

$^{31}\text{P}$  NMR study of the influence of defects on the symmetry of ferroelectric crystals of  $\text{PbHPO}_4$  above the phase transition

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 1909

(<http://iopscience.iop.org/0953-8984/3/12/021>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 10/05/2010 at 23:00

Please note that [terms and conditions apply](#).

## **$^{31}\text{P}$ NMR study of the influence of defects on the symmetry of ferroelectric crystals of $\text{PbHPO}_4$ above the phase transition**

F Ermark and U Haerberlen

Max-Planck-Institut für Medizinische Forschung, Arbeitsgruppe Molekülkristalle, Jahn-Straße 29, 6900 Heidelberg, Federal Republic of Germany

Received 2 November 1990

**Abstract.** The width  $\delta\nu$  of the  $^{31}\text{P}$  NMR in  $\text{PbHPO}_4$  is found to be larger in the paraelectric than in the ferroelectric phase. We interpret this increase of  $\delta\nu$  as an unresolved splitting due to the persistence of the low temperature ferroelectric space group  $\text{Pc}$  in the high temperature paraelectric phase, where a centrosymmetric space group is expected. A comparison of  $\delta\nu$  in a crystal grown at ambient temperature, i.e. in the ferroelectric phase, and in a crystal growth at 313 K, i.e. in the paraelectric phase, shows that  $\delta\nu$  is smaller in the latter crystal. Annealing of this crystal resulted in a further decrease of  $\delta\nu$ . This leads us to the conclusion that polar defects in real crystals conserve, locally, the symmetry of the ferroelectric phase above the transition temperature  $T_c$  and that a crystal free of defects should change its symmetry at  $T_c$  as required by Landau's theory of structural phase transitions.

### **1. Introduction**

Lead hydrogen phosphate,  $\text{PbHPO}_4$ , forms hydrogen bonded ferroelectric crystals with a quasi one-dimensional structure (Nelmes and Chaudhary 1978). The second-order phase transition from the high temperature paraelectric (P) to the low temperature ferroelectric (F) phase at the transition temperature  $T_c = 310$  K is believed to be triggered by the ordering of the hydrogens in the O—H—O hydrogen bonds (Negran *et al* 1974). The phase transition displays an intriguing feature in that a variety of experimental techniques applied to  $\text{PbHPO}_4$  including second harmonic generation (SHG) (Keens and Happ 1988, Zgonik *et al* 1987) and  $^{31}\text{P}$  nuclear magnetic resonance (NMR) indicate that the monoclinic space group of the F phase,  $\text{Pc}$ , does not change at  $T_c$ . Note that, according to Landau's theory of second-order phase transitions a change to a higher symmetric space group, of which the low temperature space group is a subgroup, is required at  $T_c$ . For  $\text{PbHPO}_4$  the transition should be from  $\text{Pc}$  to the centrosymmetric space group  $\text{P2}/c$  (Negran *et al* 1974). The  $^{31}\text{P}$  NMR evidence for the persistence of  $\text{Pc}$  symmetry in the P phase is based on measurements of the  $^{31}\text{P}$  NMR linewidth which was found to be larger in the P than in the F phase (Ermark *et al* 1989, hereafter referred to as I). In what follows we shall refer to the increment of the  $^{31}\text{P}$  NMR linewidth in the P phase compared with that in the F phase as *excess width*. In I we speculated that the persistence of  $\text{Pc}$  symmetry in the P phase is due to the presence of an inhomogeneous internal biasing field originating in polar defects. The polar defects are thought to be at

the centre of domains in which the hydrogen bonds are *asymmetric* in a uniform direction but with decreasing degree of asymmetry towards the domain boundary. Note that for  $T > T_c$  the O—H—O hydrogen bonds must be *symmetric* if the space group of the unperturbed crystal is indeed P2/c. Disregarding the spatially varying degree of asymmetry of the hydrogen bonds that destroys translational symmetry, the space group within a domain is Pc. For a general orientation of a PbHPO<sub>4</sub> crystal relative to the static field  $B_0$  and assuming Pc symmetry, the <sup>31</sup>P NMR is split into two components. A distribution of unresolved splittings has been proposed in I as the origin of the observed *excess width* of the <sup>31</sup>P NMR in the P phase of the PbHPO<sub>4</sub>.

The crystal specimen investigated in I was grown in the F phase, i.e. in the presence of a biasing field (the field accompanying the spontaneous polarization). In what follows this crystal will be referred to as the *F crystal*. It is natural to assume that defects incorporated in *F crystals* tend to become polarized. If this is actually so and if the explanation outlined above for the *excess width* of the <sup>31</sup>P NMR in the P phase is correct a crystal grown in the P phase, hereafter referred to as the *P crystal*, should contain fewer polar defects and the evidence of Pc symmetry, i.e. the amount of the *excess* <sup>31</sup>P NMR width, in the P phase of a *P crystal* should be weaker than in a *F crystal*.

It is the purpose of this paper to report on a test of this idea. Single crystals of PbHPO<sub>4</sub> grown at 313 K, i.e. in the P phase, were kindly provided by H Happ of the University of Cologne. The experimental results to be described below *are* in accordance with this idea. This is strong support for the assertion that the space group of a crystal of PbHPO<sub>4</sub> that is free of any defects indeed changes at  $T_c$  from Pc to P2/c. In a further effort to reduce the concentration of defects we additionally subjected the *P crystal* to a heat treatment as proposed by Nakatani (1987).

## 2. Experimental procedure and results

The single crystals of PbHPO<sub>4</sub> provided by H Happ were grown at 313 K and are of excellent optical quality. The specimen selected for this experiment measures  $7 \times 3 \times 1.6$  mm. A set of natural growth planes could easily be identified as (010), (110) and (011) planes by measuring the angles between them with an optical goniometer. This information was used to give the crystal a definite orientation in the magnetic field  $B_0$ , see below.

The experimental set-up was the same as that used in I. We detect the <sup>31</sup>P free induction decay (FID) after applying a  $\pi/2$ -pulse (duration  $4 \mu\text{s}$ , carrier frequency 109.29 MHz) while simultaneously decoupling the protons using a 10 W cw-irradiation at their Larmor frequency of 270 MHz. The spectrum is obtained by Fourier transforming the FID.

The first set of measurements was carried out on the virgin specimen, i.e. prior to any heat treatment. The orientation of the crystal was chosen such that  $B_0$  was lying in the *ab*-plane of the crystal, midway between *a* and *b*. For this crystal orientation the <sup>31</sup>P NMR line splitting deep in the F phase is largest (see [I]). Starting at room temperature in the F phase we measured the temperature dependences of the splitting  $\Delta\nu$  and of the width  $\delta\nu$  of the <sup>31</sup>P resonances, and in the P phase we measured the temperature dependence of  $\delta\nu$  up to 353 K. Line positions and widths (FWHM) were determined by least squares fitting the spectra to two Gaussians for  $T < T_c$ , and to one gaussian for  $T > T_c$ .

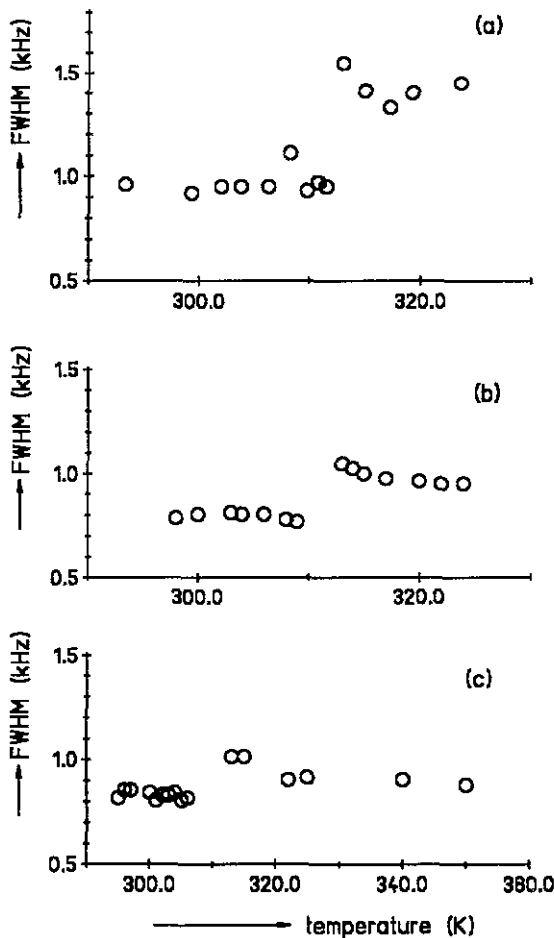


Figure 1. Temperature dependence of the line width (FWHM)  $\delta\nu$  of the  $^{31}\text{P}$  NMR in  $\text{PbHPO}_4$ : (a) crystal grown in the ferroelectric phase, reproduced from I, (b) virgin crystal grown in the paraelectric phase, and (c) after annealing of the latter crystal at a temperature of 483 K.

In figure 1 we show the temperature dependences of  $\delta\nu$  of the *virgin P crystal* (b) together with analogous data of the *F crystal* (a) from reference I. The line width  $\delta\nu$  in both crystals is constant in the F phase, increases essentially in steps at  $T_c$  and remains again constant over the whole temperature range explored in the P phase. The decisive point is that the increase of  $\delta\nu$  at  $T_c$  is about 40% for the *F crystal* while it is only 18% for the *P crystal*. As stated in the introduction, this result supports the idea that the *excess width* observed in the P phase is due to polarized domains around polar defects, and that the number (and size) of these domains can be reduced by growing the crystal in the absence of a biasing field, i.e. in the P phase.

In a second series of measurements we applied the heat treatment proposed by Nakatani (1987) to the *virgin P crystal*. The following steps were performed:

- (i) slow heating up to 483 K in an oven;
- (ii) held at  $T = 483$  K for 4 h;
- (iii) slow cooling down to room temperature, transfer of the crystal to the NMR probe;

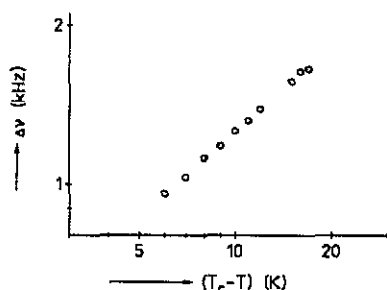


Figure 2. Log-log plot of the  $^{31}\text{P}$  NMR line splitting  $\Delta\nu$  in the ferroelectric phase against  $(T_c - T)$  of the annealed crystal grown in the paraelectric phase. The slope of  $\log \Delta\nu$  corresponds to the critical exponent of the order parameter  $p$  and is  $\beta = 0.53 \pm 0.05$ .

- (iv) heating inside the probe to 353 K and
- (v) recording  $^{31}\text{P}$  NMR spectra with slowly decreasing temperature.

Figure 1(c) shows the width of the  $^{31}\text{P}$  NMR resonances obtained in this run. As expected the heat treatment resulted in a decrease of  $\delta\nu$  in the P phase from  $\delta\nu = 960$  Hz in the virgin to  $\delta\nu = 900$  Hz in the annealed P crystal, which amounts to a decrease of the excess width from 150 Hz to 90 Hz. This strengthens our point that the excess width is a consequence of defects and demonstrates that these defects can be removed at least partially by annealing the specimen. We should point out, however, that annealing has only a small effect on the excess width which is not surprising as this excess width, conspicuous in the F crystal, is already much smaller in the virgin P crystal.

As stated in I the temperature dependence of the line splitting  $\Delta\nu$  of the  $^{31}\text{P}$  NMR in the F phase of  $\text{PbHPO}_4$  is proportional to the order parameter  $p$ . This allows us to extract the critical exponent  $\beta$  from a measurement of the temperature dependence of  $\Delta\nu$ . Defects and polarized domains in the P phase interfere, however, with the measurement of  $\beta$ : a consequence of their presence is that there is no sharply defined transition temperature  $T_c$ . This leads to a systematic error when  $\beta$  is extracted from experimental data. It will be the larger the higher the concentration of defects in the crystal. For this reason we only determined  $\beta$  for the annealed specimen where the concentration of polar defects is smallest. Figure 2 shows the temperature dependence of  $\Delta\nu$  below  $T_c$  on a doubly logarithmic scale. The fact that the data fall on a straight line for  $T_c > T > T_c - 17$  K demonstrates that the temperature dependence of  $\Delta\nu$  can indeed be represented by  $\Delta\nu(T) = \Delta\nu_0(1 - T/T_c)^\beta$ . From the slope of the straight line in figure 2 and of the scatter of the data points we infer  $\beta = 0.53 \pm 0.05$ , consistent with our previous  $^{207}\text{Pb}$  NMR result (Topič *et al* 1986) and with the results of Seliger *et al* (1983) and Smutny and Fousek (1978). According to Landau's theory of phase transitions  $\beta = 0.5$  corresponds to a phase transition in a three-dimensional system. It seems to be at variance with the idea that  $\text{PbHPO}_4$  is a quasi one-dimensional system. We think that the resolution of this apparent contradiction is contained in the idea that the para-ferroelectric phase transition in  $\text{PbHPO}_4$  consists actually in a sudden growth of already existing domains with polar defects at their centres rather than in an ordering of H-bonds along chains. The former event is a three-dimensional one, the latter would be essentially a one-dimensional phenomenon, which is not consistent with  $\beta = 0.5$ .

Measurements of the  $^{31}\text{P}$  spin lattice relaxation time  $T_1$  for  $T > T_c$  and  $T < T_c$  indicated no critical behaviour at  $T_c$ . The main observed effect is an increase of  $T_1$  from about 50 s to about 150 s at room temperature after annealing the specimen. This shows that defect-induced relaxation is significant for the  $^{31}\text{P}$  nuclei. This relaxation path appears to be stronger than that induced by critical fluctuations near  $T_c$ .

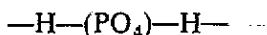
Dielectric measurements on  $\text{PbHPO}_4$  suggested that keeping an annealed crystal deeply in the F phase for an extended period leads to a stabilization of existing defects and, possibly, to the formation of new ones (Nakatani 1987). For restoring the low concentration of defects present immediately after the first annealing cycle it is, according to Nakatani (1987), sufficient to heat the crystal subsequently up to only about 353 K. It is not necessary to anneal the crystal again at  $T \approx 483$  K. To find out whether this defect behaviour can also be seen by  $^{31}\text{P}$  NMR we run a third series of measurements of the width  $\delta\nu$  on the previously annealed P crystal. Starting from room temperature the crystal was heated up to 353 K, then the temperature was lowered to 294 K.  $^{31}\text{P}$  spectra were recorded for both rising and falling temperature. These measurements were carried out three months after the first two runs. In the meantime the crystal was kept at room temperature. The results are as follows: the  $^{31}\text{P}$  line width  $\delta\nu$  in the F phase was  $\delta\nu = 781 \pm 15$  Hz, i.e. within the experimental error which is the same as that for the virgin crystal. In fact it was somewhat less than in the F phase immediately after annealing, where the value was  $\delta\nu = 826 \pm 19$  Hz. In the P phase both for rising and falling temperature  $\delta\nu$  was found to be  $\delta\nu = 903 \pm 12$  Hz and thus equal to the width found immediately after annealing:  $\delta\nu = 898 \pm 11$  Hz. The absence of any hysteresis of the  $^{31}\text{P}$  NMR width above  $T_c$  means that stabilization and formation of new polar defects by keeping the crystal in the F phase for an extended period of time cannot be detected by  $^{31}\text{P}$  NMR. It should be stressed that this finding does not rule out the phenomenon of stabilization and formation of polar defects in the F phase since other experimental techniques such as the dielectric one may well be more sensitive probes for polar defects than is the width of the  $^{31}\text{P}$  NMR.

### 3. Summary and conclusions

On the lowest level of conclusions we have demonstrated that the *excess width* of the  $^{31}\text{P}$  NMR in the P phase of  $\text{PbHPO}_4$  reported in I is *not an intrinsic property of the crystal*. The way it depends on the conditions of the growth of the crystal, and how it is influenced by heat treatment allows, on the next level, the conclusion that the *excess width* is related to *defects*. On the third level, the nature of the link between defects and the *excess width* of the  $^{31}\text{P}$  NMR in the P phase is established: as shown in I the dependence of the *excess width* on the orientation of the crystal relative to the applied field  $B_0$  matches that of the  $^{31}\text{P}$  NMR *line splitting*  $\Delta\nu$  in the F phase. The inference is that Pc persists in the P phase and that the observed *excess width* in this phase actually reflects a distribution of unresolved splittings. The combination of this result with the role of defects established in this work leads naturally to the idea of *domains* with local Pc symmetry which are induced by *polar* defects.

We point out that evidence for the persistence of the low temperature symmetry in the high temperature phase of ferroelectrics is not restricted to  $\text{PbHPO}_4$ : Bjorkstam (1990) has reported the observation of  $^{75}\text{As}$  quadrupole splittings in  $\text{KH}_2\text{AsO}_4$  which are characteristic of the symmetry of the ferroelectric phase. He observed these splittings for  $T$  as high as  $3T_c$  and came to the conclusion that the domains with ferroelectric symmetry are formed *spontaneously* and are not induced by defects. In TGS, on the other hand, a dependence of the sharpness of the phase transition on whether the crystal was grown in the ferroelectric or in the paraelectric phase indicates that in the paraelectric phase TGS, like in  $\text{PbHPO}_4$ , domains with the symmetry of the low temperature ferroelectric phase exist (Strukov and Yakushkin 1978).

From the measured critical exponent  $\beta = 0.53 \pm 0.05$  characterizing the phase transition we may infer that the domains do not extend only along chains of the type



as the quasi-one-dimensional nature of  $\text{PbHPO}_4$  might suggest, but extend in fact, in three dimensions. From the constancy of the *excess width* it follows that the size of these domains hardly changes in the P phase, at least up to 353 K, which is the highest temperature at which we have taken spectra.

The final and most important conclusion is that the phase transition of a crystal of  $\text{PbHPO}_4$  which is free of any defects is undoubtedly accompanied by a change in symmetry of the space group as is expected according to theory.

### Acknowledgment

We wish to express our thanks to Professor H Happ of the University of Cologne for providing us with high-quality  $\text{PbHPO}_4$  crystals grown at 313 K and to Professor R Blinc of the University of Ljubljana, Yugoslavia, for suggesting this kind of experiment.

### References

- Bjorkstam J L 1990 *Proc. 25th Ampere Congress (Stuttgart)* ed M Mehring, J U von Schütz and H C Wolf (Berlin: Springer) pp 388-9
- Ermark F, Topic B, Haerberlen U and Blinc R 1989 *J. Phys.: Condens. Matter* **1** 5489-96
- Keens A and Happ H 1988 *J. Phys. C: Solid State Phys.* **21** 1661-71
- Nakatani N 1987 *J. Phys. Soc. Japan* **56** 2542-8
- Negran T J, Glass A M, Brickenkamp C S, Rosenstein R D, Osterheld R K and Susott R 1974 *Ferroelectrics* **6** 179-82
- Nelmes R J and Chaudhary R N P 1978 *Ferroelectrics* **21** 467-8
- Seliger J, Zager V and Blinc R 1983 *Phys. Lett.* **93A** 149-51
- Smutny F and Fousek J 1978 *Ferroelectrics* **21** 385-6
- Strukov B A and Yakushkin E D 1978 *JETP Lett.* **28** 14-7
- Topič B, Haerberlen U, Blinc R and Arend H 1986 *J. Phys. C: Solid State Phys.* **19** 3925-32
- Zgonik M, Čopič M and Arend H 1987 *J. Phys. C: Solid State Phys.* **20** L565-9