γ-ray diffractometry: A new technique of measuring the spontaneous shear deformation in ferroelastics: Application to KH_2PO_4. Comparison with recent measurements of the birefringence

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A new accurate technique, γ-ray diffractometry, has been used to study the order parameter in KH_2PO_4 near the transition point. Results are compared to birefringence measurements. The transition is of first order with a thermal hysteresis of about 0.07°K. Unusual behavior of the order parameter has been observed for decreasing or increasing temperature near the transition.

INTRODUCTION

The phase transition in KH_2PO_4 at $T = 122°$ K is of ferroelectric-ferroelastic character ($\bar{4}2m$ to $mm2$). The polarization P_z, which is considered as the order parameter, belongs to the B_2 representation, as does the shear u_{xy} due to the piezoelectric behavior of KH_2PO_4. u_{xy} as well as the birefringence Δn_{xy} are elements of a second-order tensor and also belong to B_2. Therefore measurements of $P_z(T)$, $\Delta n_{xy}(T)$, or $u_{xy}(T)$ are usually considered as a measure of the order parameter.

Several measurements of the order parameter were performed by means of techniques which require a single-domain sample.[1] This implies the application of an external electric field, which alters the behavior of the measured quantities near the transition temperature. Furthermore, the order parameter can be determined only by extrapolation to zero field.

The temperature dependence of the shear u_{xy} has already been studied on polydomain samples by x-ray techniques[2] without application of an external field. In these experiments, the accuracy of the measured temperature values were not better than 0.1°K. Furthermore, because of the small penetration depth of the x rays, surface effects may affect the measurements.

γ-RAY DIFFRACTOMETRY

Bragg peaks are studied by taking advantage of the high degree of monochromaticity of γ lines and by using well collimated beams.[3] The diffractometers installed at the Institut Laue-Langevin generally use the 412-keV ($\lambda = 0.03$ Å) γ radiation from radioactive gold with $\Delta\lambda/\lambda = 10^{-6}$ at room temperature. The finest collimated beams are of 10″ divergence in the scattering plane. Because the absorption of this radiation is small (the mean free path, for example, being about 11 mm for copper) measurements with samples contained in ovens, cryostats, or high-pressure devices can be easily performed. Owing to the small Bragg angles, the shape of the measured diffraction pattern is caused only by lattice tilts.[4]

EXPERIMENTAL

The KH_2PO_4 crystals were grown from aqueous solution and cut along the tetragonal axis. Figure 1 shows the dimensions of the sample investigated by γ rays; the volume explored was about 12 mm^3. The c faces were electroded with evaporated gold. The electrodes were short circuited. Rocking curves were measured at the (200) lattice planes in symmetrical Laue geometry. At room temperature the sample showed a homogeneous mosaic structure with a mosaic spread of the order of 10″.

When the sample is cooled below the transition temperature, a domain texture appears as shown in Fig. 2. The rocking curves measured at the

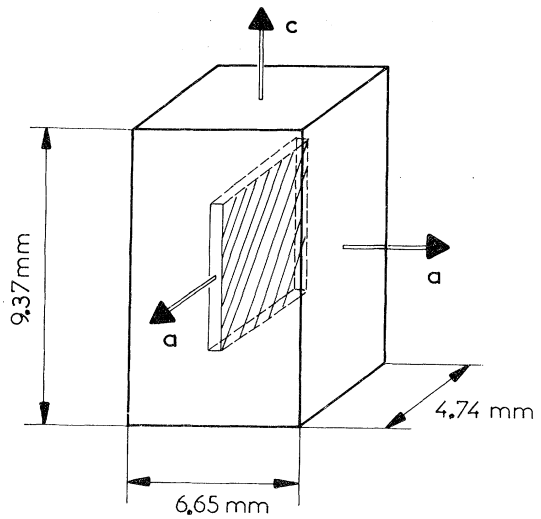

FIG. 1. Dimension and orientation of the sample; the investigated volume element is sketched by dotted lines.

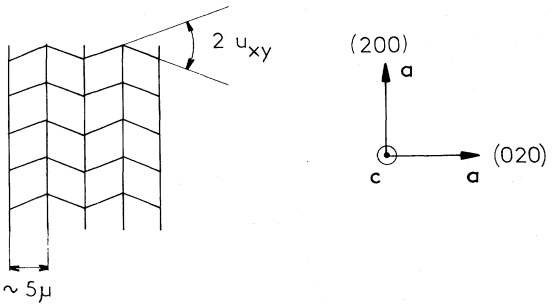

FIG. 2. Domain structure in the ferroelectric phase; u_{xy} is the shear angle.

(200) reflection split into two parts. Their angular separation is twice the shear angle u_{xy} which in general is measured with an accuracy of $\pm 4''$. If there are also domains in the direction of the other tetragonal axis, we have a third peak between the first two. The cryostat used was capable of temperature adjustment to within $\pm 5\times 10^{-3}$° K. The time necessary to measure the two Bragg peaks was of the order of 1 h. The results are plotted in Fig. 3.[5]

Using the same cryostat, the birefringence $\Delta n_{xy}(T)$ has been measured on a different sample.[6] This determination needs a single-domain sample and, therefore, the measurements were performed with an external electric field of varying strength. The values reported in Table I are obtained by extrapolation to zero field and are taken from Ref. 6.

DISCUSSION OF THE RESULTS

The results plotted in Fig. 3 confirm that the transition is of first order, showing a thermal hysteresis of about 0.07° K and a jump in the spontaneous shear of $608''\pm 10''$ for decreasing and of $552''\pm 10''$ for increasing temperature. We note the unusual shape of the thermal hystersis (the usual shape is shown on the left of Fig. 3). The experimental method guaranties that we deal with the intrinsic bulk effect because we measure the shear angle of the unit cell.

A great number of optical observations of the domain structure[7] show that the domain textures near the transition point are different for decreasing or increasing temperature. The value of the order parameter may depend on the domain width, and this would explain the observed behavior of the thermal hysteresis. In order to check this hypothesis, optical observations of the domain structure will be performed simultaneously with the γ-ray measurements.

In Fig. 4 we have plotted the birefringence $\Delta n_{xy}(T)$ versus the shear $u_{xy}(T)$ as determined by γ-ray diffractometry without any fit on the temperature (in both experiments the same platinum thermistor was used). Except in the temperature region where the thermal hysteresis occurs good proportionality is obtained with

$$\Delta n_{xy}/u_{xy} = 1.51 \pm 0.01 \ .$$

This value can be compared with the value calculated for the photoelastic effect in the paraelectric phase. The quadratic part of the free energy as a function of P_z and u_{xy} is in a Landau-type approach equal to

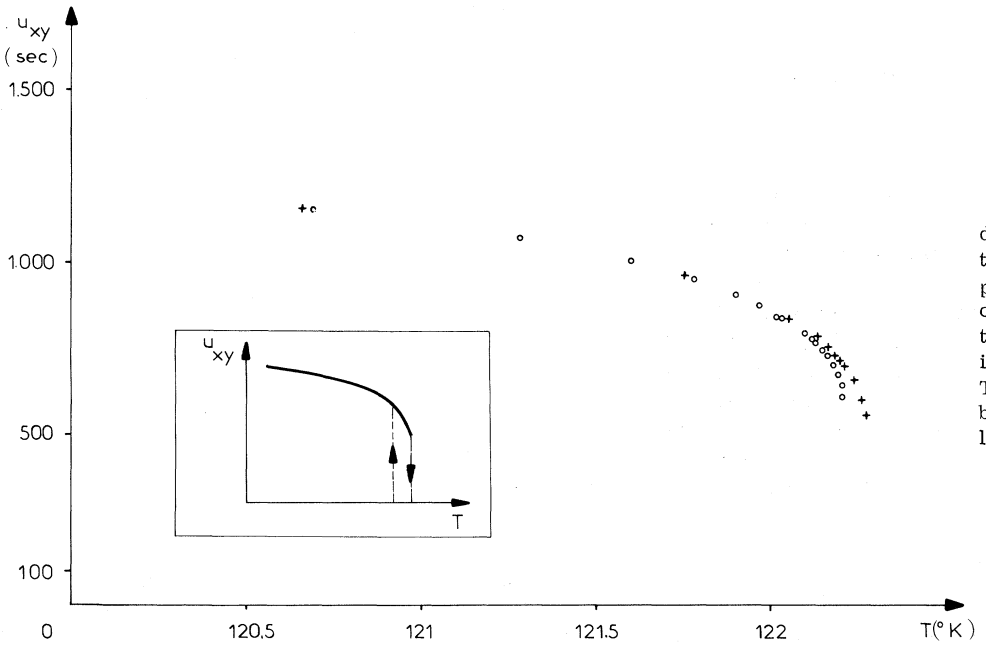

FIG. 3. Temperature dependence of the spontaneous shear. The points are related to decreasing temperature; the crosses represent increasing temperature. The usual thermodynamic behavior is shown on the left.

TABLE I. Values of the shear angle u_{xy} determined from γ-ray diffractometry for decreasing and increasing temperature, and values of the birefringence Δn_{xy} determined from measurements with applied electric field and extrapolation to zero field.

T(K)	u_{xy} (seconds of arc)	T	u_{xy}	T	u_{xy}	T	$10^3\,\Delta n$
122.204	608	122.020	839	120.663	1158	120.645	8.56
122.202	639	121.967	872	121.756	959	121.318	7.68
122.194	669	121.900	903	122.051	834	121.577	7.32
122.180	697	121.780	947	122.137	779	121.810	6.88
122.163	723	121.601	1000	122.166	751	122.060	6.17
122.149	742	121.283	1067	122.187	728	122.140	5.66
122.130	761	120.692	1151	122.199	710	122.200	5.16
122.120	775	119.614	1252	122.211	698	122.220	4.85
122.096	790	118.379	1321	122.240	654	122.240	4.26
122.036	836			122.259	597		
				122.276	552		

$$F = \tfrac{1}{2} A P_z^2 + \tfrac{1}{2} C^{\mathcal{P}}_{66} u_{xy}^2 - a_{36} u_{xy} P_z \,,$$
$$\frac{\partial F}{\partial u_{xy}} = \sigma_{xy} = C^{\mathcal{P}}_{66} u_{xy} - a_{36} P_z \,. \qquad (1)$$

We can divide the variation of birefringence in a direct elasto-optic effect produced by the strain and in an indirect effect caused by the strain-induced polarization via the electro-optic effect. So

$$\delta(1/n^2) = \rho^{x}_{36} P_z + p^{\mathcal{P}}_{66} u_{xy} \,, \qquad (2)$$

where ρ^x_{36} is the electro-optic coefficient at constant strain and $p^{\mathcal{P}}_{66}$ is the elasto-optic coefficient at constant polarization. In our experiment $\sigma_{xy} = 0$. Then from Eqs. (1) and (2) the following relation between the birefringence and the shear angle is deduced:

$$\frac{\Delta n_{xy}}{u_{xy}} = n^3 \left(\rho^{x}_{36} \frac{C^{\mathcal{P}}_{66}}{a_{36}} + p^{\mathcal{P}}_{66} \right) .$$

Using the values published in the literature[8] we calculate

$$\Delta n_{xy} / u_{xy} = 1.52 \,.$$

This result is in good agreement with our experimental determination and confirms the temperature independence of this ratio during the phase transition. The values for the spontaneous polarization deduced from our measurements are in good agreement with those obtained by Benepe and Reese[1] using polaroelectrocaloric techniques. As shown in Refs. 1 and 6 it is possible to fit the experimental result to a Landau-type formula. Because this is a first-order transition, there is no point[10] in going further and looking for critical exponents.

CONCLUSION

We have demonstrated the interest of γ-ray diffractometry to investigate a certain type of structural phase transitions. The possibility of using fine temperature control and the good accuracy of angle measurements make this technique very promising for the study of critical phenomena. Unfortunately not all domain structures which appear at a transition point, e.g., those in quartz and triglycine sulfate (TGS), can be investigated. In the case of perovskites, because of the high number of twinning possibilities, this technique can be used. For $BaTiO_3$ (the discussion is the same for $SrTiO_3$) it will not be possible to distinguish between two c domains but an a domain will give rise to an effect.[9] In this connection it may be possible to study domain structures induced by magnetostriction in high symmetrical ferro or antiferromagnetics. We can say that γ-ray diffractometry will be useful whenever the domains are, in principle, optically distinguishable.

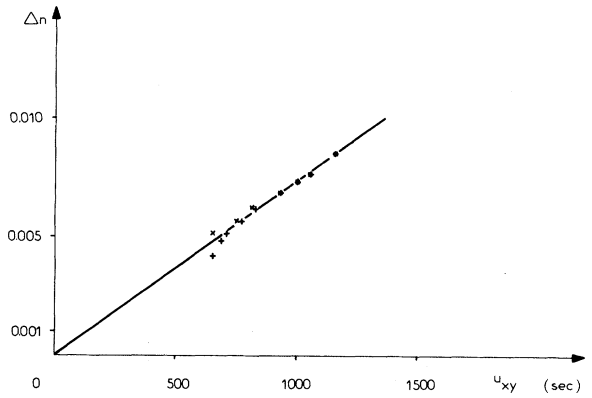

FIG. 4. Δn_{xy} vs u_{xy} for $T_c - T$ varying between 0 and 1.6 °K (+ increasing temperature, × decreasing temperature).

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