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# SEARCH FOR TRICRITICAL POINT IN $\text{KH}_2\text{PO}_4$ AT HIGH PRESSURE. I. STATIC DIELECTRIC BEHAVIOR NEAR CRITICAL POINT AT ZERO PRESSURE†

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The proposed tricritical point in KDP occurs if the critical field,  $E_{\text{cr}}$ , can be brought to zero by applying pressure. The Landau equation of state  $E = A_0(T - T_0)P + BP^3 + CP^5$  gives straight-line "isopols" in the  $T$ - $E$  plane. We obtain values for  $A_0$ ,  $B$  and  $C$  and thus  $E_{\text{cr}}$  by observing such isopols. We find  $A_0 = 4.3 \times 10^{-3}$ ;  $B = -2.35 \times 10^{-11}$ ;  $C = 5.91 \times 10^{-19}$  cgs esu for the crystal studied at ambient pressure. These values lead to  $E_{\text{cr}} = 232$  V/cm and  $\Delta P_{\text{sp on}}(T_c) = 1.82$  C/cm<sup>2</sup>. High pressure results are imminent.

The ferroelectric phase transition in  $\text{KH}_2\text{PO}_4$  (KDP) is believed to be first order, for applied electric fields smaller than the value  $E_{\text{cr}}$  at which the first-order transition line in the temperature-electric field plane terminates in a critical Curie point where the transition is second order. Values from 180 V/cm to 6500 V/cm<sup>1,2</sup> have been reported for  $E_{\text{cr}}$ . The zero-field transition temperature,  $T_c$ , decreases approximately linearly with pressure to about 8 kbar and then decreases more rapidly toward 0 K, vanishing at 17 kbar.<sup>3</sup>

One of us (VHS)<sup>4</sup> conjectured that  $E_{\text{cr}}$  decreases with increasing pressure, until the  $+E$  and  $-E$  lines of critical points merge when  $E_{\text{cr}}$  reaches zero. The transition in zero field would then be second order for all higher pressures. Such a point where three lines of critical points merge has been termed a tricritical point.<sup>5</sup> We report here our measurement of the zero-pressure critical field in an experimental configuration which allows the application of high hydrostatic pressure. We will next repeat such measurements at various pressures in a search for the possible tricritical point in KDP.

Results thus far have been obtained from a  $1 \times 1 \times 0.2$  cm single crystal obtained from Interactive Radiation, Inc. The  $c$  axis is perpendicular to the large faces onto which gold electrodes were evaporated, using a circular mask to provide a guard ring on one face. The polarization is determined by using a Cary 401 electrometer to measure the voltage on an 8  $\mu\text{f}$  polystyrene capacitor in series with the sample. The sample is

contained within a helium-filled pressure vessel, which has two capacitance thermometers with temperature sensitivity of 2 mK imbedded in its walls. The sensor closest to the incoming  $\frac{1}{4}$ " pressure line controls the heater current to the pressure vessel. Surrounding the pressure vessel is a copper can with a thermocouple-regulated heater. This can is enclosed in a brass can evacuated to  $10^{-4}$  Torr or better, which is immersed in a dewar of liquid nitrogen. Pressure vessel temperature can be held constant within  $\pm 2$  mK indefinitely. Equilibrium, defined by crystal polarization remaining constant within 0.5% for one hour, takes three to four hours to achieve.

Because polarization changes sluggishly near a critical point, we decided to take and display data along curves of constant polarization. We have not seen this approach mentioned before in the literature and believe that it offers certain advantages in interpretation. The interpretation is based on the Landau theory,<sup>6</sup> which considers the free energy as a Taylor expansion in polarization,  $P$ . We truncate the series to obtain the equation of state

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

The first term predicts Curie-Weiss behavior in the paraelectric region. The pressure dependence of  $B$  is important, because  $B$  is negative for a transition of first order, positive for second order, and zero at the tricritical point.

The equation of state with  $P$  constant yields straight-line plots of  $T$  vs.  $E$ , which we call "isopols" and display in Figure 1.

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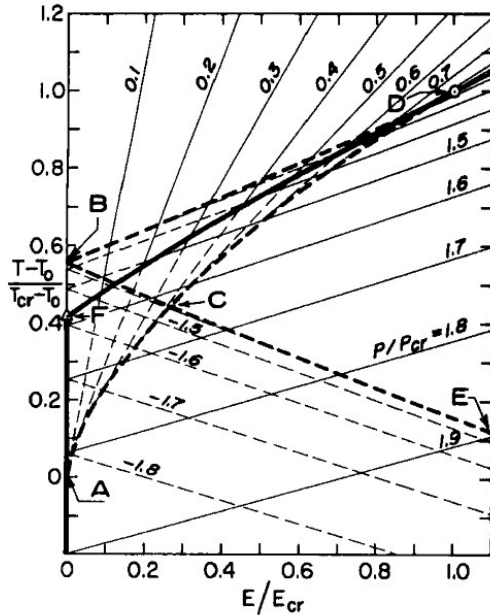


FIGURE 1 Phase diagram in  $E$ - $T$  plane obtained by keeping terms through  $P^6$  in Landau expansion. Triangle is Curie point or triple point. Circle is critical end point. Heavy solid lines indicate first-order transitions. Light solid and dashed lines correspond to isopols for stable and metastable phases respectively. Heavy dashed lines outline limits of regions of metastability.

In the small-polarization limit the  $E = 0$  intercepts approach  $T_0$ . For increasing  $P$  the intercepts at  $E = 0$  first increase and then decrease because of the negative  $B$  value associated with a first-order transition. For a second-order transition  $B$  is positive and the  $E = 0$  intercepts decrease steadily with increasing  $P$ .

The upper portion of any isopol corresponds to an absolute minimum of the free energy until the first-order line is reached. These portions are designated by solid lines in Figure 1. After crossing the first-order line the isopol corresponds to a local but not absolute minimum of the free energy. These metastable portions are indicated by dashed lines. After reaching the caustic curve which bounds the region of overlapping lines the isopol is not shown because it then corresponds to a free energy maximum. Lines with negative slope are extensions of isopols from the  $E < 0$  region not shown in Figure 1. Hysteresis can be expected in region  $ABD$  and below  $ACE$  where two or three phases can coexist.

Our results at ambient pressure are shown in Figure 2. We derive our values for the coefficients appearing in the equation of state from the straight line portions of the isopols. To find  $T_0$  the  $E = 0$  intercepts for small values of  $P$  are extrapolated to  $P = 0$ . The values

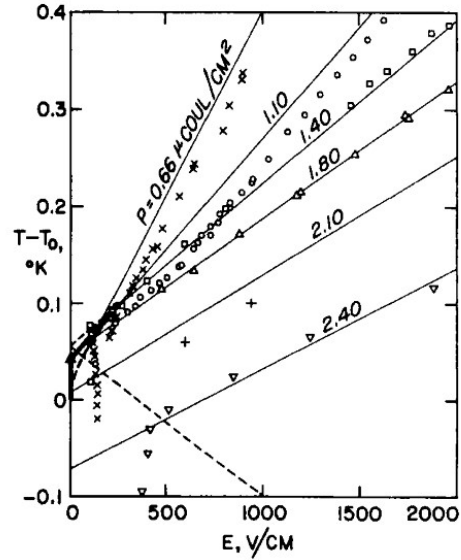


FIGURE 2 Points indicate experimental  $T$  vs.  $E$  relation for various constant polarizations. Straight lines indicate "isopols" for best fit values of  $T_0$ ,  $A_0$ ,  $B$  and  $C$ , with solid circle and triangle indicating corresponding critical point and Curie point respectively. Data for  $P = 0.66$  and  $1.10 \mu\text{C}/\text{cm}^2$  are averages of temperature drift runs which showed considerable hysteresis between increasing and decreasing  $T$ .

$A_0 = (dE/dT)_P/P$  agree for all lines with a standard deviation of 3%. We find  $B$  and  $C$  from a plot of  $-A_0(T - T_0)/P^2$  vs.  $P^2$ , in which  $B$  is the intercept and  $C$  is the slope. This plot is shown in Figure 3.

We find  $A_0 = (4.3 \pm 0.2) \times 10^{-3}$ ;  $B = -(2.35 \pm 0.4) \times 10^{-11}$ ;  $C = (5.91 \pm 1.50) \times 10^{-19}$  in cgs esu for the crystal tested. The maximum small signal ac dielectric constant for this crystal was 12,000, some-

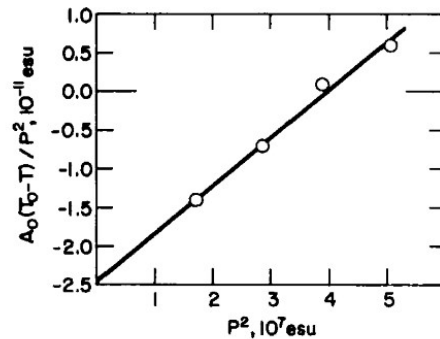


FIGURE 3 The equation of state  $E = A_0(T - T_0)P + BP^3 + CP^5$  with  $E = 0$  predicts a linear graph of  $A_0(T_0 - T)/P^2$  vs.  $P^2$  with  $B$  the intercept and  $C$  the slope. Values for  $T(E = 0)$  are taken from intercepts of isopols in Figure 2. Points for  $P = 0.66$  and  $1.10 \mu\text{C}/\text{cm}^2$  are omitted owing to the large scatter in  $(T - T_0)$  for small polarization.

what lower than the highest values reported. From these we may calculate in the usual way:

$$T_c - T_0 = 3B^2/16A_0C = 0.041 \pm 0.010 \text{ K};$$

$$T_{\text{crit}} - T_0 = 9B^2/20A_0C = 0.098 \pm 0.025 \text{ K};$$

$$E_{\text{crit}} = [2(-B/5)^5/(C/3)^3]^{1/2} = 232 \pm 70 \text{ V/cm};$$

$$P_{\text{crit}} = [-3B/10C]^{1/2} = 1.15 \pm 0.07 \text{ } \mu\text{C/cm}^2;$$

$$\Delta P_{\text{sp on}}(T_c) = (-3B/4C)^{1/2} = 1.82 \pm 0.10 \text{ } \mu\text{C/cm}^2.$$

The absolute uncertainties are rather large due primarily to uncertainty in the crystal dimensions. The precision of the experiments is much better than the accuracy, so that in an experiment designed to detect changes in  $B/C$  with pressure for a given

crystal, results for  $B/C$  may be compared within  $\pm 2\%$ . Our value for  $P_{\text{sp on}}(T_c)$ , which depends upon  $B/C$  only, agrees very well with that reported by Benepe and Reese from their electrocalorimetric experiments.<sup>6</sup>

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