# 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


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 = A0(T - T0)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 δ exponent where δ is defined by the relationship of the electric field to polarization. The measured values of the δ exponent agree within experimental accuracy with the predicted mean-field value of 5 at the tricritical point.

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Approved:

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Signature Charles R. Bacon

Date January 20, 1978

TO RACHEL

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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 $KH_2PO_4$ 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, $E = A_o(T - T_o)P + BP^3 + CP^5$. 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, $p_t$, 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.

## 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 $KH_2PO_4$ (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 $T_c$ (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 Hbonded 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 β (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 δ, 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 γ 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[1] 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.

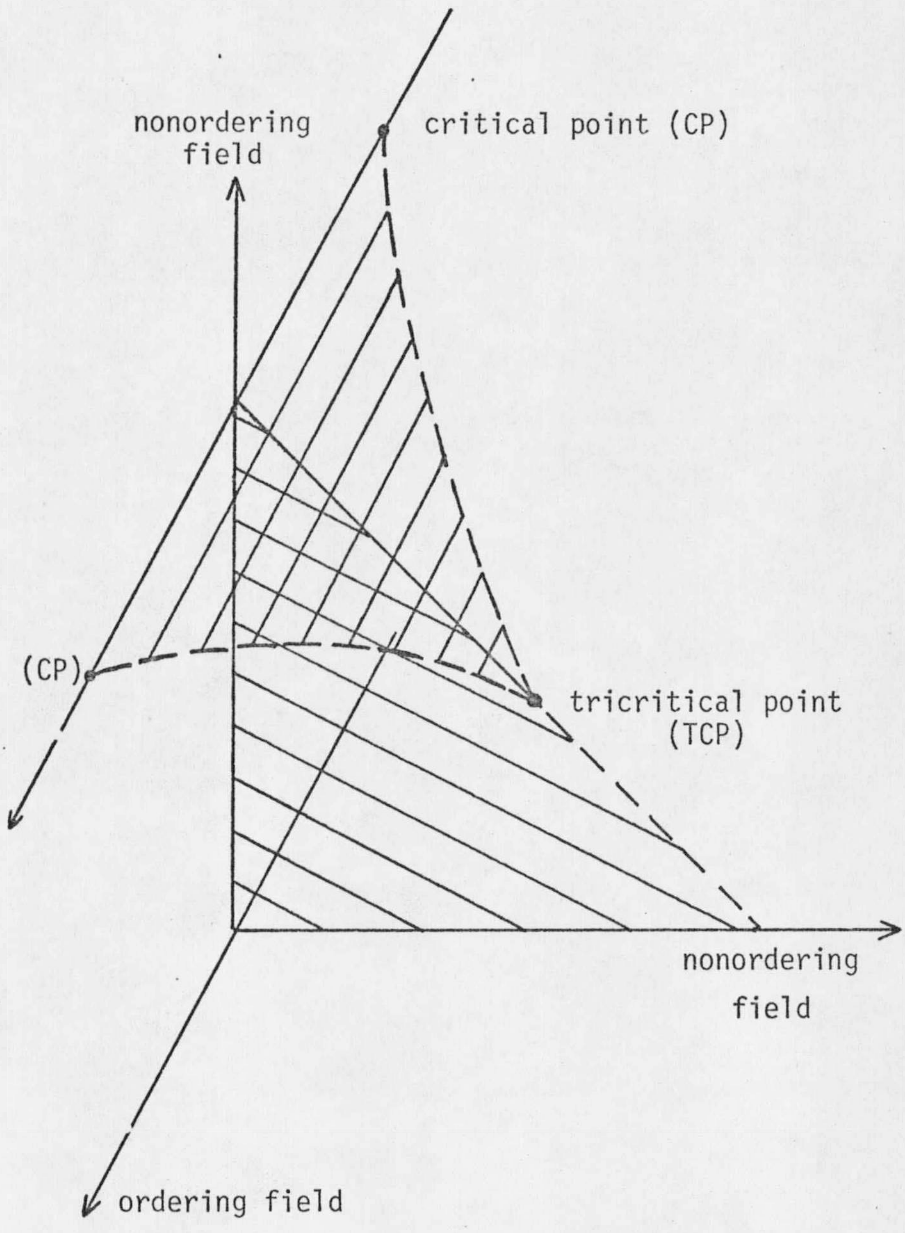


FIGURE 1. Phase diagram of the tricritical point of $KH_2PO_4$.

## Description of $KH_2PO_4$

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.

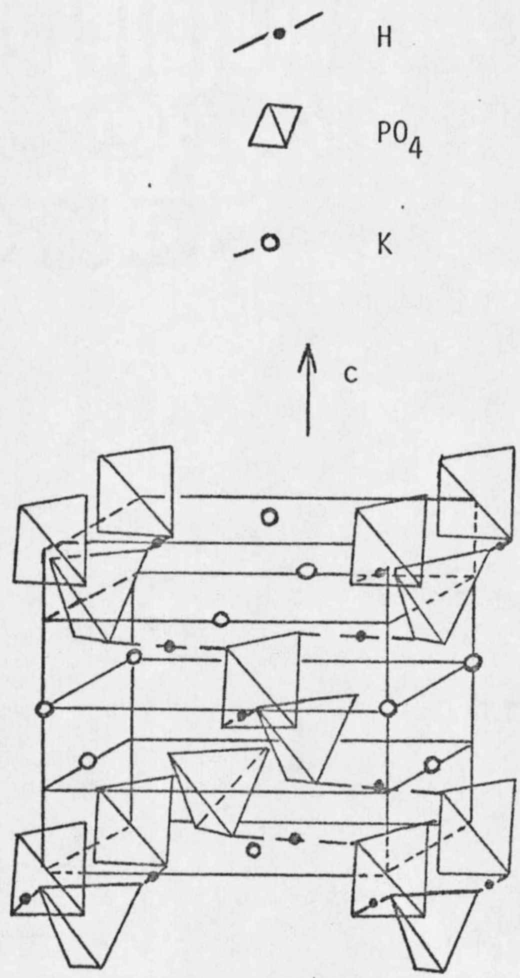


FIGURE 2. Structure of $KH_2PO_4$.[2]

## 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[1] 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 $^{o}$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 $\pm$ 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.