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TRICRITICAL POINT AND TRICRITICAL EXPONENT δ IN $KH_2PO_4^\dagger$

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Static dielectric results for a KH_2PO_4 crystal at pressures of 0, 2, and 2.4 kbar are analyzed in terms of a Landau free energy expansion using the "isopol" technique. The measured exponent δ at 2.4 kbar is consistent with the mean-field tricritical value of 5. This result and the Landau parameter values indicate a tricritical point near 2.4 kbar.

A tricritical point is a point in a three-dimensional parameter space at which three lines of critical points meet. Only in ferroelectrics have tricritical points been found for which all three parameters (pressure p, temperature T, and electric field E) are independent and experimentally accessible.

In retrospect, the first indication that KH_2PO_4 might have a tricritical point was the discovery by Silsbee, Uehling and Schmidt[1] that the Senko[2] model predicts either a first-order or second-order transition, depending on the relative magnitudes of three energy parameters. Later, Schmidt[3] predicted that KH_2PO_4 would exhibit a tricritical point at modest pressure. We have confirmed this prediction, as described below.

We have found that our experimental results are in accord with the Landau free energy expansion

$$F = \tfrac{1}{2}A_0(T - T_0)P^2 + \tfrac{1}{4}BP^4 + \tfrac{1}{6}CP^6. \qquad (1)$$

From the thermodynamic relation $E = \partial F/\partial P$ the equation of state

$$E = A_0(T - T_0)P + BP^3 + CP^5 \qquad (2)$$

is obtained, in which A_0 is the inverse of the Curie–Weiss constant and T_0 is the Curie–Weiss temperature. Because for fixed P Eq. (2) predicts a convenient linear relation between electric field E and temperature T, we obtained and analyzed data along lines of constant P. A family of such lines, which we call "isopols", is shown in Figure 2 for the case $B < 0$ which corresponds to a first-order transition. For $B > 0$ the transition is of second order, while the tricritical point occurs at the pressure p_t for which $B = 0$ when $T = T_0$.

A dc voltage was applied across the series circuit consisting of the crystal and a low-leakage capacitor, and polarization was measured by an

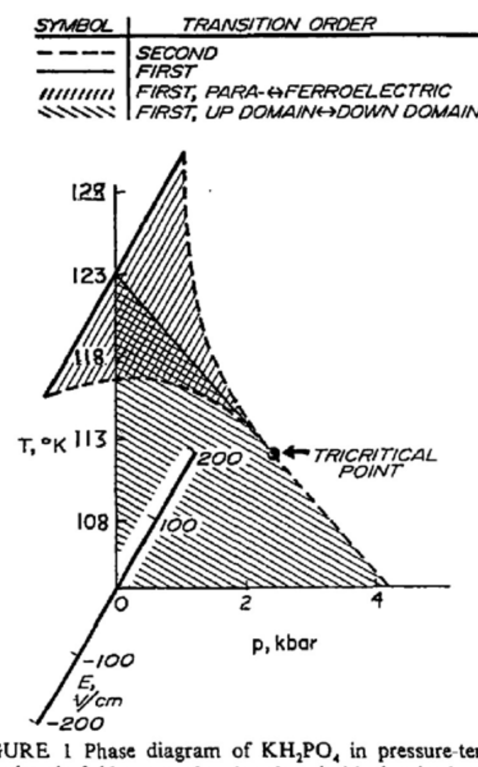

FIGURE 1 Phase diagram of KH_2PO_4 in pressure-temperature-electric field space, showing the tricritical point located at the confluence of the two wing critical lines, the zero-field critical line, and the line of triple points. The first-order transition surfaces bounded by these lines are shown also.

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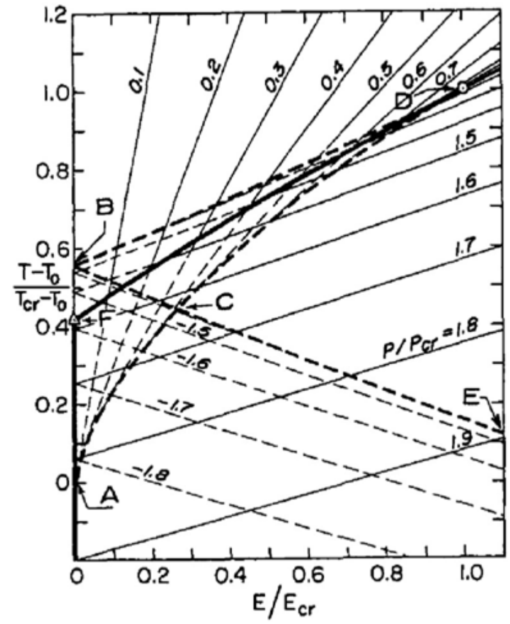

FIGURE 2 Dimensionless isopol plot for equation of state given in Eq. 2, shown for a negative Landau coefficient B, for which the transition is of first order. The ferroelectric transition temperature or Curie point T_c is at F, the Curie–Weiss temperature T_0 at A, and the wing critical point at D. Free energy minima corresponding to paraelectric and "up domain" ferroelectric phases both exist in the region BCD. Minima corresponding to "up domain" and "down domain" phases both exist in region ACE. All three minima occur in region ABC. The first-order paraelectric- "up domain" transition line is indicated by DF, while the first-order "up domain"–"down domain" transition line extends downward from F.

electrometer connected across the capacitor. The crystal was in a beryllium copper pressure vessel using helium as the pressure fluid. This vessel was surrounded by an evacuated space containing a heat shield and bounded by a can immersed in liquid nitrogen. Millidegree temperature stability was provided by automatic control of a coarse heater on the shield and a fine heater on the pressure vessel.

Results for our first two crystals have been reported previously.[4,5] The Landau parameters for

TABLE I
Landau expansion coefficients for KH_2PO_4 Crystal No. 3

Pressure (kbar)	$A_0 \times 10^3$ (cgs-esu)	$B \times 10^{11}$ (cgs-esu)	$C \times 10^{19}$ (cgs-esu)
0.001	4.14 ± 0.11	-1.26 ± 0.05	3.18 ± 0.13
2.000	4.50 ± 0.08	-0.30 ± 0.15	5.8 ± 0.6
2.400	4.31 ± 0.20	-0.03 ± 0.07	4.4 ± 0.3

the third crystal at 0, 2, and 2.4 kbar are given in Table I. The exponent δ is defined by $E \propto P^{\delta}$, with T being held at the critical or tricritical temperature. At 2.4 kbar we found $\delta = 4.9 \pm 0.3$, in accord with the tricritical value of 5 predicted by Eq. (2). For the second crystal at 3 kbar, the E *vs.* P plot shows crossover of δ from the critical value of 3 toward 5 with increasing P.

Both the isopol and the B coefficient results for our third crystal indicate a tricritical point near 2.4 kbar. Our results from the second crystal[5] as well as measurements of Bastie *et al.*[6] indicate with lower accuracy a tricritical point near 2 kbar. It is not yet clear whether p_t varies somewhat from sample to sample.

In summary, the important aspects of this work are the development of the isopol technique for analyzing the polarization results, the determination that KH_2PO_4 has a tricritical point, and the first measurement in any substance of the tricritical exponent δ.

REFERENCES

1. H. B. Silsbee, E. A. Uehling and V. H. Schmidt, *Phys. Rev.* **133**, A165 (1964).
2. M. E. Senko, *Phys. Rev.* **121**, 1599 (1961).
3. V. H. Schmidt, *Bull. Am. Phys. Soc.* **19**, 649 (1974).
4. A. B. Western, A. G. Baker, R. J. Pollina and V. H. Schmidt, *Ferroelectrics* **17**, 333 (1977).
5. V. H. Schmidt, A. B. Western and A. G. Baker, *Phys. Rev. Lett.* **37**, 839 (1976).
6. P. Bastie, M. Vallade, C. Vettier and C. M. E. Zeyen (Proc. of this Meeting).