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³¹P NMR study of the ferroelectric phase transition in PbHPO₄

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Abstract. The ³¹P chemical shift tensors were measured in the para-electric (P) and ferroelectric (F) phases of PbHPO₄. They reflect the approximate C_{2v} and C₃ point symmetries of the ³¹P sites in the P and F phases of the crystal. The transition from C_{2v} to C₃ is the result of a proton ordering in double-well potentials below the phase transition temperature. In the P phase the width of the proton decoupled ³¹P-resonances is larger than in the F phase, and the orientation dependence of the excess width is clearly correlated with that of the ³¹P line splittings in the F phase. This finding is interpreted as giving evidence that the Pc-space-group symmetry of the F phase persists in the P phase. We believe that this is due to the presence of a homogeneous internal biasing field—produced by oriented defects with a non-zero charge and dipole moment—which breaks the symmetry of the high temperature phase in a similar way to an external electric field. The orientation of these defects is due to the fact that the crystal was grown in the ferroelectric phase.

1. Introduction

In 1974 lead hydrogen phosphate, PbHPO₄, was shown to become ferroelectric at $T_c = 310$ K (Negran *et al* 1974). Owing to its simple structure it subsequently became a favourite subject for the study of paraelectric–ferroelectric phase transitions in hydrogen-bonded systems. From the first structural investigations it was concluded that the space group of the F phase is Pc while the space group of the P phase was assumed to be P2/c. Figure 1 shows a projection of PbHPO₄ on the *ac* plane which is a glide plane of both space groups. The most striking feature of this structure is the presence of sheets of zig-zag chains of hydrogen-bonded PO₄ groups separated by sheets of lead ions. The presence of hydrogen bonds within the chains and the absence of any bonds between neighbouring chains renders PbHPO₄ a highly one-dimensional system. The driving mechanism of the phase transition is assumed to be the ordering of the protons in double-well potentials below T_c , whereas above T_c the two possible sites appear to be occupied equally.

Despite its simple structure, however, PbHPO₄ is not a simple system at all. After 14 years of experimental and theoretical work we rather feel that with PbHPO₄ nature has provided us with a crystal possessing an exceptionally simple structure but undergoing a complex phase transition of which even some basic aspects have remained the subject

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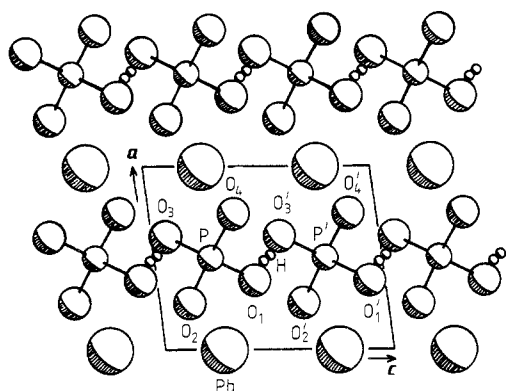


Figure 1. Projection of the atomic arrangement of PbHPO_4 on the ac plane. This plane is a glide plane of the space group.

of controversy. The centrosymmetric initially proposed structure for the P phase has, in fact, never been confirmed by subsequent structural studies. In addition to x-ray and neutron scattering, PbHPO_4 has recently been studied by Raman, hyper-Raman, IR, second-harmonic generation and NMR techniques. Some authors state that the space group of PbHPO_4 remains Pc above T_c (Happ *et al* 1985, Ohno *et al* 1987, Lockwood *et al* 1987), whereas others conclude from their experiments that it changes to $P2/c$ (Zgonik *et al* 1987, Shin *et al* 1988). Our own ^{207}Pb NMR data (Topič *et al* 1986, hereafter referred to as I) indicate a change in symmetry at T_c from Pc to $P2/c$. The nature of the bonding of the lead ions is predominantly ionic and couples them mainly to the PO_4 groups, and very little to the hydrogens. On the other hand, the coupling of the phosphorous atoms to their ligands is partly covalent and thus very sensitive to the formation of symmetric or asymmetric hydrogen bonds between the oxygens. This may be the reason why the P phase appears to possess $P2/c$ symmetry when judged by the shielding tensor of the lead nuclei. By the same token the shielding of the phosphorous nuclei should be a much more sensitive probe for the distribution of the hydrogens along the hydrogen bonds. This study shows that this is true despite the fact that the magnetic shielding of the electron-rich ^{207}Pb nuclei is intrinsically a much larger effect than that of the ^{31}P nuclei. This motivated us to study the temperature and orientation dependences of the magnetic shielding of the ^{31}P nuclei in PbHPO_4 . They sit in the centres of highly symmetric PO_4 groups. In the roughest approximation their site symmetry is tetrahedral in both the F and P phase which implies zero shielding anisotropy. In the next approximation it is C_{2v} in the P phase since two of the coordinating oxygens are hydrogen bonded and two are not. C_{2v} allows a non-zero anisotropy of the ^{31}P shielding tensor σ , but because of the underlying tetrahedral symmetry it remains small. If the C_{2v} site symmetry were exact it would completely fix the orientation of the principal axis system of σ . However, it is broken by the orientation of the hydrogen bonds and a twofold axis is the only genuine symmetry element left by the environment of the PO_4 tetrahedra. If the spacegroup is truly $P2/c$ in the P phase, the two phosphorous ions in the unit cell are magnetically equivalent and the ^{31}P NMR spectrum consists of a single line. In the F phase the hydrogen bonds become asymmetric, the ^{31}P nuclei in the unit cell become magnetically inequivalent and the NMR spectrum consists of two lines. Far below T_c the phosphorous ions are coordinated by three oxygens and one hydroxyl group, O–H. The approximate ^{31}P local site symmetry becomes C_3 instead of C_{2v} . This change manifests itself in a reorientation of σ^{P} .

Whether or not the predicted pair of lines in the F phase is really observable in an NMR spectrum depends on the ratio of the chemical shift difference of the two inequivalent ^{31}P

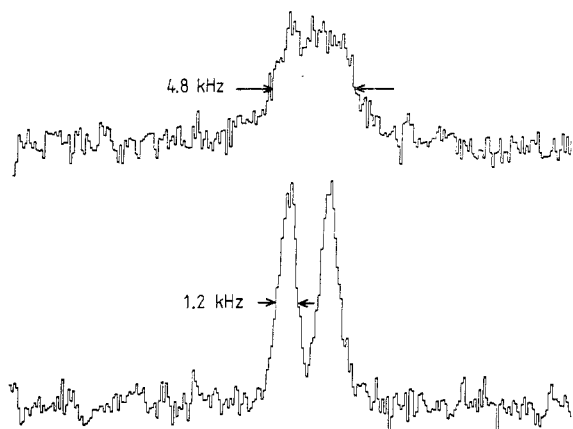


Figure 2. ^{31}P spectrum of PbHPO_4 at $T = 295\text{ K}$ and $\nu_0 = 109.3\text{ MHz}$ without (top) and with proton decoupling (bottom).

nuclei to the width of the lines. Preliminary experiments in Ljubljana have shown that the natural width of the lines is too broad to allow their resolution. In this work we therefore decouple the ^{31}P nuclei from the protons by applying a strong RF irradiation at the Larmor frequency of the protons during observation of the ^{31}P NMR. The remaining linewidth is due to the ^{31}P - ^{31}P and ^{31}P - ^{207}Pb dipole-dipole coupling. It is small enough to allow resolution of the ^{31}P lines in the F phase. In the P phase an excess linewidth but no line splitting is observed. As there is no reason for a sudden broadening of the lines at T_c , we interpret it as an unresolved line splitting giving evidence of a conservation of the space group Pc even above T_c . Whether there is one definite line splitting or a continuous distribution of unresolved line splittings over the sample crystal remains an open question.

2. Experimental procedure

The same crystal of PbHPO_4 as in I was used. For proton decoupling a single-coil, double-tuned probe was built with resonance frequencies $\nu_P = 109.29\text{ MHz}$ and $\nu_H = 270\text{ MHz}$, ν_P and ν_H being the Larmor frequencies of the ^{31}P and ^1H nuclei in a field of magnitude $B_0 = 6.4\text{ T}$. Due to the 'large' ^{31}P - ^1H distance of 2.3 \AA , a decoupling power of about 20 W at ν_H was sufficient to suppress the ^{31}P - ^1H dipole-dipole coupling. Figure 2 shows two ^{31}P spectra of PbHPO_4 , one with and one without proton decoupling. As can be seen, decoupling of the protons results in a reduction of the ^{31}P NMR linewidth by about a factor of four and the two expected lines in the F phase can be resolved clearly. The ^{31}P free induction decay (FID) was detected after excitation by a $\pi/2$ pulse of 4 \mu s duration and was Fourier transformed subsequently. Some tens of degrees both above and below T_c the spin lattice relaxation time T_1 is of the order of 300 s . Because of this rather long time we accumulated only 3 to 5 FIDs for each spectrum.

To measure the ^{31}P shielding tensor, chemical shift rotation patterns were recorded for three rotation axes x , y and z with x and y parallel to the crystallographic a and b axes, respectively, and $z \perp a, b$. The ^{31}P NMR line of a sample of about 85% saturated solution of H_3PO_4 served as shift reference.

3. Results and discussion

Figure 3 shows the angular dependence of the ^{31}P chemical shifts for $T = 316\text{ K}$ (P phase) and for $T = 213\text{ K}$ (F phase) where the saturation of the line splitting occurs. The full

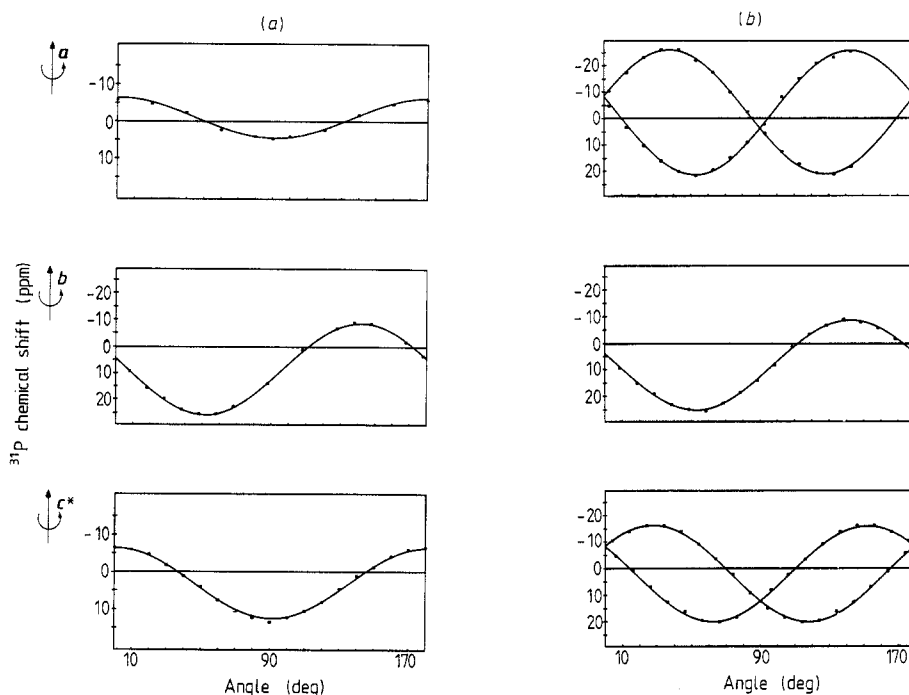


Figure 3. Angular dependence of the ^{31}P chemical shifts in PbHPO_4 (a) at $T = 316$ K assuming $P2/c$ symmetry and (b) at $T = 213$ K. The shifts are given relative to an 85% saturated solution of H_3PO_4 . The symbols at the left indicate the axis about which the crystal has been rotated. This axis is perpendicular to the applied field B_0 . At zero rotation angle B_0 is parallel to b , c^* and b , respectively, for the plots with $B_0 \perp a$, b and c^* .

curves correspond to least-squares fits of the data to symmetric second-rank tensors. These tensors are listed in table 1 in which data obtained at other temperatures are also included. We have first processed the data from the P phase under the assumption of the centrosymmetric spacegroup $P2/c$. One of the principal axes of σ^{P} is, consequently, parallel to the crystal b axis; it is associated with the intermediate principal component, σ_{22} . The indices P and, later on, F refer to the P and F phases. As expected, the orientation of the other two principal axes of σ^{P} conforms essentially to the approximate C_{2v} site symmetry of the ^{31}P nuclei: the angle between the least (most) shielded direction of the ^{31}P nuclei and the projection of the $\text{O}_2\text{-P-O}_4$ ($\text{O}_3\text{-P-O}_1$) bonds onto the ac plane is only 5° . This is illustrated in figure 4.

In the F phase with spacegroup Pc the ^{31}P nuclei sit on general positions and no symmetry restrictions are imposed on the σ^{F} tensors. However, the P-O_1 bond is now unique among the four P-O bonds because a proton is now closer to O_1 than to O_3 which implies an increased P-O_1 bond length. This is true, in particular, for $T \ll T_c$. The σ^{F} -tensor reflects this situation: the P-O_1 direction is close to a principal shielding direction which turns out to be the least shielded one. It is important to note that the change in orientation of σ^{P} on going through the phase transition is essentially jumpwise. On the other hand, the principal values of σ^{F} change continuously in the F phase. The lower the temperature the smaller σ_{11} becomes and the closer σ_{22} moves to σ_{33} , that means σ^{F} becomes more and more axially symmetric. This reflects the approximate C_3 site symmetry of the ^{31}P nucleus at $T \ll T_c$.

The variation with temperature of the anisotropic part of σ^{P} can be accounted for by the following model in which the shielding of the ^{31}P nucleus, ignoring $\sigma_{\text{isotropic}}$, is

Table 1. Eigenvalues and directions of the ^{31}P chemical shift tensors σ^{P} in PbHPO_4 above and below T_c . The shifts were measured relative to an 85% solution of H_3PO_4 . The directions are in polar coordinates of the standard orthonormal system (x, y, z) which is related to the crystals' orthonormal system (a, b, c^*) in the following way: $x \parallel a, y \parallel b, z \parallel c^*$.

Temperature phase and symmetry	Component	Eigenvalue (ppm)	Principal directions	
			ϑ (deg)	φ (deg)
$T = 316$ K Para-electric Assuming P2/c	σ_{11}	-8.5	38.4	180.0
	σ_{22}	-6.0	90.0	90.0
	σ_{33}	24.9	51.5	0
$T = 316$ K Assuming Pc	σ_{11}	-14.4	53.3	125.7
	σ_{22}	0.02	121.3	62.6
	σ_{33}	24.6	52.3	0.6
$T = 296$ K Ferroelectric phase Pc	σ_{11}	-21.2	53.8	124.8
	σ_{22}	8.0	120.4	60.3
	σ_{33}	24.5	51.0	358.7
$T = 213$ K Ferroelectric phase Pc	σ_{11}	-34.7	54.8	120.5
	σ_{22}	17.6	114.1	48.9
	σ_{33}	24.7	44.9	345.7

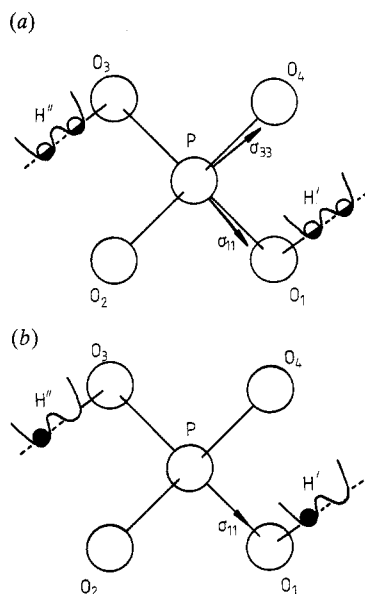


Figure 4. Occupation on the time scale of the ^{31}P NMR experiment of the hydrogen bond double-well potentials of the hydrogens and orientation of the ^{31}P shielding tensor in PbHPO_4 : (a) in the para-electric phase assuming P2/c symmetry with $\overline{\text{PO}}_1 = \overline{\text{PO}}_3 = 1.55 \text{ \AA}$, $\overline{\text{PO}}_2 = \overline{\text{PO}}_4 = 1.53 \text{ \AA}$; (b) in the ferroelectric phase with $\overline{\text{PO}}_1 = 1.57 \text{ \AA}$, $\overline{\text{PO}}_2 = 1.54 \text{ \AA}$, $\overline{\text{PO}}_3 = 1.53 \text{ \AA}$, $\overline{\text{PO}}_4 = 1.51 \text{ \AA}$. The projection is the same as in figure 1. The ^{31}P principal shielding directions in the P phase are in the plane of the projection, and perpendicular to it. In the F phase the principal direction associated with σ_{11} is essentially along the P-O₁ bond.

considered to be the sum of four tensorial temperature-dependent contributions $T_i(T)$ which are induced by the coordinating oxygens O_i , $i = 1, \dots, 4$, $\sigma^{\text{m}}(T) = \sum_{i=1}^4 T_i(T)$.

Each T_i is assumed to be traceless and axially symmetric about the respective P-O_{*i*} bond. The unique principal value will be denoted by $T_{\parallel i}$. This model corresponds to the point-dipole model of intermolecular shielding (Aravamudhan *et al* 1979), but we must be aware that the numbers for the $T_{\parallel i}$ which are obtained from a point-dipole calculation are inappropriate in accounting for σ^{P} in the present situation since any chemical

Table 2. Eigenvalues and directions of the traceless part of the ^{31}P chemical shift tensors σ^m calculated according to the model described in the text. The directions refer to the same coordinates as in table 1.

Phase and symmetry	Component	Eigenvalue (ppm)	Principal directions	
			ϑ (deg)	φ (deg)
Para-electric phase Assuming P2/c	σ_{11}	-11.9	35.5	180
	σ_{22}	-9.4	90	90
	σ_{33}	21.5	54.4	0
Ferroelectric phase $p = 1, \Delta T_{\parallel} = 12.3$ ppm	σ_{11}	-28.1	53.0	121.6
	σ_{22}	6.6	122.4	60.2
	σ_{33}	21.5	53.7	357.9
Ferroelectric phase $p = 1, \Delta T_{\parallel} = 19.8$ ppm	σ_{11}	-36.7	53.4	120.8
	σ_{22}	15.1	119.7	55.9
	σ_{33}	21.6	50.8	353.7

bonding is disregarded. We shall treat the $T_{\parallel i}$ as adjustable parameters. For the P phase it is reasonable to assume $T_{\parallel 1} = T_{\parallel 3} = T_{\parallel b}$ (b stands for hydrogen bonded oxygen) and $T_{\parallel 2} = T_{\parallel 4} = T_{\parallel n}$ (n for non-bonded oxygen). The labelling of the oxygens is as shown in figure 1. The bond directions are derived from the data of Restori *et al* 1987.

The model tensor σ^m is fitted to σ^P by minimising $\sum_{i,j=1}^3 (\sigma_{ij}^m - \sigma_{ij}^P)^2$ using $T_{\parallel n}$ and $T_{\parallel b}$ as fit parameters for which the best values turned out to be 165.3 and 153 ppm, respectively. The principal values and directions of σ^m are shown in table 2. The agreement with σ^P is quite good. In order to test the influence of the geometry and of the difference $T_{\parallel n} - T_{\parallel b}$ on σ^m we also calculated a model tensor with the correct geometry but setting $T_{\parallel 1} = T_{\parallel 2} = T_{\parallel 3} = T_{\parallel 4} = (T_{\parallel b} + T_{\parallel n})/2$. It turned out that the agreement between the orientations of the calculated and experimental principal axes remained good, but the principal values of σ^m diverged from the experimental ones. We conclude that the directions of the P-O_{*i*} bonds to a large degree fix the orientation of the phosphorous shielding tensor whereas subtle differences of the bond lengths and bond covalencies dominate its principal values.

To describe the phosphorous shielding in the F phase we keep $T_{\parallel 2} = T_{\parallel 4}$ independent of T and equal to $T_{\parallel n} = 165.3$ ppm as in the P phase, whereas we assume $T_{\parallel 1}(T) = T_{\parallel b} + \Delta T_{\parallel} p(T)$ and $T_{\parallel 3}(T) = T_{\parallel b} - \Delta T_{\parallel} p(T)$, where $p(T) = p_1(T) - p_3(T)$ is the difference of the fractional hydrogen populations in the potential wells near the oxygens O₁ and O₃, and is thus the natural order parameter. Since in the limiting case $p = 1$ we expect $T_{\parallel 3} = T_{\parallel n}$, we should set ΔT_{\parallel} equal to $T_{\parallel n} - T_{\parallel b} = 12.3$ ppm. The model tensor obtained for $\Delta T_{\parallel} = 12.3$ ppm and $p = 1$ is also shown in table 2 and may be compared with $\sigma^F(T = 213 \text{ K})$. The agreement is fair with respect to the tensor orientation, the tendency towards axial symmetry found in the experiment is also reproduced; however, a much better agreement between model and experimental shielding tensor is obtained by choosing $\Delta T_{\parallel} = 19.8$ ppm (see table 2). The need to adjust ΔT_{\parallel} shows, on the one hand, the limitations of the model and must be taken, on the other hand, as a warning against identifying uncritically normalised NMR line shifts or line splittings with order parameters. Nevertheless, measuring $\sigma^F(T)$ and fitting it to a model tensor with fixed parameters $T_{\parallel n}$, $T_{\parallel b}$ and ΔT_{\parallel} and using $p(T)$ as fit parameter would still be the most reliable way to determine the temperature dependence of the order parameter $p(T)$.

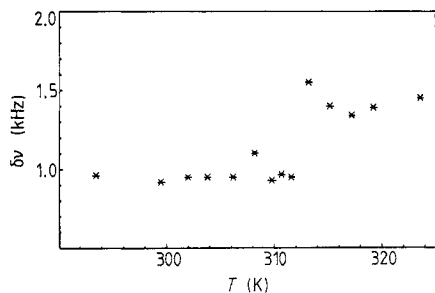


Figure 5. Temperature dependence of the width $\delta\nu$ of the ^{31}P lines.

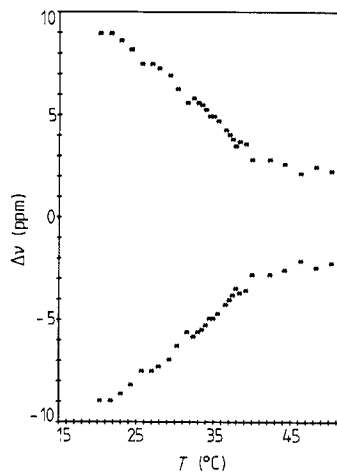


Figure 6. Temperature dependence of the ^{31}P line splitting in the ferro- and para-electric phases of PbHPO_4 assuming Pc symmetry in both phases.

by NMR. This procedure implies, however, unjustified expense in measuring time. Therefore, we selected instead the crystal orientation with the largest line splitting in the F phase and recorded the temperature dependence of the line splitting $\Delta\nu$.

To extract $\Delta\nu$ from the spectra we fitted them to two Gaussians in the F phase and (initially) to one Gaussian in the P phase. Height, width $\delta\nu$ and splitting $\Delta\nu$ of the Gaussians were fit parameters. The results with regard to $\Delta\nu(T)$ for $T < T_c$ were, apart from a trivial scaling factor, essentially the same as obtained in I for the ^{207}Pb nuclei and are therefore not reproduced here.

The widths $\delta\nu(T)$ of the Gaussians contained a surprise: in the F phase they are constant until T_c , then there is a clear jump and in the P phase $\delta\nu$ is about 40% larger than in the F phase (see figure 5). As we cannot see any reason why the homogeneous width of the ^{31}P resonance should increase at T_c , we suspect that the excess width represents inhomogeneous broadening reflecting persistence of Pc symmetry in the P phase. We subjected this hypothesis to two tests:

(i) first, we measured the temperature dependence of the ^{31}P linewidth for $\mathbf{B}_0 \parallel \mathbf{a}$, i.e., for an orientation where the two traces in the chemical shift rotation pattern of the F phase cross. For this case a persistence of Pc symmetry into the P phase will cause no excess line broadening. The result of the experiment is that the linewidths for T above and below T_c are equal to each other within the accuracy of measurement.

(ii) Second, we asked the computer to fit the ^{31}P spectra from the P phase with the linewidths fixed to their values in the F phase and to try to compensate the excess broadening by a line separation $\Delta\nu$. The results were systematic in the sense that the angular dependence of $\Delta\nu$ definitely followed the trend of the resolved line splittings in the F phase. Taking the orientation dependence of $\Delta\nu$ obtained by this procedure and fitting it to second-rank tensors produced two symmetry related σ^{P} tensors for the P phase whose orientations were practically equal to those of the σ^{F} tensors in the F phase recorded at $T = 296 \text{ K}$ (see table 1).

In figure 6 we present a plot of $\Delta\nu$ against T for the crystal orientation with the maximum splitting in the F phase. It demonstrates that it would be futile to try to extract a critical exponent from the ^{31}P NMR line-splitting data. We recognise that the residual

line splitting $\Delta\nu$ in the P phase amounts to 18% of the line splitting in the F phase for $T \ll T_c$. For comparison we cite Ohno and Lockwood (1978) who report that the intensities of Raman lines in the P phase which would be zero under P2/c symmetry, remain at about 30% of their values at $T \ll T_c$.

Instead of fitting the spectra to the two Gaussians with variable splitting $\Delta\nu$ and fixed width $\delta\nu$, we could equally well have postulated a Gaussian distribution of line splittings and fixed widths. The width of the distribution would then have been the fit parameter and it would have followed the same trends as $\Delta\nu$. Regardless of whether the splitting of the lines in the P phase is discrete or continuous we must conclude that the non-centrosymmetric spacegroup Pc persists into the P phase of PbHPO₄. We point out that this statement is based on measurements on one single crystal of PbHPO₄. The temperature range explored extended to 55 °C. For fear of destroying the practically irreplaceable crystal we did not subject it to a thermal treatment like that of Nakatani (1987).

We believe that the persistence of the ferroelectric Pc symmetry in the P phase is due to the presence of an internal biasing field produced by oriented defects with a non-zero charge and dipole moment. This field breaks the symmetry of the high temperature phase in a similar way to an external electric field. The orientation of these defects is due to the fact that the crystal was grown in the ferroelectric phase. A similar effect has been seen in tri-glycine sulphate doped with β -alanine when the crystals are grown below T_c . The viewpoint that the persistence of Pc symmetry deeply into the P phase is due to defects has been upheld by Zgonik *et al* (1987) and Nakatani *et al* (1987). Experiments with crystals grown in the P phase should definitely clear up this problem.

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