysis also yielded results that enabled a determination of the \( \delta \) exponent where \( \delta \) is defined by the relationship of the electric field to polarization. The measured values of the \( \delta \) exponent agree within experimental accuracy with the predicted mean-field value of 5 at the tricritical point.
Introduction

A tricritical point has been defined as a point where three lines of critical points meet. For ferroelectrics which possess tricritical points, all three parameters of the three-dimensional parameter space of pressure-temperature-electric field, in which the tricritical point lies, are experimentally accessible. This thesis reports on a continuation of studies of critical and tricritical behavior of $KHPO_4$ (hereafter referred to as KDP) by means of static dielectric measurements at high pressure.

Pyroelectric crystals are defined as crystals whose natural primitive cells have a nonvanishing dipole moment in equilibrium. The stablest structure of certain crystals is nonpyroelectric above a certain temperature $T$ (the Curie temperature) and pyroelectric below it. Not all pyroelectric or ferroelectric crystals exhibit phase transitions. There can also be a range of temperatures for the pyroelectric phase, above and below which the crystal is unpolarized. Ferroelectrics are pyroelectric crystals whose polarization can be reversed by applying a strong electric field. In a ferroelectric the distortion of the primitive cell from the unpolarized configuration is small and it is therefore possible to reverse the polarization by applying an electric field. The structure of KDP is presented in the next section.

Potassium dihydrogen phosphate draws interest because the relevant variables are experimentally accessible, and because it is a simple H-
bonded order-disorder ferroelectric. The large amount of literature published on KDP also makes it a good research subject. Many systems possess experimentally inaccessible ordering fields, precluding determination of the behavior in a three-dimensional parameter space in the vicinity of the tricritical point. Consider, for example, an antiferromagnetic cubic crystal. In such a system nearest neighbor cell spins tend to point in opposite directions, and so spin direction becomes ordered and alternates from cell to cell at low temperature. This can be viewed as two interpenetrating sublattices, one with average magnetization \( m \) and the other with \(-m\). The average magnetization, usually referred to as the staggered magnetization, vanishes above the critical temperature \( T_C \) (called the Neél temperature) and so is taken to be the order parameter for the transitions. The dependence of \( m \) upon the temperature \( T \) defines the critical exponent \( \beta \) (see later section) and is a measurable quantity. However, for antiferromagnetic systems the dependence of \( m \) on the staggered magnetic field \( h \) defines the critical exponent \( \delta \), which is unmeasurable because the direction of \( h \) alternates from cell to cell and therefore \( h \) cannot in general be applied externally (in certain antiferromagnets, however, an applied field \( H \) in certain directions also generates a staggered field \( h \)). This also eliminates the \( \gamma \) exponent (determined from the relationship between the zero field susceptibility and the temperature) from being directly measurable.

This thesis reports on the determination of the Landau parameters
(described in a later section) from the measurements of pressure-temperature-electric field in the vicinity of the phase transition. Determination of the $\delta$ exponent is also reported on. Previous work showed the $\gamma$ exponent to equal the mean field value of 1. The determination of these results due to the accessibility of all relevant fields is what makes KDP experimentally valuable.

For KDP we use the phenomenological theory of Landau (described in a later section) as a model of the crystal's behavior. The equation of state in the Landau theory relates the electric field $E$ to the temperature $T$ and the net polarization $P$ of the crystal. The coefficients in this equation of state are pressure-dependent. In this work we determined the relations between temperature, electric field, and net polarization near the ferroelectric transition at pressures of 0, 2, and 2.4 kbar. The data is analyzed by examining the $T$ and $E$ dependence along lines of constant polarization, i.e. isopols.

The origin of the tricritical point is evident from the phase diagram shown in Figure 1. Data points taken along the critical lines (CP) converge on the tricritical point.
FIGURE 1. Phase diagram of the tricritical point of $\text{KH}_2\text{PO}_4$. 
Potassium dihydrogen phosphate is a hydrogen-bonded ferroelectric, that is, it develops a spontaneous electric dipole moment below its transition temperature. As Figure 2 shows, the PO$_4$ groups along with potassium ions make up a structure in which K and P ions alternate in the direction of the crystallographic c axis. Every PO$_4$ group is connected to four other PO$_4$ groups by hydrogen bonds. The hydrogen bonds are perpendicular to the c axis, which is the direction of the polarization.

Above the transition temperature the protons are randomly located in off-center positions in the four hydrogen bonds associated with a PO$_4$ tetrahedron, subject to the "ice rule" that two protons are near each PO$_4$. However, below the transition temperature the two near hydrogens are always found at the top (or at the bottom) of the PO$_4$ tetrahedron. The dipole moment is produced by the movement of the K and P ions along the c axis induced by the ordering of the hydrogen bonds.
FIGURE 2. Structure of $\text{KH}_2\text{PO}_4^2$. 
Samples and Apparatus

The KDP sample used was obtained from Cleveland Crystals, Inc. The crystal dimensions were 1 x 1 x 0.2 cm with the large faces covered with chrome-gold-plated electrodes by the supplier. The crystal was allowed to hang freely in the pressure vessel. The crystal was connected to a coaxial three-conductor cable by two tiny wires connected to the chrome-gold-plated faces of the crystal.

The experimental apparatus is excellently described in the thesis of A. Western and will only briefly be described here. The cryostat assembly consists of three separate cans, the innermost being the pressure vessel, surrounded by two other cans. The outermost can is vacuum tight and connected directly to the vacuum system. The electrical leads are fed to the pressure vessel through high pressure tubing. This entire assembly is immersed in a liquid nitrogen bath that is filled automatically from an external source. The can surrounding the pressure vessel is temperature regulated to approximately 0.1 °K, and kept about one degree below the pressure vessel temperature. The pressure vessel temperature is regulated by a temperature-sensitive capacitor which controls a heater wound around the top of the pressure vessel. This capacitor's temperature was kept constant to within ±2 mK. A second capacitor is placed at the bottom of the pressure vessel where the temperature is presumed to approximately that of the crystal.

A diagram of the pressure generating system is shown in Figure 3.
FIGURE 3. Pressure system.
A liquid-gas system was used to produce pressures up to 45,000 psi. Pressurizing by means of the remote head produced pressures of nearly 20,000 psi, and then switching to the gas intensifier enabled us to reach pressures necessary to determine the tricritical point of KDP.

The setup used in collecting data at constant polarization is shown in Figure 4. An electric field was supplied to the crystal by means of a battery and voltage divider, and the polarization charge was then stored on an 8 μF polystyrene capacitor. The voltage on this capacitor was measured by a vibrating reed electrometer, and the recorder output was kept constant during measurements at constant polarization while changing the electric field and temperature.
FIGURE 4. DC polarization measurement circuit.
The Landau Theory of Phase Transitions

In this Section the phenomenological theory of Landau will be discussed. Referring to Figure 5 as a crude model of the experimental setup being dealt with, we can write the first law of Thermodynamics in differential form,

\( \text{(1)} \quad dU = dQ - dW \)

or, in terms of quantities which are represented in the Figure,

\( \text{(2)} \quad dU = TdS + EdP . \)

The Legendre transform of this expression yields the Helmholtz free energy, \( F \),

\( \text{(3)} \quad F = U - TS . \)

The differential form of the Helmholtz free energy can be written as

\( \text{(4)} \quad dF = EdP - SdT \)

so we see that the free energy is a function of temperature and polarization, \( F(T,P) \). By definition the ordering field is the first partial derivative of the free energy, \( E = \partial F/\partial P \), and the response function is the second partial derivative of the free energy, \( \chi = \partial^2 F/\partial P^2 \). The behavior of the inverse susceptibility, \( \chi \), determines whether the transition is first or second order, as shown in Figures 6 and 7, respectively. For dielectrics the susceptibility must be greater than or equal to zero, and so when \( \chi = 0 \) the following conditions must be fulfilled:

\( \text{(5)} \quad \frac{3}{4} \frac{\partial^3 F}{\partial P^3} = 0 , \)

\( \text{(6)} \quad \frac{3}{4} \frac{\partial^4 F}{\partial P^4} \geq 0 . \)
FIGURE 5. Experimental setup.
FIGURE 6. First order transition.

FIGURE 7. Second order transition.
The foundation of the Landau theory of phase transitions is the assumption that the free energy, \( F(T, P) \), can be expanded in an infinite series, such that

\[
F(T, P) = \sum_{n=0}^{\infty} A_n(T)P^n.
\]

Due to the symmetry of KDP the free energy is an even function of polarization, \( F(T, P) = F(T, -P) \), so \( A_n = 0 \) for \( n \) odd. The Landau expansion for the free energy thus takes the form

\[
F(T, P) = A(T)P^2/2 + B(T)P^4/4 + C(T)P^6/6 + \ldots.
\]

and the ordering field is given by,

\[
E = AP + BP^3 + CP^5 + \ldots.
\]

In order to predict Curie-Weiss behavior in the paraelectric region it is necessary that \( A = A_0(T - T^\circ) \), where \( T^\circ \) is the Curie-Weiss temperature. The Landau equation of state becomes

\[
E = A_0(T - T^\circ)P + BP^3 + CP^5,
\]

where \( B \) and \( C \) may be functions of temperature and/or pressure. The sign of \( B \) is an indication of the order of the transition. A negative \( B \) indicates a first order transition, whereas a positive \( B \) indicates a second order transition. A zero value of \( B \) occurs at the tricritical pressure.

A graph of the equation of state in the \( T-E \) plane for constant polarization yields straight-line plots called isopol, as shown in Figure 8.
Isopols

As was shown earlier the Landau equation of state enables us to graph straight-line plots in the T−E plane. These straight lines at constant polarization are referred to as isopols. An isopol plot is shown in Figure 8 as predicted by the Landau equation of state. For small P the terms in P³ and P⁵ become negligibly small so that for E = 0 the T intercept tends to Tₒ.

The sign of B affects the nature of the isopol plots. For negative B and increasing P the isopol intercepts rise above Tₒ, while increasing P further drives the E = 0 intercepts below Tₒ due to the onset of domination by the CP⁵ term in the equation of state. For positive B the E = 0 intercepts simply fall with increasing P.

The order of the transition is determined by the sign of B. A negative B indicates a first order transition, and a positive B indicates a second order transition. The tricritical point occurs at B = 0.
FIGURE 8. Isopols predicted by the Landau equation of state.
Data Analysis

The experimental results subjected to analysis were the measured values of the temperature $T$, the electric field $E$, the polarization $P$, and the pressure $p$.

A standard least squares analysis was done on the isopols to determine the slope, intercept, and mean values of $T$ and $E$. The standard deviations of these quantities were also found.

Two methods were used to determine the Landau parameters and the Curie-Weiss temperature. In both methods $A_0$ is found as the weighted average of the $A_{0i}$ for the various isopols. To each isopol there is an associated $A_{0i}$. From the Landau equation of state

$$E = A_0(T - T_0)P + BP^3 + CP^5$$

we get

$$\frac{dT}{dE} = \frac{1}{A_{0i}}P.$$  

Using the chain rule we can write

$$\frac{dT}{dE} = \left(\frac{dT}{dB'}\right)\left(\frac{dB'}{dE'}\right)\left(\frac{dE'}{dE}\right)$$

where $B'$ is the capacitor sensor reading of the temperature. This reading was defined to be in "B units" and could be converted into degrees Kelvin from an experimentally determined linear relationship between the two. Figure 9 shows this linearity between the capacitor sensor reading and the actual temperature in degrees Kelvin. The slope of this line is $\frac{dT}{dE'} = -4.25 \text{ K/B unit}$ in this temperature range.

The voltage applied across the 0.2 cm crystal is $E'$ in Equation (13). To put this quantity in electrostatic units (esu), as the polar-
FIGURE 9. Temperature/capacitor sensor linearity.
ization is, we use 1 esu volt = 300 volts, and so

\[ \frac{\partial E'}{\partial E} = \left( \frac{1 \text{ volt}}{(1 \text{ esu/300})/(0.2 \text{ cm})} \right). \]

The final quantity in Equation (13) is \( \frac{\partial B'}{\partial E'} \). The parameters \( B' \) and \( E' \) are precisely the measured values that are plotted to graph the isopols. For each constant polarization \( P_i \), the slope of the \( i \)th isopol is \( \frac{\partial B'}{\partial E'} \). Combining these results we rewrite Equation (13) as

\[ A_{o1} = (P_i)^{-1}(\partial E/\partial E)^{-1} \]
\[ = (P_i)^{-1} ("B unit"/\approx 2.5 \text{ oK}) \times \]
\[ (\text{esu/(60 V/cm)}) (\frac{\partial B'/\partial E'}{\partial E'})^{-1}. \]

The error is

\[ \Delta A_{o1} = -(\Delta B'/E')A_o/(\partial B'/\partial E') \]
\[ = (\Delta B'/E')/255(\partial B'/\partial E')^2 P_i \]

where \( \Delta B'/E' \) is the error in the slope of the \( i \)th isopol. These results are averaged to give \( A_o \) and \( \Delta A_o \).

The first method used to obtain the Landau parameters is one described in detail in a doctoral thesis by A. Western. Briefly, his method involves finding the Curie-Weiss temperature by plotting \( T(E \approx 0) \) vs. \( P^2 \) for low polarization. A straight-line fit to this graph yields an intercept which is identified as \( T_o \). The remaining Landau parameters \( B \) and \( C \) are obtained by doing a straight-line analysis of a graph of 
\[ -A_o(T(E = 0) - T_o)/P^2 \] vs. \( P^2 \). The intercept at \( P^2 = 0 \) is \( B \), and the slope is equal to \( C \). Results from this method were used as a check on the second method, yet to be described.
The first method has certain drawbacks. While the procedure for finding $A_0$ is very accurate, it is not known beforehand whether the $T_0$ determination is also as accurate. The size of the contribution of the $CP^5$ term is uncertain so the discarding of the higher $P$ isopols could be crucial. This leads to another drawback in the determination of the $B$ parameter. The value of $B$ is strongly sensitive to the value of $T_0$ used, as Figure 10 exhibits. In this Figure a small variation of $T_0$ induces a large change in $B$. The $C$ parameter, given by the slope of the line, is less sensitive to the value of $T_0$. The second method, described below, was developed to eliminate these problems.

In this approach we solve for $A_0$ in the same manner, and then solve for $T_0$, $B$, and $C$ simultaneously. We use as input the average temperatures of the isopols, $\bar{T}_1$, instead of the $T(E=0)$ values which have larger standard deviations. Writing the Landau equation of state in the following form,

\begin{equation}
\bar{T}_1 = T_0 + \langle \overline{E_1/A_0 P_1} \rangle - \langle P_1^2/B/A_0 \rangle - \langle P_1^2 C/A_0 \rangle,
\end{equation}

the best fit values of the parameters $T_0$, $B$, and $C$ maximize the probability

\begin{equation}
W(T_0, B, C) = c \exp \left(-\frac{1}{2}(\bar{T}_1 - T_0 - \overline{E_1/A_0 P_1}) - \frac{E_1^2}{2B_1 A_0} + \right.
\left. \frac{P_1^2}{2B_1 A_0} + \right.
\left. \frac{G P_1^4}{4A_0} \right)^2/2(\Delta T_1)^2
\end{equation}

that the parameters have their true values. Then $T_0$, $B$, and $C$ are found by setting the partial derivatives of $W(T_0, B, C)$ with respect to $T_0$, $B$, and $C$ equal to zero. This gives three equations in three unknowns,
FIGURE 10. $T_0$ variation.

$A_0(T - T_0)/P^2$, $10^{-10}$ esu

$T_0 - .02$ °K

$T_0 - .01$ °K

$T_0 + .005$ °K

$T_0 + .01$ °K

$T_0 + .015$ °K

$T_0 + .02$ °K

$p^2$, $10^7$ esu
(19) \[ \sum (\frac{T_i - T_o - \beta_i/\alpha_i p_i + P_i^2 B/\alpha_i + P_i^4 C/\alpha_i}{(\Delta T_i)^2}) = 0 \]
(20) \[ \sum (\frac{T_i - T_o - \beta_i/\alpha_i p_i + P_i^2 B/\alpha_i + P_i^4 C/\alpha_i}{(\Delta T_i)^2}) = 0 \]
(21) \[ \sum (T_i - T_o + \beta_i/\alpha_i p_i + P_i^2 B/\alpha_i + P_i^4 C/\alpha_i)^2 = 0 \]
which are solves simultaneously for the best fit values of T_o, B, and C.

The analysis of the experimental data yields the results listed in Table I. These results when compared with the results obtained by Western et al. show the characteristic change of sign of the B parameter indicating a second order phase transition at higher pressure.

A graph of the B parameter vs. the pressure, p, is shown in Figure 11. A least squares fit to the data indicates values of the tricritical pressure. These values are listed in Table II, (a), (b), and (c). The variation of the tricritical pressure is from 2.16 kbar to 2.44 kbar with a weighted average of 2.35 kbar. The results are based on the assumption that the pressure dependence of B is linear.
FIGURE 11. Tricritical pressure prediction for linear B vs p relationship.
**TABLE I. Tabulated Values of the Landau Parameters**

<table>
<thead>
<tr>
<th>( p^*, \text{kbar} )</th>
<th>( T^*_{\text{O}_K} )</th>
<th>( A_0 \cdot 10^{-3} ) esu</th>
<th>( B, 10^{-11} ) esu</th>
<th>( C, 10^{-19} ) esu</th>
<th>( T_{\text{cr}} - T^*_{\text{O}_K} )</th>
<th>( E_{\text{cr}}, \text{V/cm} )</th>
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<tr>
<td>0.00</td>
<td>122.12 ± 0.01</td>
<td>4.273 ± 0.029</td>
<td>-1.83 ± 0.03</td>
<td>5.66 ± 0.13</td>
<td>0.062</td>
<td>132.8</td>
</tr>
<tr>
<td>2.00</td>
<td>113.12 ± 0.01</td>
<td>3.751 ± 0.041</td>
<td>-0.22 ± 0.17</td>
<td>4.24 ± 0.06</td>
<td>0.001</td>
<td>2.8</td>
</tr>
<tr>
<td>2.40</td>
<td>111.22 ± 0.01</td>
<td>3.975 ± 0.023</td>
<td>-0.00 ± 0.08</td>
<td>4.08 ± 0.33</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>111.23 ± 0.01</td>
<td>3.804 ± 0.039</td>
<td>0.22 ± 0.35</td>
<td>4.83 ± 1.90</td>
<td>NA</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>111.21 ± 0.01</td>
<td>3.255 ± 0.077</td>
<td>0.12 ± 0.23</td>
<td>3.65 ± 0.62</td>
<td>NA</td>
<td>NA</td>
<td></td>
</tr>
</tbody>
</table>

*Stable to within ± 0.0005 kbar.*

# Absolute calibration not tied to National Bureau of Standards

NA—Not applicable, transition is second-order.
TABLE II. Predicted Values of the Tricritical Pressure

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Tricritical Pressure</th>
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<tr>
<td>1</td>
<td>2.24</td>
</tr>
<tr>
<td>2</td>
<td>2.16</td>
</tr>
<tr>
<td>3</td>
<td>2.44</td>
</tr>
</tbody>
</table>
Critical and Tricritical Exponents

The Landau expansion of the free energy is a mean field treatment of the crystal behavior in the paraelectric region. Mean field theory is accurate for ferroelectrics because of the long-range nature of the electric dipole interaction.

To find the critical exponents one makes a Taylor series expansion of the free energy, \( F \), about the critical polarization \( P_{cr} \),

\[
F(T, P) = F_{cr} + (A - A_{cr})P_{cr} \left( P - P_{cr} \right) + B P_{cr} \left( P - P_{cr} \right) + CP_{cr} \left( P - P_{cr} \right)^2 + DP_{cr} \left( P - P_{cr} \right)^3 + \ldots
\]

\[
F(T, P) = F_{cr} + \left( A - A_{cr} \right) \left( P - P_{cr} \right) + \left( A - A_{cr} \right) \left( P - P_{cr} \right) + \ldots
\]

The \( \gamma \) exponent is defined by

\[
\left( \frac{F(T) - F_{cr}}{F(T_{cr}) - F_{cr}} \right)^\gamma = \left( \frac{T - T_{cr}}{T_{cr}} \right)^\gamma.
\]

The mean field value of \( \gamma = 1 \) is obtained from Equation (23).

The exponent of prime interest in this work was the tricritical exponent \( \delta \). The \( \delta \) exponent is defined by

\[
(E - E_{cr}) = (P - P_{cr})^\delta.
\]

At the tricritical point and for pressures greater than the tricritical pressure \( P_{t} \), \( E_{cr} = P_{cr} = 0 \) so Equation (25) becomes

\[
E = P^\delta.
\]

Since \( E = \partial F/\partial P \), Equation (23) gives

\[
E = (B + 5CP_{cr}/2)(P - P_{cr})^3 + 5CP_{cr}(P - P_{cr})^4 + C(P - P_{cr})^5.
\]
so that

\[ E - E_{cr} = (B + 5CP_{cr}/2)(P - P_{cr})^3 + \ldots \]

At the tricritical point, \( B = 0 \), giving

\[ E = CP^5 \]

so the mean field tricritical exponent \( \delta = 5 \). From the data analysis (see Appendix A), values for the \( \delta \) exponent are determined from the high polarization data. Table III shows the values predicted from the data for the three separate runs done with the sample. Within experimental accuracy a value of \( \delta = 5 \) is indicated by each data run.

The exponent \( \beta \) is defined by

\[ (P - P_{cr}) = (T - T_{cr})^\beta \]

The Landau equation of state can be written so that

\[ (T - T_{cr}) = B(P - P_{cr})^2 + C(P - P_{cr})^4 \]

This gives \( \beta = 1/2 \) for the critical lines and \( \beta = 1/4 \) at the tricritical point. Recent results by a group in France working with \( \gamma \)-ray diffraction to study the lattice parameter (which is related to the spontaneous polarization) below \( T_c \) showed the tricritical exponent \( \beta = 1/4 \) at 2 kbar and the critical exponent \( \beta = 1/2 \) at 3.5 kbar. They concluded that the tricritical pressure \( p_t = 2 \) kbar, in general agreement with our results.
TABLE III. Measured Values of the $\delta$
Exponent and Errors

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<th>Pressure, kbar</th>
<th>$\delta$</th>
<th>$\Delta \delta$</th>
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Summary

Using the method of "isopols" to analyze the static dielectric data obtained for KH₂PO₄ at 0, 2, and 2.4 kbar we find values for the tricritical pressure, pₜ, and the δ exponent. The method of "isopols" was developed from consideration of the Landau free energy expansion. Analysis of the data along these isopols yielded values of the Landau parameters. Assuming a dominant linear relationship between the pressure, p, and the Landau B coefficient we calculate a tricritical pressure near 2.4 kbar.

By expanding the free energy in a Taylor series expansion about the critical polarization, Pₜ, we arrive at an expression which defines the δ exponent. The Landau theory is a mean-field treatment and predicts a value of 5 for the δ exponent. It has been shown that at 2.4 kbar we have calculated a δ exponent which is consistent with the predicted mean-field value.
Conclusions and Recommendations for Further Study

Our results have shown us that the data analysis based on the Landau theory of phase transitions does indeed give the anticipated values for the Landau coefficients and the critical exponents. This study and previous work\(^1\) confirms that the transition at 2 kbar is first order and that it is second order at 3 kbar. Based on these results data was obtained at 2.4 kbar. At this pressure we found that we were very near the tricritical pressure which was calculated to be 2.4 ± 0.2 kbar. The calculation of the \(\delta\) exponent served as another confirmation that we were near the tricritical pressure. In going from first to second order the exponent is expected to change from a value of 3 to 5 respectively, which is experimentally seen in the data. We conclude that the tricritical point does exist for \(\text{KH}_2\text{PO}_4\), and that the tricritical pressure, \(p_t\), is 2.4 ± 0.2 kbar.

A further significance of this study was the measurement of the \(\delta\) exponent. This exponent had never been determined experimentally in any ferroelectric previously.

Our predictions of the tricritical pressure were based on assumptions about the pressure dependence of the \(B\) coefficient. Further study at higher pressures would be useful in order to verify these assumptions.

Since our measurement of the \(\delta\) exponent was the first of its kind
determination of the exponent in other substances would be very interesting. One such substance is SbSI, but because of the way the crystal grows, i.e. needle-like, it has so far been too hard to experimentally handle. When these problems are overcome an experiment similar to the one reported on in this thesis would yield valuable results that could answer questions as to the validity of the use of the Landau theory in a region very close to the transition.
APPENDIX

One method used to analyze the KDP isopol data is presented here in detail. While the presentation will be in terms of the Landau theory parameters, the results should have general applicability.

We will consider the following three problems:

A. Find $A_0$ in the Landau equation of state.
B. Solve for $T_0$, $B$, and $C$ simultaneously.
C. Determine the exponent $\delta$ in $E = P^\delta$.

In order to deal with A. we will review the problem of obtaining the best fit straight line to a collection of data points. Referring to Figure A-1 we assume that $X_i$ is known exactly, and $y_i$ has a standard deviation $\Delta y_i$. The probability that a given $y$ is the true value $y_i$ is given by

\[
W(y) = (\Delta y_i / 2\pi)^{-1} \exp\left(-\frac{(y - y_i)^2}{2(\Delta y_i)^2}\right),
\]

which is properly normalized. For an arbitrary straight line $y = ax + b$ the probability that it represents the true data points is the joint probability,

\[
W(a, b) = c \exp\left(-\frac{(ax_i + b - y_i)^2}{2(\Delta y_i)^2}\right),
\]

where $\sigma_i = \Delta y_i$.

The two conditions that maximize $W(a, b)$ are

\[
\Sigma_i ((ax_i + b - y_i)x_i/\sigma_i) = 0, \quad \Sigma_i ((ax_i + b - y_i)^2)/\sigma_i = 0,
\]

where $\bar{a}$ and $\bar{b}$ represent the best fit values. Solving for these we find,

\[
\bar{a} = \frac{(\Sigma_i x_i y_i/\sigma_i^2)\Sigma(1/\sigma_i^2) - \Sigma_i (x_i/\sigma_i^2)(y_i/\sigma_i^2)\Sigma(1/\sigma_i^2)}{(\Sigma_i x_i/\sigma_i^2)(\Sigma(1/\sigma_i^2)) - (\Sigma_i y_i/\sigma_i^2)(\Sigma(1/\sigma_i^2)) - \Sigma_i (x_i/\sigma_i^2)(y_i/\sigma_i^2)}.
\]
FIGURE 12. Coordinate transformation.
(A-5) cont.
\[(\Sigma(x_i^2/\sigma_i^2))^2)\),

(A-6) \[\overline{b} = (\Sigma(y_i^2/\sigma_i^2) \Sigma(x_i^2/\sigma_i^2) - \Sigma(x_i^2/\sigma_i^2) \Sigma(x_i y_i/\sigma_i^2))/(\Sigma(x_i^2/\sigma_i^2) \Sigma(1/\sigma_i^2) - (\Sigma(x_i/\sigma_i^2))^2)\].

If we make a linear transformation to new variables (see Figure A-1),

(A-7) \[u = x - \overline{x}, \quad v = y - \overline{b}\]

where

(A-8) \[\overline{x} = \Sigma(x_i^2/\sigma_i^2)/\Sigma(1/\sigma_i^2)\]

so that

(A-9) \[\Sigma(u_i^2/\sigma_i^2) = 0\]

In terms of these new variables we have,

(A-10) \[\overline{b}(u_1, v_1) = 0\]

and

(A-11) \[\overline{a}(u_1, v_1) = \Sigma(u_i v_i/\sigma_i^2)/\Sigma(u_i^2/\sigma_i^2)\].

To find the standard deviations in \(\overline{a}\) and \(\overline{b}\), define \(\alpha = a - \overline{a}\) and \(\beta = b - \overline{b}\), and use the \(u, v\) variables so that \(\overline{b} = 0\). The joint probability becomes,

(A-12) \[W(\alpha, \beta) = C \exp(-\Sigma(\overline{au}_i - v_i + au_i + \beta)^2/2\sigma_i^2)\]

\[= C \exp(-\Sigma(\overline{au}_i - v_i)^2/2\sigma_i^2) \exp(-\Sigma\beta^2/2\sigma_i^2) \times \exp(-\Sigma(\alpha^2 u_i^2/2\sigma_i^2))\]

where terms in \(\alpha, \beta,\) and \(\alpha\beta\) vanish as a result of Equation (A-3). The standard deviations are

(A-13) \[\Delta a = 1/\Sigma(u_i^2/\sigma_i^2)^2\]
As an example we apply these results to the individual isopols. Assume $\sigma_i = \sigma$, the same for all data points. For $n$ data points,

\begin{align*}
\bar{x} &= \frac{1}{n} \sum_{j=1}^{n} x_j, \quad \bar{y} = \frac{1}{n} \sum_{j=1}^{n} y_j ,
\end{align*}

or

\begin{align*}
\bar{E} &= \frac{1}{n} \sum_{j=1}^{n} E_j , \quad \bar{T} = \frac{1}{n} \sum_{j=1}^{n} T_j ,
\end{align*}

\begin{align*}
\bar{a} &= \sum_{j=1}^{n} \frac{(E_j - \bar{E})(T_j - \bar{T})}{\Sigma (E_j - \bar{E})^2} ,
\end{align*}

\begin{align*}
\Delta a &= \sigma / \sqrt{\Sigma (E_j - \bar{E})^2} , \quad \Delta b = \sigma / \sqrt{n}
\end{align*}

where,

\begin{align*}
\sigma &= \left( \frac{1}{n} \sum_{j=1}^{n} (T_j - \bar{T} - \bar{a}(E_j - \bar{E}))^2/(n-2) \right)^{1/2}.
\end{align*}

In order to find $A_0$ in step A, we find from the equation,

\begin{align*}
T &= \frac{E}{A_{oi} P_1} + \frac{P_0 - BP_1^2}{A_{oi}^2 - CP_i^2} ,
\end{align*}

that

\begin{align*}
\frac{\partial T}{\partial E} &= \frac{1}{A_{oi} P_1} .
\end{align*}

Here $A_{oi}$ is obtained from Equation (A-17) with $\bar{a}_i = 1/A_{oi} P_1$. The standard deviation is,

\begin{align*}
\Delta A_{oi} &= 1/255(\Delta a_{i1}/a_{i1} (1/P_i a_{i1}))
\end{align*}

where $\Delta a_{i1}$ is obtained from Equation (A-18). From this we find the weighted average for $A_0$ and its standard deviation as

\begin{align*}
A_0 &= \Sigma (A_{oi})^2 / \Sigma (1/(\Delta A_{oi})^2)
\end{align*}

and

\begin{align*}
\Delta A_0 &= (1/\Sigma_i / (\Delta A_{oi})^2)^{1/2} ,
\end{align*}
respectively.

Having determined $A_0$, we now want to find $T_0$, $B$, and $C$ simultaneously. We rearrange the Landau equation of state such that

$$T_1 = T_0 + \frac{E_1}{A_0} P_1 - \frac{P_1^2 B/A_0 - P_1^4 C/A_0}{2}.$$  

The best fit values of $T_0$, $B$, and $C$ maximize the probability

$$W(T_0, B, C) = c \exp\left(-\sum_i \left(\frac{T_i - T_0 - \frac{E_i}{A_0} P_i + P_i^2 B/A_0 + P_i^4 C/A_0}{2}\right)^2 \times \frac{1}{2(A_i^2)} \right),$$

that the parameters have their true values. Having previously determined $A_0$, we define

$$\alpha_i = \frac{E_i}{A_0} P_i, \quad \beta_i = \frac{P_i^2}{A_0}, \quad \gamma_i = \frac{P_i^4}{A_0}, \quad \sigma_i = \Delta T_i$$

in order to simplify the notation. Setting the partial derivatives of $W$ with respect to $T_0$, $B$, and $C$ equal to zero, we obtain three equations

$$\begin{align*}
\sum_i \left(\frac{T_i - T_0 - \alpha_i + \beta_i B + \gamma_i C}{\sigma_i^2}\right) &= 0, \\
\sum_i \left(\frac{T_i - T_0 - \alpha_i + \beta_i B + \gamma_i C}{\sigma_i^2}\right) &= 0, \\
\sum_i \left(\frac{T_i - T_0 - \alpha_i + \beta_i B + \gamma_i C}{\sigma_i^2}\right) &= 0,
\end{align*}$$

which enables us to solve for the best fit values of $T_0$, $B$, and $C$.

In order to determine the form of the standard deviations we return to the general problem of the three parameter probability $W(x, y, z)$, such that,

$$W(x, y, z) = c \exp\left(-\sum_i \left(-a_i + b_i x + c_i y + d_i z^2\right)^2\right).$$

As an example we will find the standard deviation of $x$. In order to find $\sigma_x$, we must integrate out the contributions that $y$ and $z$ make in the probability. This will leave us with the single function probability
\( W(x) \) from which we can find the standard deviation by inspection. The mathematical derivation begins with

\[
W(x) = \int W(x, y) dy = \int W(x, y, z) dz dy
\]

Putting the form of \( W(x, y, z) \) gives,

\[
W(x) = \int c \exp\left(-\sum_{i} -a_i + b_i x + c_i y + d_i z\right)^2 dz dy
\]

Carrying out the integration over \( z \) leaves,

\[
W(x) = c' \int \exp\left(-\sum_{i} -a_i + b_i x + c_i y\right)^2 \left(\sum_{i} a_i - b_i x - c_i y\right) dy
\]

Since we are interested only in terms in \( x \) and \( x^2 \) the integration over \( y \) is carried out and all irrelevant factors are placed in the constant coefficient. The probability \( W(x) \) becomes,

\[
W(x) = c'' \exp\left(-\sum_{i} b_i^2 + \left(\sum_{i} c_i d_i\right)^2/\sum_{i} d_i^2 + \left(\sum_{i} \frac{c_i^2}{d_i} + \sum_{i} \frac{c_i^2}{d_i} + \sum_{i} \frac{c_i^2}{d_i} + \sum_{i} \frac{c_i^2}{d_i} \right)\right) x
\]

which gives for the standard deviation in the \( x \) direction

\[
\sigma_x = \frac{1}{2} \left(\sum_{i} \frac{c_i^2}{d_i} - \left(\sum_{i} c_i d_i\right)^2/\sum_{i} d_i^2 + \left(\sum_{i} \frac{c_i^2}{d_i} + \sum_{i} \frac{c_i^2}{d_i} + \sum_{i} \frac{c_i^2}{d_i} + \sum_{i} \frac{c_i^2}{d_i} \right)\right) x
\]

In terms of the parameters of the Landau equation of state the probability can be written as,

\[
W(T_0, B, C) = c \exp\left(-\sum_{i} \frac{\tilde{T}_i - \tilde{E}_i}{A_i P_i} + T_0 - P_1 B/A_0 - P_1 C/A_0\right)^2 x \left(\sum_{i} \frac{1}{\lambda(T_0)^2}\right)
\]
therefore we can make the identifications,

\[(A-38) \quad a_i = \left( T_i - \bar{E}_i / A_{o i} \right) / (2(\Delta T_i)^2)^{1/2} \]

\[(A-39) \quad b_i = 1/(2(\Delta T_i)^2)^{1/2} \]

\[(A-40) \quad c_i = \frac{p_i}{A_o} (2(\Delta T_i)^2)^{1/2} \]

\[(A-41) \quad d_i = \frac{-p_i^2}{A_o} (2(\Delta T_i)^2)^{1/2} \]

with \( x = T_o, y = B, \) and \( z = C. \) From \( (A-36) \) we can find \( \sigma_T, \sigma_B, \) and \( \sigma_C. \)

To get the standard deviation of \( B \) from \( (A-36) \) replace \( b \) with \( c, \) and \( c \) with \( b \) leaving \( d \) unchanged. To obtain the standard deviation of \( C \) from 
\( (A-36) \) replace \( b \) with \( d, \) \( d \) with \( c, \) and \( c \) with \( b. \)

The final application of these results is in determining the \( \delta \) exponent. Let \( x_i = \log P_i, y_i = \log E_i, \) and define

\[(A-42) \quad i = \log (E_{o i} + E_{o i}) / (E_{o i} - E_{o i}) \]

We find \( \bar{E}_{o i} \) from the equation

\[(A-43) \quad T_i - \bar{T}_i = \bar{a}_i (E_i - \bar{E}_i) \]

for the \( i \)th isopol in terms of \( (u, v) \)-variables, and evaluate it at 
\( T_i = T_o; \) the best fit \( T_o \) from all the isopol data. Equation \( (A-43) \) be-
comes

\[(A-44) \quad \bar{E}_{o i} = \bar{E}_i + (T_o - \bar{T}_i) / \bar{a}_i \]

Since \( \bar{E}_i \) and \( \bar{a}_i \) are independent parameters

\[(A-45) \quad \Delta E_{o i} = \left( (\Delta \bar{E}_i)^2 + (T_o - \bar{T}_i) \bar{a}_i / a_i \right)^{1/2} \]

where \( \Delta \bar{E}_i \) is \( \Delta b \) in Equation \( (A-14) \) and \( \Delta a_i \) is \( \Delta a \) in Equation \( (A-13). \)

Using these results we find the weighted mean values

\[(A-46) \quad \log \bar{E}_o = \bar{\log} \bar{E}_{o i} / \sigma_{o i}^2 \]

\[\left[ \sum_i \sigma_{o i}^2 \right] \]
(A-46) cont. \[ \log \bar{P} = \frac{\sum \log P_i / \sigma_i^2}{\sum (1/\sigma_i^2)} . \]

From this we find the best fit exponent,

\[ \delta = \frac{\sum (\log(P_i/\bar{P}) \log(E_{0i}/E_0)/\sigma_i^2)}{(\sum (\log(P_i/\bar{P})/\sigma_i)^2)} . \]

The standard deviation is

\[ \Delta \delta = \left( \frac{\sum (\log(P_i/\bar{P})A_{0i} P_i) \Delta T_0}{\sum (\log(P_i/\bar{P})/\sigma_i)^2} \right) + \frac{1}{\sum (\log(P_i/\bar{P})/\sigma_i)^2} . \]
REFERENCES


3. Cleveland Crystals, Inc., Box 3157, Cleveland, Ohio 44117.


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