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## Pressure dependence of the crystal structure of lead hydrogen phosphate (PbHPO<sub>4</sub>)

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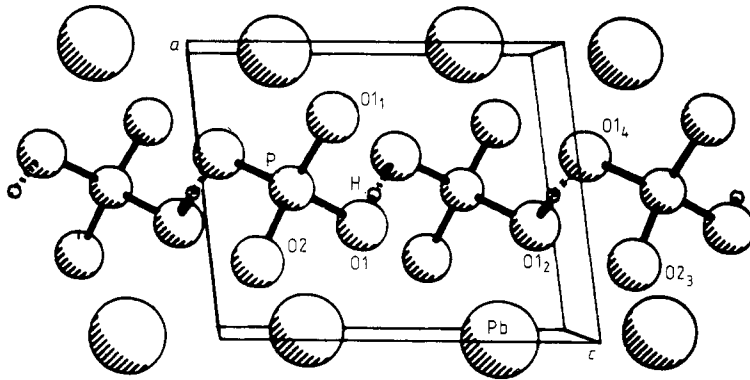
**Abstract.** Lead monohydrogen phosphate (PbHPO<sub>4</sub>) undergoes a ferroelectric phase transition at  $T_c = 310$  K at atmospheric pressure.  $T_c$  falls to room temperature at a pressure of about 0.125 GPa. The crystal structure of PbHPO<sub>4</sub> has been determined by x-ray diffraction at 2.0 and 2.3 GPa and the lattice parameters have been measured at a number of pressures between 0.1 MPa and 3.8 GPa. The unit-cell dimensions change anisotropically under high pressure: the compressibility of  $b$  is approximately twice that of  $a$  and  $c$ . The principal structural changes with pressure are shown to be compression of the distance between the sheets (parallel to the  $ac$  plane) of electrostatically interacting Pb<sup>2+</sup> and HPO<sub>4</sub><sup>3-</sup> ions, and compression of the hydrogen bond connecting the PO<sub>4</sub> anions of the neighbouring sheets.

### 1. Introduction

Since the discovery of the ferroelectric–paraelectric phase transition in lead monohydrogen phosphate (hereinafter referred to as LHP) at 310 K by Negran *et al* (1974), LHP and its analogues have attracted considerable interest in relation to studies of phase transitions involving ordering of hydrogen atoms in hydrogen bonds. The reason for this is that the LHP structure is relatively simple and that its second-order phase transition saturates over an unusually wide range in temperature of about 100 K, making it a convenient material for studying a phase transition at different stages of ordering.

Figure 1 shows a perspective view of the LHP structure along its  $b$  axis, when it is ordered in its low-temperature phase. The phosphate anions are linked into chains along the [001] direction by short hydrogen bonds between oxygen atoms 01 and 01<sub>1</sub> (see the caption to figure 1). The hydrogen bond is acentric—i.e. the hydrogen atom lies closer to one of the oxygen atoms—and is nearly linear. The chains are not cross-linked to one another and therefore LHP is often regarded as a model structure of a one-dimensionally ordered ferroelectric. With increasing temperature, starting from about  $T_c - 100$  K, the hydrogen atom begins to disorder, with its second position lying on the other side of the midpoint between 01 and 01<sub>1</sub>. Above  $T_c$  the hydrogen atom is disordered 50:50 over

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**Figure 1.** A perspective drawing of the  $\text{PbHPO}_4$  structure viewed down  $b$  in its low-temperature (ordered) phase, made with the PLUTO program of Motherwell (1976). Dotted lines represent the  $\text{H} \cdots \text{O}$  contacts in the hydrogen bonds (more readily seen in figure 3). The atoms labelled P, Pb, O1 and O2 have the coordinates given in table 2. Atoms O1<sub>1</sub> and O1<sub>4</sub> are not symmetry-related to atom O1 in the low-temperature phase, but become so above  $T_c$  (see table 3). Apart from the disordering of the H atoms (see the text), atomic positions differ very little between the two phases.

these two positions. Below  $T_c$  the structure is monoclinic, space group  $Pc$ , with the non-hydrogen atom framework approximating the symmetry of space group  $P2/c$  (Negran *et al* 1974). Structural changes in LHP such as H-atom ordering, shifts of the atoms and the changes of their temperature factors through the phase transition, have been studied extensively by neutron-diffraction methods (Zhong and Nelmes 1981, Nelmes 1984, Tun *et al* 1990, Nelmes *et al* 1990). The more recent analyses have indicated that the structure above  $T_c$  still remains non-centrosymmetric in the space group  $Pc$ , though the departures from  $P2/c$  symmetry consist only of very small (but significant) relative displacements of the non-hydrogen atoms and small misorientations of their thermal ellipsoids. This surprising result has been supported by Raman work studying the dynamics of the heavy atoms (Lockwood *et al* 1985).

The phase transition temperature in LHP is strongly pressure dependent. Dielectric constant measurements by Mylov *et al* (1979) showed the pressure dependence of  $T_c$  to be  $dT_c/dP = -1.15 \text{ K GPa}^{-1}$ ; earlier, Yasuda *et al* (1978) obtained  $-1.40 \text{ K GPa}^{-1}$ . According to these measurements, the phase transition in LHP at room temperature should take place at a pressure of about 0.125 GPa.

Most recently, the LHP structure has been determined in its disordered phase at 1.5 GPa by neutron diffraction (Restori *et al* 1987). The high-pressure x-ray study of LHP presented here was to determine the pressure dependence of the unit-cell dimensions for pressure calibration in the neutron-diffraction experiments, and to extend the structural studies of LHP to pressures above 2.0 GPa. Because of the strong domination of x-ray scattering by the lead atoms and because of the limitations of the high-pressure techniques (Katrasiak and Nelmes 1986a), this study could not provide any information about the hydrogen atom positions or compete with the neutron-diffraction techniques in the accuracy of the positions of the phosphorus or oxygen atoms. But we hoped to obtain useful additional information about the pressure dependence of this strongly anisotropic structure.

**Table 1.** The pressure dependence of the unit-cell dimensions for  $PbHPO_4$  at room temperature.

	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (deg)
0.10 MPa	4.6789(5)	6.6375(5)	5.7753(5)	97.135(8)
0.10 MPa†	4.6902(2)	6.6550(5)	5.7891(2)	97.248(2)
0.20 GPa†	4.6840(3)	6.6331(7)	5.7804(3)	97.079(3)
0.70 GPa	4.6605(8)	6.5827(14)	5.7466(14)	96.883(18)
0.85 GPa	4.6548(5)	6.5755(11)	5.7453(9)	96.870(11)
1.00 GPa	4.6492(6)	6.5636(10)	5.7392(9)	96.812(12)
1.00 GPa†	4.6614(2)	6.5831(4)	5.7566(2)	96.842(2)
1.12 GPa	4.6482(6)	6.5612(10)	5.7381(8)	96.806(11)
1.51 GPa	4.6363(4)	6.5357(11)	5.7275(8)	96.718(10)
2.00 GPa	4.6227(4)	6.5142(6)	5.7186(6)	96.616(8)
2.12 GPa	4.6225(4)	6.5022(18)	5.7137(6)	96.566(8)
2.30 GPa	4.6153(4)	6.4899(7)	5.7070(6)	96.529(8)
3.80 GPa	4.5717(6)	6.4213(12)	5.6715(7)	96.284(10)

† The parameters obtained by Howard (1986) from a powder neutron-diffraction experiment.

## 2. Experiment

Small LHP crystals were kindly provided by Dr B Březina of the Institute of Physics, Prague. The crystal used for measurements had dimensions of  $0.100 \times 0.095 \times 0.030$  mm<sup>3</sup> and was a piece cut off a longer crystal approximately along the (100) plane. The crystal was mounted into a Merrill–Bassett diamond-anvil high-pressure cell (Merrill and Bassett 1974), and fastened to the diamond surface with a dab of silicon vacuum grease. The  $b$  axis of the crystal was perpendicular to the face of the diamond. An Inconel gasket, 0.20 mm thick with a 0.30 mm hole, was used and a 4:1 mixture of methanol and ethanol was the hydrostatic fluid (Hazen and Finger 1982). The pressure inside the diamond cell was measured using the pressure dependence of the  $R_1$  ruby fluorescence line (Piermarini *et al* 1975) with an accuracy of 0.05 GPa. The high-pressure cell was mounted on a CAD4 diffractometer, and graphite-monochromated Mo  $K\alpha$  radiation was used. The unit-cell dimensions were measured at 0.1 MPa (a bare-crystal sample) and several higher pressures up to 3.8 GPa, and the results are listed in table 1 together with some obtained by Howard (1986).

Compared with the precision of measurements on bare-crystal samples, the precision of high-pressure x-ray measurements is significantly affected by the experimental restrictions imposed by the high-pressure cell—such as the limited data set, high background, and absorption of the cell etc (Katrusiak and Nelmes 1986a). Therefore pressures much higher than  $P_c = 0.125$  GPa were chosen for our structural experiments, assuming that the magnitudes of changes in the atomic positions would increase with increasing pressure and thence would be easier to detect. The measurements were performed at 2.0 and 2.3 GPa at room temperature. The  $\omega$ -scan method was adopted, with the diffractometer-angle settings optimal for the high-pressure cell (Finger and King 1978). All the accessible data were measured at both the high pressures, including all the equivalent reflections. Reflections for which either the incident or reflected beam lay beyond  $37.5^\circ$  from the cylindrical symmetry axis of the cell were not accepted for further analysis, this angle leaving a small safety margin on the limit ( $40^\circ$ ) imposed by the steel mounting of the

beryllium discs (Hazen and Finger 1982). The reflection intensities were corrected for the LP factor, absorption by the crystal and absorption by the high-pressure cell. The absorption of the crystal was calculated analytically, and gave transmission coefficients in the range 0.20 to 0.28. The absorption of the high-pressure cell was measured experimentally as a function of the angle between the axis of the cell and the x-ray beam, according to the procedure described by King (1981).

Since the departures of the high-temperature phase structure from the centrosymmetric space group  $P2/c$  found by Tun *et al* (1990) are too small to show up in this high-pressure x-ray experiment, the centrosymmetric structure was used as a starting model for the analysis of both data sets. In space group  $P2/c$ , the Pb and P atoms lie on two-fold axes and only two oxygen atoms are symmetry-independent. For all except the lead atom, only isotropic temperature factors were refined. The position and isotropic temperature factor of the hydrogen atom 50:50 disordered over two sites (symmetry-related in space group  $P2/c$ ) were taken from the previous neutron-diffraction experiments (Tun *et al* 1990)—the hydrogen atom was included in the structure factor calculations, but was not refined. No positional constraints were applied to the non-hydrogen atoms beyond those imposed by the space group symmetry. The final cycles of refinement included an isotropic extinction factor. The results of this refinement are given in table 2.

Various other models of the LHP structure were also tested in the refinement. They included (i) the structure in space group  $Pc$  with all atoms, except for H, free to refine, (ii) the structure in space group  $Pc$  with the  $PO_4$  group rigid, but free to rotate, and finally (iii) the structure in space group  $P2/c$  with the  $PO_4$  group rigid and free to rotate. None of these models was finally accepted: the *R*-factor ratio test (Hamilton 1974) did not reject space group  $P2/c$ , while the unconstrained model of the structure in space group  $P2/c$  gave a better fit than model (iii).

The structure refinements were carried out with the SHELX76 computer program (Sheldrick 1976), using the neutral-atom scattering factors from the *International Tables for X-ray Crystallography* (1974).

### 3. Results and discussion

Table 1 presents the unit-cell dimensions of LHP at various pressures up to 3.8 GPa measured in this experiment, and those from a powder neutron-diffraction study of LHP by Howard (1986) are given for comparison. The neutron results are in very good agreement after applying a common factor of 0.998 to them, this being almost certainly attributable to a small error in the neutron-wavelength calibration. The relative changes of the unit-cell dimensions with pressure are shown in figure 2. The compressibility of the crystal is significantly anisotropic and non-linear. The rate of change of parameters *a* and *c* with pressure is the same within error up to about 1.0 GPa, but at high pressures parameter *a* becomes significantly more compressible than *c*. The compressibility of the crystal along *b* is about twice as high as along *a* or *c* at all points within the range of pressure covered. The increase of pressure also causes a small decrease of angle  $\beta$  by  $0.85(1)^\circ$ , or 0.88%, in 3.8 GPa. The compressibilities of all the unit-cell dimensions, except *a*, are clearly non-linear.

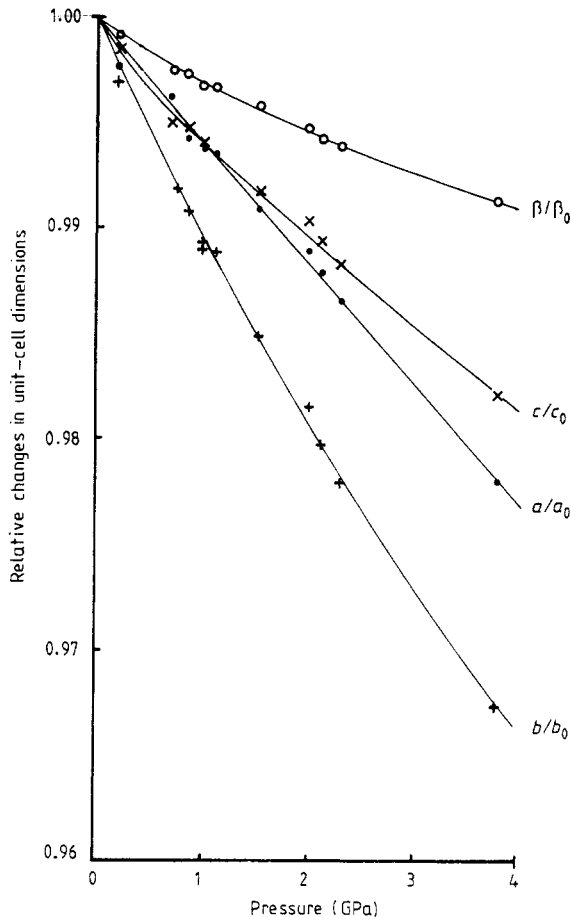
Because of the experimental limitations, only the structure of non-hydrogen atoms can be discussed in this paper. The largest significant changes in positions of these atoms following the increase of pressure are the shifts of atom Pb along the *b* axis—see

**Table 2.** The refined fractional coordinates (and their EDSS in parentheses on the last quoted places) for  $\text{PbHPO}_4$  in its high-temperature phase at 2.0 and 2.3 GPa from this study compared with those obtained by neutron diffraction at atmospheric pressure (0.1 MPa) and 316 K by Tun *et al* (1990) and at 1.5 GPa and 293 K by Restori *et al* (1987). The values of  $x$  and  $z$  are fixed by symmetry for the Pb and P atoms in space group  $\text{P2}/c$ . (The Pb coordinates given for 0.1 MPa and 1.5 GPa are related by the  $c$ -glide to those quoted in Restori *et al* (1987).) For this study (2.0 and 2.3 GPa at 293 K) the isotropic temperature factors  $U_{\text{iso}}$  ( $\text{\AA}^2$ ), number of independent reflections  $N$  and conventional agreement factors  $R$  and  $R_w$  are also given. Pb was refined with anisotropic temperature factors, but the equivalent isotropic value,  $U_{\text{eq}}$  ( $\text{\AA}^2$ ), is given here.

	Tun <i>et al</i> (1990) 316 K/0.1 MPa	Restori <i>et al</i> (1987) 293 K/1.5 GPa	This study 293 K/2.0 GPa	This study 293 K/2.3 GPa
Pb $x$	0.0	0.0	0.0	0.0
$y$	0.80016(4)	0.7922(2)	0.7924(3)	0.7911(4)
$z$	0.75	0.75	0.75	0.75
$U_{\text{eq}}$			0.0088	0.0099
P $x$	0.5	0.5	0.5	0.5
$y$	0.79345(6)	0.7934(3)	0.7936(16)	0.7915(24)
$z$	0.25	0.25	0.25	0.25
$U_{\text{iso}}$			0.009(1)	0.011(1)
O1 $x$	0.37936(8)	0.3714(3)	0.373(2)	0.371(2)
$y$	0.65892(5)	0.6558(3)	0.659(4)	0.637(6)
$z$	0.43421(7)	0.4326(3)	0.431(2)	0.433(2)
$U_{\text{iso}}$			0.014(1)	0.019(2)
O2 $x$	0.25625(6)	0.2565(2)	0.2571(16)	0.243(2)
$y$	0.92255(4)	0.9242(2)	0.934(5)	0.933(7)
$z$	0.12780(5)	0.1245(2)	0.1270(13)	0.1222(17)
$U_{\text{iso}}$			0.014(1)	0.019(2)
$N$			169	169
$R$			0.026	0.029
$R_w$			0.028	0.027

table 2. The implications of these changes can be assessed from figure 3, presenting a perspective view of the LHP structure along  $a$  (like figure 1, the structure in the low-temperature phase is shown, with the H atoms ordered onto one site). As clearly seen from this diagram, cations  $\text{Pb}^{2+}$  and anions  $\text{HPO}_4^{2-}$  can be considered to be arranged in sheets perpendicular to direction  $b$ , the  $y$ -coordinates of Pb and P being almost the same within a sheet. Each such sheet has two neighbouring ones, which are the images of itself in the crystallographic  $c$ -glide planes (located at  $y = 0$  and  $y = \frac{1}{2}$ ). The interactions between one of these sheets and each of its two neighbours are, however, different: while on one side there are only electrostatic interactions between the ions, on the other there are additionally the hydrogen bonds between the oxygen atoms. There is also a considerable difference in the distances from a sheet to its two neighbouring sheets: the distance ( $l_1$ ) between the electrostatically interacting sheets is much shorter than the distance ( $l_2$ ) between the sheets that are linked by the hydrogen bonds (distances  $l_1$  and  $l_2$  are shown in figure 3).

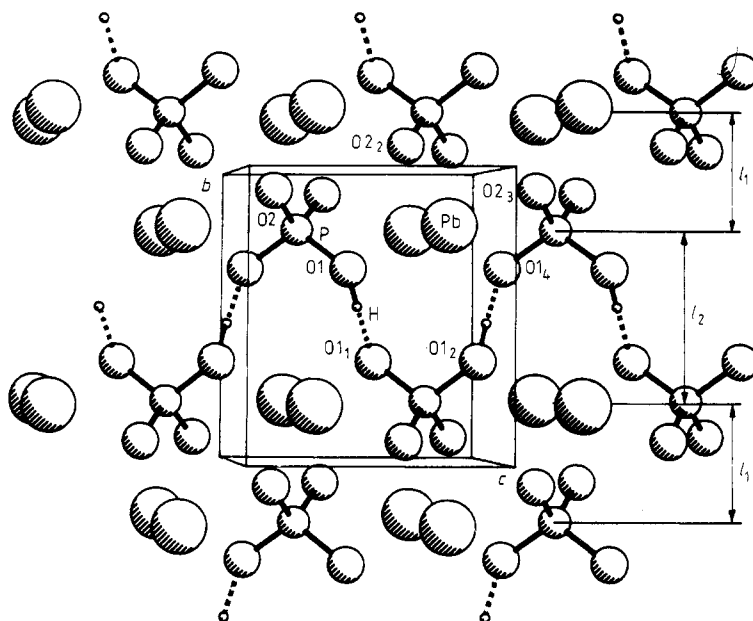
The pressure dependence of  $l_1$  and  $l_2$  is presented in table 3 and figure 4, as determined in the structure refinements, together with the distances  $l_1$  and  $l_2$  determined in



**Figure 2.** Relative changes in the unit-cell dimensions of  $\text{PbHPO}_4$  with pressure—the results obtained by Howard (1986) at 0.20 and 1.00 GPa from a powder neutron-diffraction experiment are included.

the neutron-diffraction experiments at 316 K/0.1 MPa (Tun *et al* 1990)<sup>†</sup> and at 293 K/1.5 GPa (Restori *et al* 1987). The  $l_1$  and  $l_2$  values calculated for  $\text{Pb}^{2+}$  and  $\text{HPO}_4^{2-}$  at 0.1 MPa differ by nearly 0.1 Å, but this relative displacement along  $b$  of the ions in one sheet is reduced to  $\approx 0.02$  Å at 1.5 GPa and the higher pressures. The strongest compression is observed for  $l_2(\text{Pb})$ , which is changed significantly more than  $l_2(\text{P})$  and  $l_1(\text{P})$ . While these distances all decrease with pressure,  $l_1(\text{Pb})$  increases its value between the measurements at 0.1 MPa and 1.5 GPa. Above 1.5 GPa the pressure dependences of  $l_2(\text{Pb})$  and  $l_2(\text{P})$  are almost the same, taking into account the low precision of the P-positions determined by x-rays (see figure 4)—and this is also true for  $l_1(\text{Pb})$  and  $l_1(\text{P})$  since  $l_1$  and  $l_2$  are dependent through  $l_1 + l_2 = b$ . (The similar pressure dependence of

<sup>†</sup> Atmospheric pressure values have to be obtained above room temperature to be in the high-temperature (disordered) phase. The effect of the 23 K difference in temperature from the other studies is negligibly small compared with the changes due to pressure.



**Figure 3.** A perspective drawing (like figure 1) of the  $\text{PbHPO}_4$  structure viewed along  $a$  in its low-temperature phase with the H atoms ordered. Dotted lines represent the hydrogen bonds;  $l_1$  and  $l_2$  are discussed in the text. The atom labelling refers to the interatomic distances quoted in table 3. The atoms labelled P, Pb, O1 and O2 have the coordinates given in table 2. Atoms O1<sub>1</sub> and O1<sub>4</sub> are not symmetry related to atom O1 in the low-temperature phase, but become so above  $T_c$  (see table 3). Apart from the disordering of the H atoms (see the text), atomic positions differ very little between the two phases.

$l_1$  and  $l_2$  for Pb and P could start at pressures lower than 1.5 GPa, and further measurements are needed to check this point.) If we consider distances  $l_1$  and  $l_2$  defined as the average of  $l_1(\text{Pb})$  and  $l_1(\text{P})$  and of  $l_2(\text{Pb})$  and  $l_2(\text{P})$ , respectively, it can be seen that  $l_2$  is compressed very significantly, by 4.2% over 2.3 GPa, while there is no change at all in  $l_1$  within the experimental error. This means that the compression of  $l_2$  accounts for all the contraction of the unit-cell dimension  $b$ , which is the most pressure-dependent of all the unit-cell dimensions (figure 2).

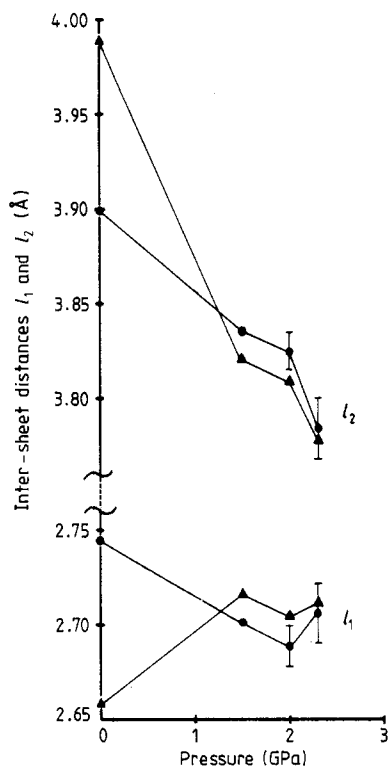
The basis for this behaviour probably lies in the strong electrostatic interactions between the ions. The shortest inter-ionic distances and hence the strongest electrostatic forces are present between cation  $\text{Pb}^{2+}$  and atom O2 of the  $\text{HPO}_4^{2-}$  anion. This can be seen from the interatomic distances given in table 3. The shortest anion to cation distance is  $\text{Pb} \dots \text{O}_{22}$ , linking adjacent electrostatically interacting sheets; this distance is about 0.1 Å less than the shortest contact within the sheets,  $\text{Pb} \dots \text{O}_{23}$  (see table 3 and figure 3). The interatomic distances between the hydrogen-bonded sheets are much longer: the shortest contact is between the hydrogen-bonded atoms  $\text{O1} \dots \text{O1}_1$ , but the shortest contact of cation  $\text{Pb}^{2+}$  is to  $\text{O1}_2$ —about 1 Å longer than the  $\text{Pb} \dots \text{O}$  distances within the sheets or between the electrostatically interacting sheets (see table 3 and figure 3). The absence of short electrostatic interactions between the hydrogen-bonded sheets probably accounts for the strong pressure dependence of  $l_2$ .

The positions of the oxygen atoms were not determined very precisely in this experiment, as explained before, but precisely enough to illustrate another interesting feature



**Table 3.** The pressure dependence of the distances  $l_1$  and  $l_2$  between the sheets of  $\text{Pb}^{2+}$  and  $\text{HPO}_4^{2-}$  ions in the structure of  $\text{PbHPO}_4$  ( $l_1$  and  $l_2$  are defined as the distances along  $b$  between the Pb and P atoms lying in neighbouring sheets—see figure 3) and of other interatomic distances discussed in the text. The 293 K/1.5 GPa and 316 K/0.1 MPa reference results were both determined in neutron-diffraction experiments (Restori *et al* 1987, Tun *et al* 1990). In the interatomic distances, atom symbols without subscripts are located at the positions  $(x, y, z)$  given in table 2; those with subscripts are at the symmetry-related positions given in the final column. (Atom O1<sub>1</sub> is denoted O3' by Restori *et al* (1987).)

	Tun <i>et al</i> (1990) 316 K/0.1 MPa	Restori <i>et al</i> (1987) 293 K/1.5 GPa	This study 293 K/2.0 GPa	This study 293 K/2.3 GPa	Symmetry-related positions
$l_1(\text{Pb})$	2.6557(3) Å	2.717(2) Å	2.705(3) Å	2.711(4) Å	
$l_2(\text{Pb})$	3.9890(3)	3.820(2)	3.810(3)	3.778(4)	
$l_1(\text{P})$	2.7449(3)	2.701(3)	2.69(1)	2.71(2)	
$l_2(\text{P})$	3.8998(3)	3.836(3)	3.83(1)	3.78(2)	
Pb ... O1	2.8593(5)	2.792(2)	2.79(2)	2.81(2)	$x, 1-y, 0.5+z$
Pb ... O1 <sub>2</sub>	3.6228(5)	3.496(3)	3.50(2)	3.37(3)	$1-x, y, 1.5-z$
Pb ... O1 <sub>4</sub>	3.3674(5)	3.372(2)	3.36(2)	3.37(2)	$x, 2-y, 0.5+z$
Pb ... O2 <sub>2</sub>	2.3548(4)	2.360(2)	2.50(2)	2.30(3)	$x, y, 1+z$
Pb ... O2 <sub>3</sub>	2.4935(4)	2.485(2)	2.49(2)	2.49(2)	$1-x, 1-y, 1-z$
O1 ... O1 <sub>1</sub>	2.4701(7)	2.441(3)	2.47(3)	2.23(4)	



**Figure 4.** The pressure dependence of distances  $l_1$  and  $l_2$  calculated from the y-coordinates of atoms Pb ( $\blacktriangle$ ) and P ( $\bullet$ ) (see table 3 and figure 3). The values at atmospheric pressure (at 316 K) and at 1.5 GPa are calculated from the neutron-diffraction measurements by Tun *et al* (1990) and Restori *et al* (1987), respectively. The full lines are guides to the eye only.

of the LHP structure. The  $\text{PO}_4$  groups, apart from shifts along the  $b$  axis, are also allowed to rotate about the two-fold axis in  $\text{P2}/c$ . The orientation of the  $\text{PO}_4$  groups around the two-fold axis can be characterised by two angles between the  $c$  axis and each of the directions of bonds P–O1 and P–O2 projected onto the  $ac$  plane. The mean change of these two angles can be used to describe the rotation of the  $\text{PO}_4$  groups in their orientation relative to the  $\text{PO}_4$  chain direction. This rotation calculated for the 293 K/1.5 GPa LHP structure (Restori *et al* 1987), relative to the atmospheric pressure structure at 316 K, is  $2.90(4)^\circ$  in a sense that reduces the compression of the  $\text{O1} \dots \text{O1}_1$  hydrogen bonds. Our x-ray determinations at 2.0 and 2.3 GPa give similar angles of  $2.4(5)^\circ$  and  $2.1(6)^\circ$ , respectively. The  $\text{KH}_2\text{PO}_4$  and squaric acid ( $\text{H}_2\text{C}_4\text{O}_4$ ) structures also respond to pressure in this way, in that the  $\text{PO}_4$  or  $\text{C}_4\text{O}_4$  groups rotate to reduce the compression of the hydrogen bonds: this rotation is  $1.00(4)^\circ$  for  $\text{KH}_2\text{PO}_4$  at 1.7 GPa (Nelmes 1987) and  $0.45(6)^\circ$  for squaric acid at 2.75 GPa (Katrusiak and Nelmes 1986b). In all these crystals, despite their quite different structures, the compressibility of the hydrogen bonds has very similar values:  $-0.018 \text{ \AA GPa}^{-1}$  for  $\text{KH}_2\text{PO}_4$ ,  $-0.022 \text{ \AA GPa}^{-1}$  for squaric acid and  $-0.019 \text{ \AA GPa}^{-1}$  for LHP (these are average values as the compressibilities are slightly non-linear: see Restori *et al* (1987) and the references therein).

### Acknowledgments

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**References**

- Finger L W and King H E Jr 1978 *Am. Mineral.* **63** 337
- Hamilton W C 1974 *International Tables for X-ray Crystallography* vol 4 (Birmingham: Kynoch)
- Hazen R M and Finger L W 1982 *Comparative Crystal Chemistry* (New York: Wiley)
- Howard C J 1986 private communication
- International Tables for X-ray Crystallography* 1974 vol 4 (Birmingham: Kynoch)
- Katrusiak A and Nemes R J 1986a *J. Appl. Crystallogr.* **19** 73
- 1986b *J. Phys. C: Solid State Phys.* **19** L765
- Lockwood D J, Ohno N, Nelmes R J and Arend H 1985 *J. Phys. C: Solid State Phys.* **18** L559
- King H E Jr 1981 *High-Pressure Crystallography with a CAD4* instruction manual, Enraf-Nonius, Delft
- Merrill L and Bassett W A 1974 *Rev. Sci. Instrum.* **45** 290
- Motherwell W D S 1976 PLUTO (program for plotting molecular and crystal structures) University of Cambridge
- Mylov V P, Shirokov A M, Shuvalov L A, Kharitonov V N and Březina B 1979 *Sov. Phys.-Crystallogr.* **24** 738
- Negran T J, Glass A M, Brickenkamp C S, Rosenstein R P, Osterheld R K and Sussot R 1974 *Ferroelectrics* **6** 176
- Nelmes R J 1984 *Ferroelectrics* **53** 207
- 1987 *Ferroelectrics* **71** 125
- Nelmes R J, Katrusiak A, Zhong W-L, Choudhary R N P and Březina B 1990 in preparation
- Piermarini G J, Block S, Barnett J D and Forman R A 1975 *J. Appl. Phys.* **46** 2274
- Restori R, Tun Z, Nelmes R J and McIntyre G J 1987 *J. Phys. C: Solid State Phys.* **20** L591
- Sheldrick G 1976 SHELX 76 'Program System for Crystal Structure Determination' University of Cambridge
- Tun Z, Nelmes R J and Kuhs W F 1990 in preparation
- Yasuda N, Okomoto M, Shimuzu H, Fujimoto K and Inuishi Y 1978 *Japan. J. Appl. Phys.* **17** 103
- Zhong W-L and Nelmes R J 1981 *Ferroelectrics* **39** 1120