

Hydrogen-Atom Ordering in Lead Hydrogen Arsenate Monitored by Neutron Time-of-Flight Laue Diffraction using Single-Frame Methods

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The ordering of the hydrogen atom in a single crystal of lead hydrogen arsenate in the temperature range 320 to 80 K is described. The details of the ordering at small temperature steps are determined from single frames of data collected using the neutron time-of-flight Laue method. The constrained refinements obtained from these data yield lower precision than full data sets but allow the ordering to be characterized rapidly and reliably. This is the first example of the use of this single-frame method of monitoring such phase transitions. The approach used here with neutrons, stimulated in part by synchrotron Laue diffraction, will be of interest for all time-resolved experiments with synchrotron radiation or neutrons.

Keywords: time-of-flight Laue diffraction; neutron diffraction; phase transformations; time-resolved studies; single-frame method.

1. Introduction

The possibilities of monitoring phase transitions using data collected with the Laue method have been the subject of some interest since the advent of intense wide-wavelength-band synchrotron sources and the realization that the problems of data overlap in Laue diffraction are not as serious as once feared (Cruickshank, Helliwell & Moffat, 1987; Helliwell *et al.*, 1989; Allinson *et al.*, 1992; Moffat, Szebenyi & Bilderback, 1984; Moffat, Schildkamp, Bilderback & Volz, 1986; Hajdu *et al.*, 1987). More recently, the possibilities of monitoring structural changes using limited ('single shot') data collected using neutron time-of-flight Laue diffraction have been discussed (Wilson, 1995). The single-frame methods proposed allow a more rapid characterization of the broad details of a structural change, especially one in which few parameters vary significantly. This overcomes one of the main problems of studying structural variation with single crystals – the large data-collection time required for full neutron data sets.

One structural change which lends itself ideally to study using this method is the hydrogen-atom ordering in lead hydrogen arsenate (Fig. 1), the structure of which is known from single-crystal X-ray (Effenberger & Pertlik, 1986) and neutron (Wilson, Cox & Stewart, 1991) techniques. This material undergoes a paraelectric–ferroelectric phase transition at 313 K (Lavrencic & Petzelt, 1977), and below this temperature the hydrogen atom gradually orders onto one of two initially equivalent sites, the ordering becoming complete some 100 K or more below the transition temperature (Wilson, 1994). There are other structural changes as the symmetry is lowered from $P2/c$ to Pc , but in this work only the hydrogen-atom ordering is considered. Changes in hydrogen-atom parameters, such as that studied

here, are particularly well suited to study using neutron diffraction, for which the scattering from hydrogen atoms is more on a par with that from other elements [*e.g.* $(b_H)^2/(b_{Pb})^2 = 0.158$ for neutrons, *cf.* the ratio of $(Z_H)^2/(Z_{Pb})^2 = 0.000149$ for X-rays, making the neutron technique a much more sensitive probe of hydrogen-atom parameters].

The Laue time-of-flight diffraction technique exploits the ability of an instrument equipped with a two-dimensional position-sensitive detector (PSD) on a pulsed neutron source to access large volumes of reciprocal space in a single measurement (a 'frame'). Time-of-flight Laue diffraction is thus ideal for this type of measurement in that the group of reflections in a single shot are measured at genuinely the same time and under the same conditions.

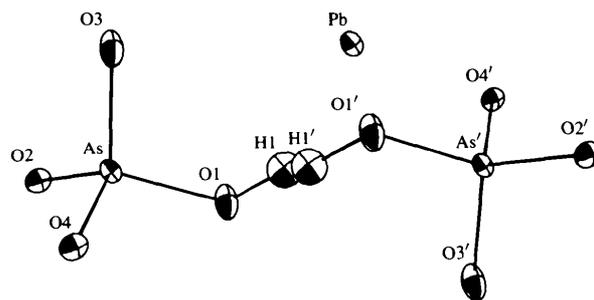


Figure 1
ORTEP (Johnson, 1965) view of the structure of $PbHAsO_4$, showing the hydrogen atom disordered over the two sites related by the centre of symmetry in the high-symmetry ($P2/c$) phase. This symmetry centre is lost below ~ 313 K and the hydrogen atom preferentially orders onto a single site as the temperature is lowered.

Typically, such an experiment comprises full examination of the structure at the two end points to allow appropriate parameter constraints to be set up for the restricted refinements from the limited data sets. These are subsequently collected at a range of intermediate temperatures and limited refinements of the relevant parameters carried out, to yield rapid characterization of the changing structural trends in the system under study.

2. Data collection and structural refinements

Data were collected from a large ($2 \times 2 \times 1$ mm) single crystal of lead hydrogen arsenate, grown from a polyacrylamide hydrogel by means of a controlled chemical reaction (Brezina & Havrankova, 1980), using the time-of-flight Laue diffractometer SXD at the ISIS spallation neutron source at the Rutherford Appleton Laboratory (Wilson, 1990). Neutrons with wavelengths in the range 0.48–4.8 Å were used, sorted using the time-of-flight technique. The detector used on SXD is a large-area (192×192 mm²) position-sensitive detector comprising 64×64 3 mm elements, placed for this experiment with its centre at $2\theta = 90^\circ$ at a distance of 109 mm from the sample. The detector thus subtends large angles at the sample. The sample was mounted on a χ/φ circle and data collected in one or more frames, each containing a volume of reciprocal space and hence many reflections. The unit cell of lead hydrogen arsenate is monoclinic, with space group $P2/c$ in the high-temperature phase, lowering to Pc in the low-temperature phase. The cell parameters at 320 K are $a = 4.872$ (6), $b = 6.758$ (8), $c = 5.886$ (6) Å, $\beta = 95.4$ (5) $^\circ$. The low-symmetry nature of the unit cell makes this material a good test of a data-collection procedure accessing a limited region of reciprocal space; the small unit-cell volume should, of course, help to make the procedure tenable.

Two ‘full’ data sets were collected, at 320 and 80 K, involving the collection of 28 data frames at each temperature, each frame taking around 1 h of data-collection time. These led to data sets comprising 2784 and 4306 observed reflections [$I > 3\sigma(I)$], respectively (1222 and 2169 unique reflections), allowing full structural refinements to be carried out for these ‘end points’. Refinements were carried out (on F) in the local *SFLSQ* program, using the low-symmetry space group but, in the refinement at 320 K, constraining all non-hydrogen atoms to their equivalent high-symmetry parameters. The results of these refinements are shown in Table 1, from which it is clear that the end points of the hydrogen-ordering transition have been well defined, with site occupancies of ~ 0.5 and ~ 1.0 found at 320 and 80 K, respectively, within experimental error. The total hydrogen-atom stoichiometry was constrained to equal unity. To allow for the calculation of the frame which best allows the hydrogen-atom ordering to be followed, further refinements were carried out on these data sets in which all atomic coordinates were fixed at the values found in the high-temperature high-symmetry structure, and only

Table 1

Refined atomic parameters for PbHAsO_4 (e.s.d.’s are given in parentheses).

(a) Using the full data set at 320 K ($wR = 0.065$ for 1222 unique reflections).

	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso} (Å ²)	Site
Pb		0.2032 (2)		0.897 (14)	
As		0.7960 (2)		0.543 (16)	
O1	0.3500 (8)	0.6420 (5)	0.4293 (7)	1.21 (5)	
O2	0.2488 (9)	0.9371 (5)	0.1123 (8)	0.67 (5)	
O3	0.6298 (8)	0.6555 (5)	0.0414 (7)	1.30 (5)	
O4	0.7533 (9)	0.9265 (5)	0.3888 (9)	0.72 (5)	
H1	0.4772 (11)	0.5194 (8)	0.4831 (10)	1.66 (7)	0.518 (29)

(b) Using the full data set at 80 K ($wR = 0.062$ for 2169 unique reflections).

	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso} (Å ²)	Site
Pb		0.2036 (1)		0.296 (9)	
As		0.7977 (1)		0.278 (10)	
O1	0.3610 (5)	0.6462 (3)	0.4254 (5)	0.442 (22)	
O2	0.2438 (5)	0.9271 (3)	0.1077 (4)	0.127 (18)	
O3	0.6460 (5)	0.6548 (3)	0.0378 (5)	0.412 (21)	
O4	0.7472 (5)	0.9394 (3)	0.3887 (5)	0.294 (21)	
H1	0.4829 (9)	0.5215 (6)	0.4750 (8)	1.34 (5)	0.983 (18)

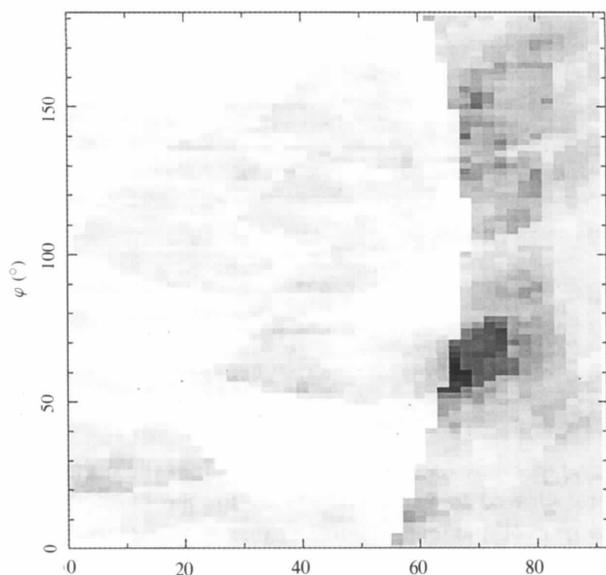
the temperature factors and hydrogen-atom site occupancies were allowed to vary. The results for the hydrogen-atom ordering at the end points in this restricted refinement scheme were essentially identical to those found in the full refinements.

3. Optimizing the single-frame data collection

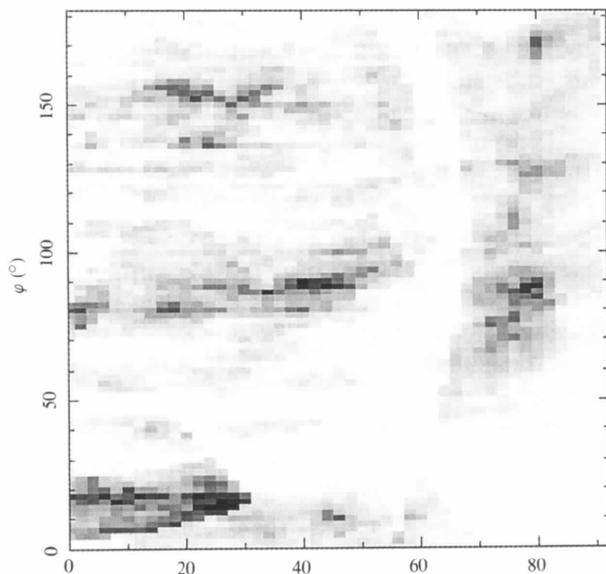
Using the atomic parameters determined in these refinements, structure-factor sets were simulated for these end points, to a minimum d spacing of 1 Å. Using the two sets of structure-factor data, a series of calculations were carried out for the whole range of accessible crystal orientations ($0 < \chi < 90^\circ$; $0 < \varphi < 180^\circ$) to locate the regions in which the maximum structure-factor changes occur. As discussed earlier (Wilson, 1995) orientations which maximize both ΔF and $\Delta F/F$ were searched for, since either criterion may be of use in optimizing the $\Delta F/\Delta(\text{parameter})$ path. The results of these calculations are shown in Fig. 2. It can be seen from this that the optimized region in the $\Delta F/F$ map is more clearly defined and coincides with a relatively high value in the ΔF map, whereas the optimized value in the ΔF map is less convincing and less well supported by the complementary $\Delta F/F$ results. The orientation indicated as giving the maximum structure-factor changes on hydrogen ordering was thus chosen from the $\Delta F/F$ map, corresponding to values of $(\chi, \varphi) = (66^\circ, 62^\circ)$.

Single frames of data were collected in this orientation at temperatures from 320 to 80 K, in 10 K steps again with 1 h of data-collection time per frame, yielding the data sets indicated in Table 2. It is worthy of note that >300 observed [$I > 3\sigma(I)$] reflections are extracted from this single frame in the lowest temperature data (80 K) and that even at 320 K there remain >170 observed reflections per single measurement. Refinements were carried out on each of these single-frame data sets, in each case allowing isotropic temperature factors to vary for all atoms and subsequently allowing the

hydrogen-atom site occupancies to vary. As above, the total hydrogen stoichiometry was constrained to equal unity. The results found for the hydrogen-atom occupancy are plotted in Fig. 3, from which it is clear that the expected ordering



(a)



(b)

Figure 2

(a) The optimal $(\Delta F/F) - \Delta(\text{parameter})$ map for the hydrogen-atom ordering in PbHAsO_4 . The plot shows the degree of change of $\Delta F/F$ as the hydrogen-atom occupancy on site H1 changes from 0.5 (high T) to 1.0 (low T), as a function of crystal orientator angles χ and φ for the particular crystal orientation in this experiment. Reflections to a d_{\min} of 1.0 \AA were used in the simulations. The highest point in the map occurs at $(\chi, \varphi) = (66^\circ, 62^\circ)$. (b) The optimal $\Delta F - \Delta(\text{parameter})$ map for the hydrogen-atom ordering in PbHAsO_4 , analogous to (a). The highest point in this map occurs at $(\chi, \varphi) = (28^\circ, 14^\circ)$.

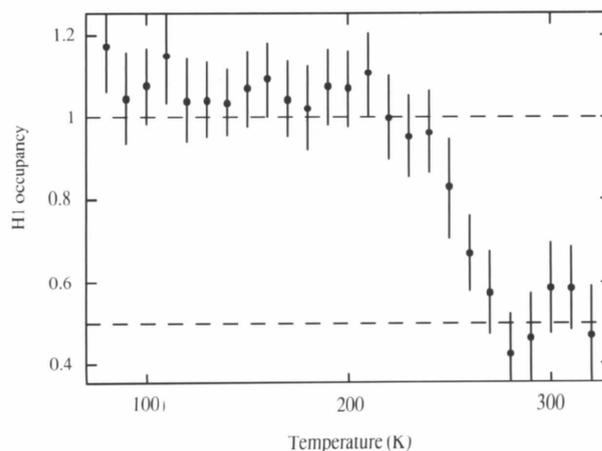
Table 2

Refined atomic parameters for PbHAsO_4 using the $\Delta F/F$ -optimized single-frame data sets at various temperatures (e.s.d.'s are given in parentheses).

T (K)	No. of reflections	wR (%)	H_1 occupancy	$H_1 B_{\text{iso}}$ (\AA^2)	$\text{Pb } B_{\text{iso}}$ (\AA^2)	$\text{As } B_{\text{iso}}$ (\AA^2)	$O_{\text{av}} B_{\text{iso}}$ (\AA^2)
80	303	9.8	1.17 (11)	1.66 (25)	0.26 (3)	0.19 (4)	0.26 (8)
90	279	9.1	1.04 (11)	1.44 (21)	0.29 (3)	0.21 (4)	0.28 (8)
100	283	8.8	1.07 (9)	1.23 (18)	0.34 (3)	0.22 (4)	0.34 (8)
110	276	9.2	1.15 (11)	1.35 (20)	0.34 (4)	0.27 (4)	0.38 (9)
120	278	9.3	1.04 (10)	1.40 (21)	0.42 (4)	0.21 (4)	0.40 (10)
130	272	8.9	1.04 (9)	1.38 (19)	0.42 (4)	0.26 (4)	0.46 (10)
140	277	9.2	1.03 (8)	1.24 (17)	0.44 (4)	0.29 (4)	0.48 (9)
150	249	8.7	1.06 (9)	1.42 (19)	0.45 (4)	0.29 (4)	0.50 (10)
160	245	8.7	1.09 (9)	1.34 (19)	0.51 (4)	0.30 (4)	0.52 (11)
170	241	8.8	1.04 (9)	1.45 (20)	0.51 (4)	0.30 (5)	0.58 (11)
180	238	8.6	1.02 (10)	1.48 (21)	0.61 (4)	0.33 (5)	0.63 (12)
190	233	8.2	1.07 (9)	1.62 (20)	0.59 (4)	0.33 (4)	0.65 (11)
200	231	8.3	1.06 (9)	1.48 (18)	0.59 (4)	0.34 (4)	0.62 (12)
210	218	8.3	1.10 (10)	1.61 (21)	0.64 (4)	0.33 (5)	0.70 (13)
220	219	8.4	1.00 (10)	1.59 (21)	0.64 (4)	0.41 (5)	0.76 (14)
230	211	8.6	0.95 (10)	1.49 (20)	0.73 (4)	0.39 (5)	0.79 (13)
240	213	8.6	0.96 (10)	1.67 (23)	0.74 (5)	0.37 (5)	0.83 (15)
250	203	8.6	0.83 (12)	1.54 (23)	0.78 (5)	0.38 (5)	0.87 (15)
260	206	8.2	0.66 (9)	1.98 (24)	0.81 (4)	0.42 (4)	1.13 (13)
270	201	8.0	0.57 (10)	1.94 (26)	0.88 (5)	0.49 (5)	1.11 (14)
280	190	8.1	0.42 (10)	1.74 (21)	0.86 (5)	0.47 (5)	1.15 (14)
290	193	8.0	0.46 (11)	1.87 (25)	0.83 (5)	0.45 (5)	1.17 (15)
300	184	7.2	0.58 (11)	2.08 (25)	0.82 (4)	0.44 (5)	1.16 (17)
310	173	8.0	0.58 (10)	1.92 (26)	0.90 (5)	0.43 (5)	1.19 (17)
320	173	7.8	0.46 (12)	2.03 (27)	0.97 (5)	0.48 (6)	1.29 (18)

pattern for this hydrogen atom (Wilson, 1994) is reproduced well. An initially rapid ordering of the hydrogen onto the preferred site is followed by a more gradual increase to total ordering at around 220 K, below which the hydrogen atom is essentially fully ordered within experimental error.

Subsequent to this experiment, data were collected in the optimized ΔF orientation of $(\chi, \varphi) = (28^\circ, 14^\circ)$, with the temperature this time rising from 80 to 320 K in the same 10 K steps. The results are displayed in Fig. 4, from which it is clear that the general trend is still recognizable but that the results are considerably less convincing. It is wrong to draw

**Figure 3**

The refined hydrogen-atom occupancy on site H1 as determined from the single frames collected in the $\Delta F/F$ -optimized frame. The ordering trend is clear. The dotted lines represent the fully ordered (1.0) and fully disordered (0.5) H1 occupancy values.

general conclusions from a single experiment, but in this case it appears that the $\Delta F/F$ optimization is the most reliable to use for the single-frame procedure.

4. Concluding remarks

The results obtained from the $\Delta F/F$ -optimized frame (Fig. 3), and to a lesser extent those from the best ΔF frame (Fig. 4), are compelling evidence that the single-frame procedure can yield important information regarding atomic parameter changes. The ability to monitor structural changes by neutron diffraction from a single crystal at 25 temperatures in around one day of data collection is extremely welcome and only made possible by exploiting the benefits of the time-of-flight Laue technique. Possible extension of the single-frame technique to still shorter timescales is being investigated and some preliminary data will be obtained shortly. In this way the limits of the procedure should become better understood in the near future.

The limitations of the procedure in terms of accuracy and precision are of course also of concern. As was noted before (Wilson, 1995), the accuracy of the results obtained depends on the availability of good, reliable end-point refinements

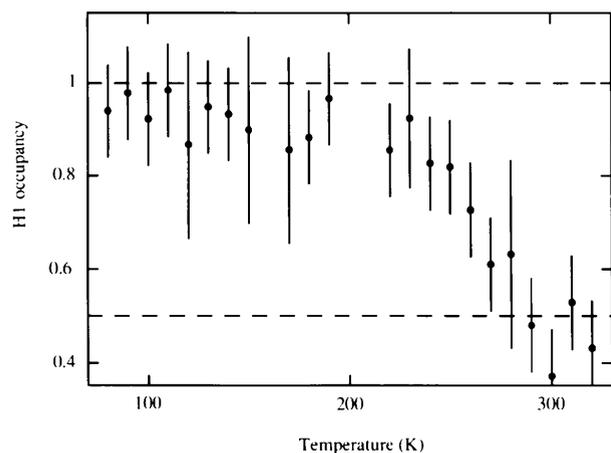


Figure 4

The refined hydrogen-atom occupancy on site H1 as determined from the single frames collected in the ΔF -optimized frame. There is again evidence for the ordering trend but this is less clear than in Fig. 3.

and is also critically dependent on the choice of sensible parameters and constraints for the limited refinements to which the technique is necessarily confined. The precision of each individual refined value is also limited, of course, by the restricted range of structure factors available in a single frame. This factor may be amenable for inclusion in the procedure to optimize the choice of the frame collected. To some extent, however, this lack of precision in individual values is offset by the opportunity to measure many more points in a given time, in which case trends may well be identified more reliably than with just a few, highly precise measurements at a more restricted number of points, the more typical domain of single-crystal studies.

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