Study of the Tricritical Point in KH_2PO_4 by γ-Ray and Neutron Diffractometry

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The existence of a pressure-induced tricritical point in potassium dihydrogen phosphate was investigated by direct measurements of the spontaneous shear angle as a function of temperature using γ-ray diffractometry at pressures up to 2.15 kbar. High-resolution neutron diffractometry was applied to the measurement of the critical behavior of the lattice constant c at various pressures up to 3.5 kbar. The results of the two methods agree and indicate tricritical behavior at a pressure of about 2 kbar.

Active experimental studies have shown that a number of physical systems have more than two field variables. As a consequence, considerable attention has been paid to systems that display "higher order" critical points.[1,2] He^3-He^4 mixtures exhibit a tricritical point[3] in the (T, s, η) field-variable space,[4] where T is the temperature, s the difference in the chemical potentials, and η the field conjugate to the superfluid order parameter. Magnetic field-induced transitions in DyAlG (dysprosium aluminum garnet)[5] and $FeCl_2$[6] have provided examples of magnetic tricritical points (TCP) in the $(H_{\text{applied}}, H_{\text{staggered}}, T)$ space; furthermore, applied pressure generates tricritical lines in a four-dimensional space.[7] Applied pressure or stress has also been found to induce changes in critical phenomena in the antiferromagnet MnO,[8] the perovskite crystal $SrTiO_3$,[9] ammonium halides,[10] and the ferroelectrics SbSI[11] and KH_2PO_4 (KDP).[12]

In ferroelectrics, two field (or intensive) variables are temperature T and electric field E; pressure plays an important role by modifying the strength of certain terms in the Hamiltonian and can be considered as a fieldlike variable. Indeed, hydrostatic pressure induces a change in the order of the ferroelectric transition in SbSI[11] and KDP[12] at zero electric field. The latter material was investigated recently by Schmidt and co-workers[12] using static dielectric measurements under pressures up to 3 kbar. The ferroelectric phase transformation which is first order at ambient pressure was found to be second order at a pressure of 3 kbar.

Here we report the first direct microscopic measurements of the spontaneous shear u_{xy} using γ-ray diffractometry and of the variation u_{zz} of the lattice parameter c using neutron diffraction in the vicinity of the ferroelectric transition of KDP at pressures up to 3.5 kbar at $E=0$. The two quantities u_{xy} and u_{zz} are related to the order parameter, i.e., the spontaneous polarization P_z, in the following way: u_{xy} is linearly coupled to P_z via piezoelectricity, and recent studies[13,14] at ambient pressure have established the proportionality of these two quantities near T_c. Electrostriction causes u_{zz} to be proportional to the square of P_z.

In contrast to the previous dielectric measurements[12] which determine the macroscopic polarization, both the γ-ray[13] and neutron[14] scattering techniques yield microscopic values of the order parameter and do not require an external field. With an electric field E applied, these methods allow study of the entire tricritical region in the variable space (T, E, p), whereas the dielectric method is not useful in that part of the region in which the crystal breaks up into domains. Furthermore, these techniques provide information from a relatively large bulk sample, whereas x rays can penetrate only a short distance and may yield results affected by surface strains.

The $4\times6\times7$-mm^3 KH_2PO_4 samples used were perfect single crystals. The pressure cell[15] consisted of an autofrettaged high-strength aluminum alloy body and its associated safety shield. The pressure medium was helium. A primary two-stage compressor, together with a pressure intensifier, were used. The pressure was measured by a Manganin gauge. The pressure cell was immersed in a cryostat. Slow temperature slopes of typically 0.1 K per hour were run through the temperature range of interest. The precision of the temperature measurement was 0.01 K.[16]

Both the γ-ray and the neutron experiments were performed at the Institut Laue-Langevin with the same pressure-cell/cryostat system. For the first experiment we used the γ-ray diffractometer[17] at a wavelength of $\lambda = 0.03$ Å and an angular collimation in the scattering plane of 30 seconds of arc to measure directly[13] the spontaneous shear angle at different pressures as a function of the sample temperature.

For the second experiment a neutron high-resolution parallel-crystal arrangement was used.[18] The monochromator was a KD_2PO_4 single crystal plate. At a wavelength of 3.2 Å the angular position (resolution 0.01°) of the (004) reflection was monitored as a function of temperature to yield the corresponding variation of the constant lattice c. The studied range in pressure was 0.001 to 3.5 kbar.

A comparison of the shear data at 1 bar, 1 kbar, and 2.15 kbar (Fig. 1) shows that the step at T_c characteristic of a first-order transition decreases with increasing pressure. Given the uncertainty due to the temperature inhomogeneity of the sample, it is difficult to know whether this step has really disappeared for the pressure of 2.15 kbar. Further studies are necessary to clear up this point conclusively.

The shear u_{xy} is connected to the polarization by the relationship

$$u_{xy} = b_{36} P_z,$$

where b_{36} is a piezoelectric constant. At ambient pressure the value of this constant can be obtained within the temperature range of $0 \leq T_c - T \leq 1$°K by comparing the spontaneous shear measurements of Bastie *et al.*[13] and Zeyen and Meister,[14] both in good agreement, with polarization data of Benepe and Reese.[19] This leads to a value of $b_{36} = (4.83 \pm 0.02) \times 10^{-7}$ esu.

Neglecting the pressure dependence of b_{36},[20] an attempt has been made to compare our results to the polarization curves deduced by Schmidt *et al.* from their static dielectric data at various pressures (Fig. 1). Although the agreement is not quantitatively good, both types of experiments

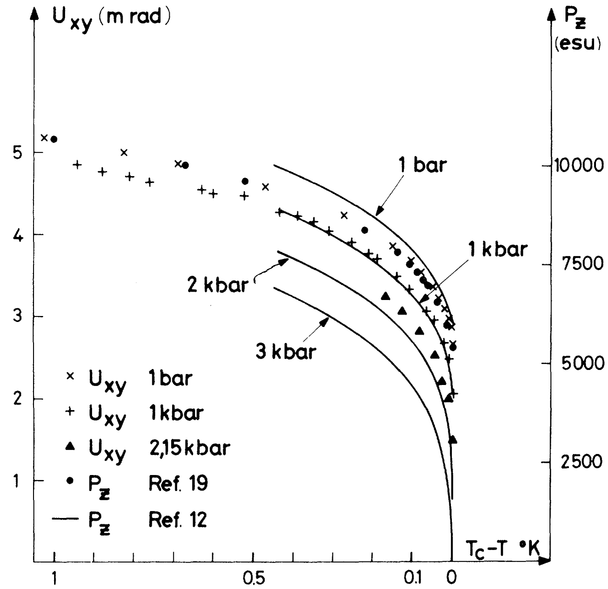

FIG. 1. Temperature dependence of the spontaneous shear u_{xy} from γ-ray measurements for various pressures. These data are compared with polarization measurements by Benepe and Reese (Ref. 19). Full lines are calculated from the work of Schmidt *et al.* (Ref. 12) and Baker *et al.* (Ref. 12).

are compatible with the existence of a TCP at a pressure close to 2 kbar.

The temperature behavior of u_{zz} in the vicinity of T_c can be written as[21]

$$u_{zz}(T) = \alpha_3 T + Q_{33} P_z^2,$$

where $\alpha_3 T$ stands for the usual thermal expansion and Q_{33} is an electrostriction coefficient describing an elongation of the lattice parameter c resulting from the appearance of the spontaneous polarization P_z. Figure 2 shows that the step in u_{zz} at T_c disappears completely at the pressure of 3.5 kbar. An extrapolation of α_3 for temperatures below T_c yields the purely electrostrictive part

$$\Delta u_{zz}(T) = u_{zz}(T) - \alpha_3 T = Q_{33} P_z^2(T) \text{ for } T < T_c.$$

A comparison of $\Delta u_{zz}(T)$ and $P_z(T)$ at ambient pressure within the temperature range of $0 < T_c - T < 2$ K gives a value of $Q_{33} = (3.2 \pm 0.2) \times 10^{-12}$ esu practically independent of temperature and in good agreement with the value reported in the literature.[22]

Because of the long-range character of dipolar interactions, the critical behavior of uniaxial three-dimensional ferroelectrics is expected to be essentially classical.[23] In particular, renormalization-group theory[24] indicates that the temperature dependence of the order parameter is described by the classical exponent $\beta=\frac{1}{2}$ for a second-order phase transition (apart from small logarithmic corrections). When a tricritical point is approached a value of $\beta=\frac{1}{4}$ is expected in three-dimensional systems.[26] Therefore we have attempted to fit our results using a classical Landau-type expansion of the free energy,

$$F=a(T-T_c)P_z^2+bP_z^4+cP_z^6+\ldots.$$

The temperature dependence of P_z is obtained by setting $\partial F/\partial P_z=0$; near T_c this leads to

$$P_z=\left[\frac{a(T_c-T)}{b}\right]^{1/2} \text{ for } b>0,\ c>0$$

$$(\beta=\tfrac{1}{2},\ \text{second-order transition}),$$

and

$$P_z=\left[\frac{a(T_c-T)}{c}\right]^{1/4} \text{ for } b=0,\ c>0$$

$$(\beta=\tfrac{1}{4},\ \text{tricritical point}).$$

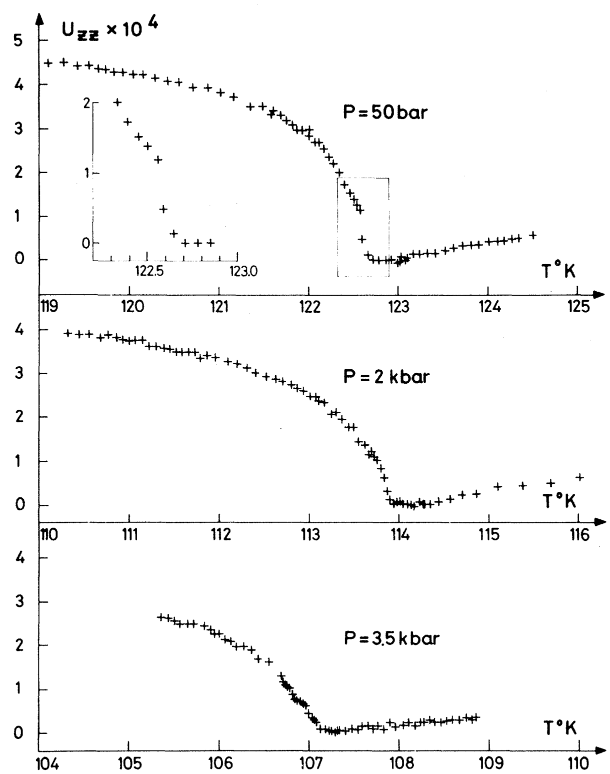

FIG. 2. Temperature dependence of the spontaneous strain u_{zz} from neutron measurements for various pressures. The inset shows the discontinuity at room pressure.

Figure 3 shows clearly that near T_c, $u_{zz}=Q_{33}P_z^2$ is proportional to T_c-T at 3.5 kbar and proportional to $(T_c-T)^{1/2}$ at 2 kbar. This indicates that the coefficient b vanishes for a pressure of $p\simeq 2$ kbar, i.e., that a TCP exists at this pressure.

An attempt to fit our results by a Landau expansion over the wider temperature range T_c-2 K $<T<T_c$ has been made, but the introduction of higher order terms up to the eighth power of P_z is required to obtain good agreement. As a result the number of adjustable parameters is large and their determination is not very accurate. Nevertheless, the fitting procedure always leads to a value of the coefficient b which is negative at 50 bar, positive at 3.5 kbar, and vanishingly positive at 2 kbar. Consequently the present measurements of the spontaneous shear u_{xy} and strain u_{zz} confirm the results of the dielectric measurements as far as the existence of the pressure induced tricritical point is concerned.

Finally, one may note that the change of the order of the transition with pressure in KDP is not unexpected and may be qualitatively explained by an increase of the tunnelling frequency Ω of the protons with pressure. This increase of Ω has been invoked[26] to explain the pressure dependence of T_c. According to the theory of Blinc and Svetina,[27] this leads to a decrease of the jump of the order parameter. A quantitative comparison with this theory requires additional accurate data.

In order to determine the tridimensional phase diagram, high-resolution neutron-diffraction measurements of both u_{xy} and u_{zz} for various pressures, temperatures and electric fields ap-

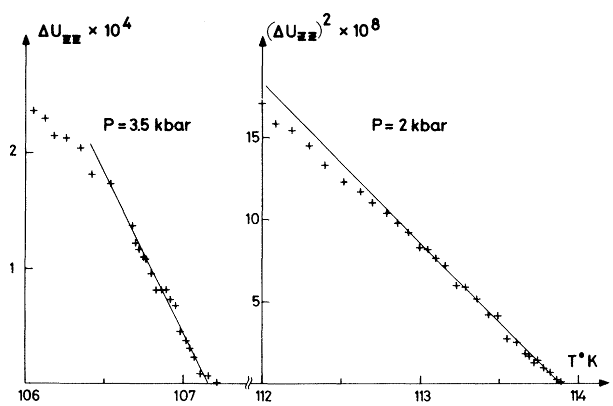

FIG. 3. Temperature dependence of the first and second powers of the polarization-induced strain Δu_{zz}. These plots indicate the change in β from $\beta=\frac{1}{2}$ at $p=3.5$ kbar to $\beta\simeq\frac{1}{4}$ at $p=2$ kbar.

plied to the sample crystal are currently under way.

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[21]This expression is valid in the mean-field approximation where the fluctuations of the order parameter are neglected. These fluctuations give rise to a term in the volume thermal expansion coefficient proportional to the "anomalous" part Δc of the specific heat (Pippard's relation). From the measurements of Δc in the paraelectric phase at atmospheric pressure one can note that this contribution is rather small, but this may no longer be true when the transition becomes second order. In particular near the TCP, the "classical" value of the critical exponent α is $\frac{1}{2}$, and the fluctuations would introduce a term in $\Delta u_{zz}(T)$ proportional to $|T-T_c|^{1/2}$. This may explain the apparent "anomalous" drop of α_3 with increasing pressure just above T_c.

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