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DIELECTRIC STUDIES OF CRITICAL AND TRICRITICAL PHENOMENA IN KDP AND RDP

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Our method of obtaining and analyzing dielectric data for KDP is reviewed, which demonstrated that KDP has a tricritical point between two and three kbar pressure. We also describe our method for obtaining the critical exponents \( \gamma \) and \( \delta \). Our experimental results for KDP are summarized. New results are presented for RDP which agree with the conclusion of others that its transition is of second order at ambient pressure.

INTRODUCTION

It is well known by now that \( \text{KH}_2\text{PO}_4 \) (KDP) has a tricritical point between 2 and 3 kbar pressure. We review here the method used for analyzing dielectric data in terms of isopols to determine the coefficients in the Landau equation of state which appears to describe accurately static dielectric phenomena in this uniaxial ferroelectric. We describe also our method for determining critical and tricritical exponents. Finally, we review our results for KDP and present our new results for \( \text{RH}_2\text{PO}_4 \) (RDP).

PRINCIPLE OF ISOPOL MEASUREMENTS

For systems having free energy \( F \) symmetric in the order parameter \( P \), the Landau expansion for the free energy is

\[
F = A P^2 + B P^4 + C P^6 + \ldots
\]  

(1)

If we expand \( A \) and \( B \) to first order in temperature \( T \) and pressure \( p \), and note that the constant term in \( A \) vanishes if the Curie-Weiss temperature \( T_c \) is chosen for the reference temperature, we obtain the following equation of state for electric field \( E \) by differentiating \( F \) with respect to \( F \) at fixed \( T \) and \( p \):
\[ E = A_0 (T - T_0)^p + A_0^p + B_0 (T - T_0)^p + B_0^p (T - T_0)^p + CP^5. \] (2)

In this linear approximation, lines of constant polarization \( P \) (isopols) appear as straight lines on a plot of \( T \) vs. \( E \). Because of this linear relation, analysis of the data is much simplified if a few fixed values of \( P \) are used in collecting and analyzing data.

An example of such an isopol plot is provided by our recent results for an RDP crystal shown in Fig. 1. The plot is only valid in regions in which the crystal does not exist metastably in two phases, as has been explained previously. The points lying on nearly vertical lines in Fig. 1 indicate a region of metastability, and such points are not used in the analysis.

The first step in the isopol analysis is measurement of the slopes of the isopols, which in our approximation obey the relation

\[ (\partial E/\partial T)_p = A_0^p + B_0^p P^2. \] (3)

By plotting against \( P^2 \) this slope divided by \( P \), one obtains \( A_0 \) as the intercept at \( P^2 = 0 \) and \( B_0 \) as the slope of the line.

After the best fit line for \( A_0^p + B_0^p P^2 \) is found in this manner, values from this line can be put into Eq. (2) rearranged as follows (for the \( p=0 \) case) to provide values for \( B_c \) and \( C \):

\[ B_c + C P^2 = E P^{-3} (A_0^p + B_0^p P^2) (T - T_0)^{-2}. \] (4)

A similar analysis can be carried out for nonzero pressure if the \( A_p P \) and \( B_p P^2 \) terms are eliminated by suitably redefining \( T_0 \) and \( B_c \). One plots the right side of Eq. (4) against \( P^2 \), using one point from the best-fit line for each isopol. It is simplest to use the point where the isopol crosses the \( E=0 \) axis. However, it is more accurate to use the "center of gravity" or mean value of the experimental points for the isopol. From this plot, \( B_c \) is found as the \( P^2=0 \) intercept and \( C \) as the slope. Of course, one can make simpler assumptions; in our previous analysis for KDP we assumed that \( B_0^p = 0 \).

The transition order is determined by the sign of \( B_p (T - T_0)^p + B_0^p P \) at the Curie-Weiss temperature \( T_0 - A_0^p / A_0 \) at a given pressure \( P \). If \( B \) is positive at that temperature and pressure, the transition is of second order. If \( B \) is negative there, the transition is of first order and there exist two "wing" critical points at temperature \( T_{Cr} \) and fields \( H_{Cr} \) as discussed previously. If \( A_0^p (T - T_0)^p + A_0 P \) and \( B \) vanish simultaneously, there exists a tricritical point at that temperature \( T_{tr} \), pressure \( p_{tr} \), and field \( E=0 \). The term "tricritical" reflects the fact that in a three-dimensional pTE space there are three lines of critical points which meet at the tricritical point. One of these lines lies in the \( pT \) plane, while the other two consist of wing critical points on both sides of that plane.

Additional details concerning the use of the isopol method appear elsewhere.
METHOD OF DETERMINING EXONENTS

The exponents $\beta$, $\gamma$, and $\delta$ are associated with dielectric properties. However, we cannot determine $\beta$ from macroscopic dielectric measurements because it is associated with the growth of the order parameter below $T_c$ at zero field, and the coexistence of domains of both orientations in this temperature and field region causes the observed polarization to be much smaller than that corresponding to a single domain. Fortunately the polarization is proportional in first order to the square of the change below $T_c$ in the $c$ unit cell dimension, and neutron diffraction measurements of this change have provided the exponent $\beta$ for KDP. The polarization is also proportional in first order to the $x$-$y$ shear, so in principle this exponent could also be determined from diffraction experiments which simultaneously provide the shear angle for both types of domains.

The exponent $\gamma$ is defined by $\chi \propto (T-T_0)^{-\gamma}$, where $\chi$ is the dielectric susceptibility. To determine $\gamma$ from an isopol plot such as shown in Fig. 1, one examines the isopols for small polarization $P$. If at a given temperature $P$ is proportional to $E$ for the first two isopols, then $\chi=P/E$ represents the susceptibility at that temperature. If in addition the isopols are straight as in Fig. 1, then the above relation indicates a critical exponent $\gamma=1$. Of course the $E=0$ intercepts of the isopols must approach the actual transition temperature as $P$ approaches zero; otherwise the transition is of first order and critical exponents cannot be defined.

The exponent $\delta$ is defined by $E=\delta P$, with measurements made at the transition temperature. In practice the transition temperature is not known exactly in advance, so there generally will not be experimental points exactly at that temperature. A reasonable procedure for obtaining the desired $E$ vs. $P$ plot is as follows: The best-fit line is determined independently for each isopol. One then uses for $E$ and $P$ the values corresponding to the points at which the $T=T_0$ line crosses these best-fit lines. Only those isopols should be used which have data points both above and below $T_0$; in other words, the data should not be extrapolated.

EXPERIMENTAL RESULTS

For KDP our results have been reported in detail elsewhere and will merely be summarized here. Data from three crystals agree in indicating a first-order transition at ambient pressure. The two crystals for which we obtained results at pressures of 1, 2, 2.4, and 3 kbar provided the basis for our reported tricritical point in the 2.3+0.3 kbar pressure range. Bastie and Vallade have recently reported a tricritical pressure of 2.8 kbar for KDP.

The critical and tricritical exponents found to date for KDP agree with predictions of Landau's mean-field theory. Our results for $\delta$ at 2.4 kbar indicated a tricritical exponent of 5 as predicted, while at 3 kbar the data were in the crossover region between the critical value of 3 and the tricritical value of 5.
FIGURE 1. Isopols for RDP at ambient pressure.
For $\beta$ we obtained the value 1 for both the critical and tricritical exponent for KDP as predicted by Landau theory.

Neutron diffraction measurements by Bastie, Vallade, Vettier, and Zeyen$^2$ of the KDP $c$-axis unit cell length change below $T_c$ indicated an exponent $\beta$ at 2 kbar near the Landau tricritical value of 0.25, and near the critical value of 0.5 at 3.5 kbar, thus providing additional evidence for a tricritical point in KDP.

For RDP a preliminary analysis of our ambient pressure results for a crystal grown by us yield $A_0 = (3.97 \pm 0.1) \times 10^{-3}$ esu if a temperature-dependent $B$ is assumed; $B_0$ is found to be $-(2.43 \pm 0.9) \times 10^{-10}$ esu which is a surprisingly large temperature dependence. We then find $B_0 = (1.7 \pm 0.3) \times 10^{-10}$ esu, indicating a second-order transition quite far from the tricritical point.

Our value for $C$ is quite uncertain; we obtain $-(9 \pm 9) \times 10^{-18}$ esu. Of course, a negative value for $C$ requires for stability a positive term of higher order in $P$ in the free energy, such as $DP^2/2$. In this context we remark that there appear in Fig. 1 vertical portions of isopoles at temperatures above $T_0$. This indicates the presence of metastable phases above $T_0$, whereas our free energy function in Eq. (1) does not possess any metastable minima above $T_0$ because it is truncated at the $P^2$ term and $B$ is positive as required for a second-order transition. We note also that for KDP at 3 kbar in the second-order transition pressure range there were no such vertical portions of isopoles above $T_0$. Measurements on other RDP crystals will be necessary to determine whether this metastability is intrinsic, or is caused by crystal imperfection.

We also analyzed our RDP data assuming $B$ to be temperature-independent, but the results were less satisfactory because the plot of $B+CP^2$ vs. $P$ then is a curve from which a value for $C$ cannot be abstracted unambiguously. This type of fit with $B$ temperature-independent was made by Bastie, Lajzerowicz, and Schneider$^4$, for their ambient-pressure RDP shear results obtained by gamma-ray diffractometry. They found $A_0 = 4.20 \times 10^{-3}$ esu, $B = 7.61 \times 10^{-11}$ esu, and $C = 2.85 \times 10^{-19}$ esu.

We have just obtained dielectric results at 0.9 kbar pressure from another crystal grown by us. These results appear to be good, but they have not yet been analyzed.

CONCLUSIONS

Our dielectric studies of KDP near $T_c$ at several hydrostatic pressures showed that this crystal has a tricritical point between 2 and 3 kbar, and demonstrated that the critical and tricritical exponents $\alpha$ and $\beta$ have the values predicted by mean field theory.$^6$

Our recent dielectric results for RDP at ambient pressure agree with previous$^4$ reports that this transition is of second order.

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