

Structural studies of schultenite in the temperature range 125–324 K by pulsed single crystal neutron diffraction — hydrogen ordering and structural distortions

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Abstract

The structure of the mineral schultenite, PbHAsO_4 , has been studied using pulsed neutron single crystal diffraction. The low-temperature, low-symmetry structure is found to exhibit substantial ordering of the hydrogen atom onto one of two possible sites, which are equally occupied in the high-temperature phase above 313 K. The occupancies found at low temperature agree well with the normal behaviour for such a hydrogen ordering phase transition in this type of material. In addition the heavy atom lattice distortion has been characterised as a function of temperature and found to follow broadly the pattern of hydrogen ordering. Higher-temperature measurements at and above the phase transition confirm the high symmetry nature of the structure in this region, with no significant distortions from this within the resolution of the present data.

KEYWORDS: hydrogen ordering, pulsed single crystal neutron diffraction, phase transition, schultenite

Introduction

LEAD hydrogen arsenate (PbHAsO_4), which occurs naturally as the mineral schultenite, undergoes a paraelectric–ferroelectric phase transition at 313 K (Lavrencic and Petzelt, 1977). The structure of the high-temperature, paraelectric phase has space group $P2/c$ and the hydrogen atom is disordered (necessarily 50:50) about the centre of symmetry (Fig. 1). In the low-temperature, ferroelectric phase, however, the space group is Pc , with the loss of the centre of symmetry. The structural phase transition is manifest as an ordering of the hydrogen atom onto one of the two, now non-equivalent, sites. In addition, the loss of the two-fold axis allows the heavy-atom lattice to distort significantly (Lockwood *et al.*, 1985). The hydrogen ordering in this type of phase transition is typically gradual, becoming complete some 100° below the transition temperature in the isotypic compound lead hydrogen phosphate, LHP (Lockwood *et al.*, 1985).

The phase transition observed in materials such as schultenite is related to the ordering of hydrogen atoms involved in strong hydrogen bonds, and hence is intimately connected to the nature of hydrogen bonding. The relation of ordering characteristics to the separation of the disordered hydrogen atoms above the phase transition, and to the separation of the relevant oxygen atoms, should give significant information regarding the hydrogen atom potentials in such a material, and hence help to elucidate the factors influencing the structure. One purpose of the present work is to examine the structure of schultenite at temperatures below the phase transition, to elucidate the structural changes with temperature, especially with regard to hydrogen atom ordering and structural distortions.

In addition, determination of the structure in the high-temperature phase will serve two further aims—to verify the equal occupancies of the two hydrogen atoms (equivalent in the high-symmetry structure) and to look for any deviations of the

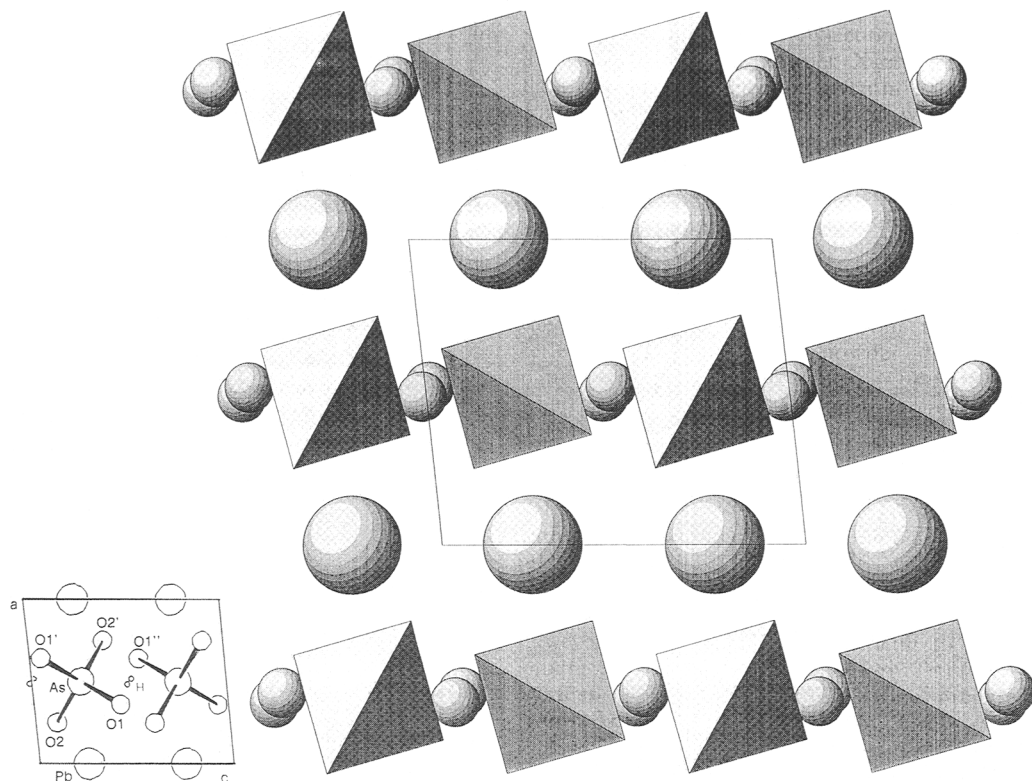


FIG. 1. The structure of schultenite at room temperature ($P2/c$), projected onto the ac plane, depicting the AsO_4 tetrahedra and the partially occupied H atom sites between the two oxygen atoms (drawn using ATOMS (Dowty, 1992)). The atom and unit cell labelling is given in the inset. The basic structure is very similar to that of the phosphate analogue LHP, with a separation between the two partially occupied hydrogen atom positions of 0.388(19) Å. In the low-temperature phase, O1' and O2' are no longer symmetry related to O1 and O2, the two hydrogen atom positions are non-equivalent and deviate from 50:50 occupancy, and the Pb and As atoms are no longer on special positions.

heavy atom structure, for which there is some evidence in the case of LHP (Lockwood *et al.*, 1985).

For phase transitions such as that discussed here, neutron diffraction is the obvious method to use, as the scattering cross-section of hydrogen is of the same order as those of most other elements. Unlike the X-ray method, therefore, hydrogen atom parameters can be obtained with equal precision to the rest of the structure.

Experimental

A single crystal sample of schultenite was obtained from the Natural History Museum, London, collection [BM 1926,205]. The crystal was transparent, of dimension $4 \times 3 \times 1 \text{ mm}^3$, and contained a small amount of a green inclusion (*c.*

$0.75 \times 0.75 \times 0.25 \text{ mm}^3$), probably mimetite [$Pb_5Cl(AsO_4)_3$]. For neutron diffraction, a bulk probe, the presence of this inclusion, of some 1% of the crystal volume, should not present a serious problem.

Data were collected on the single crystal diffractometer (SXD; Wilson, 1990) at the ISIS Spallation Neutron Source (Rutherford Appleton Laboratory, Oxon, UK). This instrument is a time-of-flight Laue diffractometer exploiting the pulsed, white beam nature of the ISIS source along with large area position-sensitive detectors to measure large volumes of reciprocal space simultaneously. This means a single data frame contains many reflections and the mode of data collection is to measure a series of such frames, with crystal and detector stationary during the collection. In the present experiment neutrons in

TABLE 1. Refinements of schultenite at high and low temperatures

<i>T</i> (K)	No. of reflections	Space group	No. of parameters	Thermal parameters*	<i>R</i>
324	316	<i>P2/c</i>	34	All aniso except H	0.062
		<i>Pc</i>	43	Pb and As aniso	0.065
300	350	<i>P2/c</i>	34	All aniso except H	0.061
		<i>Pc</i>	43	Pb and As aniso	0.065
305	467	<i>P2/c</i>	34 [†]	All aniso except H	0.071
		<i>Pc</i>	39	All isotropic	0.082
290	106	<i>Pc</i>	39 [‡]	All isotropic	0.070
275	217	<i>Pc</i>	39	All isotropic	0.075
250	196	<i>Pc</i>	39	All isotropic	0.098
200	244	<i>Pc</i>	39	All isotropic	0.069
125	155	<i>Pc</i>	39 [‡]	All isotropic	0.070

*Choice of refined parameters discussed in text.

[†]High symmetry refinement from Wilson *et al.* (1991).

[‡]Blocked matrix refinements used for these data sets due to the low number of data available.

the wavelength range 0.4–4.8 Å were used in the data collection, with the detector in its normal position centred around $2\theta = 90^\circ$, subtending angles of some 60° at the sample in both horizontal and vertical directions.

To allow for the measurement of several temperatures in a short experimental period, only limited data sets were collected for the low-temperature studies. While reducing the precision obtained for the atomic parameters, such limited data do allow trends in structural parameters to be elucidated. This is discussed more fully elsewhere (Wilson, 1994).

Data were collected in two experimental periods. First, some 6–8 data frames were collected at each of six temperatures below T_c at 305, 290, 275, 250, 200 and 125 K (see Table 1). Secondly, data were accumulated at 300 K and at 324 K (above T_c), each comprising 12 data frames (see Table 1). Further details of the data collection procedures have been given previously in work on the high-symmetry structure of the title material (Wilson *et al.*, 1991). Refinement of all data sets was carried out using the least-squares program SFLSQ, a member of the Cambridge Crystallographic suite of subroutines and programs (Brown and Mattheuman, 1987). The structural refinements in the high-symmetry space group included anisotropic thermal parameters on all the non-hydrogen atoms, but those in the low-symmetry space group used isotropic thermal parameters at all temperatures.

Given the problems with obtaining reliable determination of the hydrogen atom anisotropic thermal parameters even in the full room-temperature data set (Wilson *et al.*, 1991), only isotropic thermal parameters were believed to be reliable for these in the low-temperature refinements, with their more limited data sets. In the room-temperature case, the relevant bonding parameters were in fact not found to be significantly affected by including anisotropic temperature factors on the hydrogen atom. The low temperature refinements were carried out using both the cells refined at the individual temperatures and also using the monoclinic unit cell determined at 275 K: space group *Pc* (no. 7); $a = 4.873(5)$, $b = 6.783(6)$, $c = 5.946(6)$ Å, $\beta = 95.53(6)^\circ$. At the level of precision of the results quoted, there was found to be no significant change in the structural parameters found in these two cases.

High-temperature structure

The structure of schultenite determined at room temperature (Wilson *et al.*, 1991) is shown in Fig. 1, with bonding parameters as shown in Table 2. From this table it can be seen that the separation $2R$ of the oxygen atoms involved in the O–H...O hydrogen bond in schultenite is 2.503(5) Å, compared with 2.470 Å in LHP, and that the separation of the two disordered hydrogen atom positions is 0.388(19) Å (0.393 Å in LHP). In

TABLE 2. Selected bonding parameters in schultenite at the higher temperatures, with the room temperature values for LHP given for comparison. Typical estimated standard deviations are indicated in each column, for heavy atom and for hydrogen atom parameters

Bonds	Schultenite neutron data				305K <i>P2/c*</i> 0.005 <i>0.015</i>	X-ray (RT) <i>P2/c†</i> 0.006	LHP Neutron <i>P2/c‡</i> 2.860
	324K		300K				
	<i>P2/c</i> 0.004 <i>0.012</i>	<i>Pc</i> 0.04 <i>0.05</i>	<i>P2/c</i> 0.005 <i>0.012</i>	<i>Pc</i> 0.04 <i>0.05</i>			
Pb—O(1)	2.841	2.833/2.922	2.832	2.772/2.963	2.836	2.810	2.860
Pb—O(2)	2.391	2.402/2.416	2.396	2.407/2.408	2.402	2.398	2.354
Pb—O(2 ^m)	2.507	2.539/2.542	2.503	2.516/2.549	2.492	2.496	2.493
As—O(1)	1.703	1.714/1.745	1.707	1.735/1.726	1.711	1.701	1.550 (P)
As—O(2)	1.684	1.661/1.722	1.686	1.711/1.685	1.683	1.681	1.529 (P)
O(1)...O(1') (2R)	2.486	2.491	2.505	2.515	2.503	2.471	2.470
O(1)—H	1.062	1.052/1.074	1.069	1.124/1.048	1.061		1.048
H...O(1')	1.429	1.430/1.445	1.440	1.481/1.439	1.443		1.424
H...H'(δ)	0.404	0.393	0.398	0.395	0.388		0.392
Δ(As—O)		0.03(4)		0.03(4)			
H _{occ}		0.52(5)		0.60(5)			

*From Wilson *et al.* (1991)

†X-ray parameters from Effenberger and Pertlik (1986)

‡LHP parameters from Lockwood *et al.* (1985)

general, the bonding parameters for schultenite agree reasonably well with those in LHP, as expected, but the value of 2R is somewhat higher in the former.

Given the similarity of the structures at room temperature, it might reasonably be expected that the phase transition behaviour in the two will also be similar. To this end, the structure of schultenite was investigated at a range of temperatures above and below the phase transition.

To examine any structural changes evident just above the phase transition temperature, it was most convenient to collect, in a second experiment, more complete data sets at 324 K (high temperature, above the phase transition) and, for comparison purposes, at 300 K.

Comparisons of the results from these two data sets were most conveniently made by using refinements carried out in both the high-symmetry (*P2/c*) and low-symmetry (*Pc*) space groups. The final refinement details are shown in Table 1.

The results of the refinements are shown in Table 2, which shows selected bond lengths in each case. Several points are worthy of note from this. (1) The H...H separation at each temperature is close to the 0.388(19) Å determined in the original, room-temperature refinement (Wilson *et al.*, 1991). (2) The hydrogen atom occupancies in the

low-symmetry refinement of the high-temperature phase (324 K) are equal (and =0.5) to within experimental error, as expected, whereas those in the low-temperature phase (300 K) showed clear preferential ordering onto one of the two sites. This confirms the importance of the hydrogen atom ordering in the phase transition. (3) The deviations of the heavy atoms from the high-symmetry structure (as indicated in Table 2 by the As—O differences) are small at both temperatures. Within the accuracy of the present measurements it is seen that the significance of these deviations is not clear, but such deviations are by no means excluded. Crystallographic determinations of such small deviations involve some difficulties, as can be seen from the relative precision of the parameters determined in the high- and low-symmetry space groups. This problem, caused by high correlations between parameters due to the small deviations from symmetry, illustrates the necessity for using only the highest resolution, highest precision data collected from the best possible crystal in such cases if conclusive results are to be obtained.

Low-temperature structure — hydrogen ordering

The variation of hydrogen ordering with temperature is shown in Fig. 2. The ordering character-

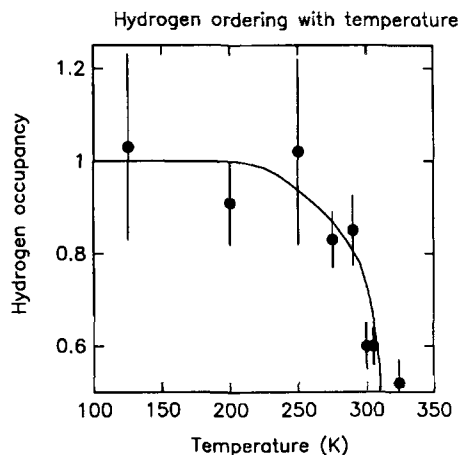


FIG. 2. Hydrogen atom ordering in schultenite as a function of temperature. The line drawn is a guide to the eye.

istics closely follow the pattern found in LHP (Nelmes, 1980; Lockwood *et al.*, 1985), with the ordering rising rapidly to some 30% of the fully ordered value within 10° below the phase transition. Full ordering is reached at some 100° below T_c as expected. The present data are not of sufficient quality (reflected in the large error bars) to test the hypothesis that the onset of proton ordering occurs not at T_c but significantly below T_c , as found in LHP (Lockwood *et al.*, 1985). Further, high-precision data would be required for examination of this effect. The distortion of the heavy atom structure from the centrosymmetric $P2/c$ arrangement, follows approximately the same behaviour as the proton ordering, mirroring the situation in LHP (Lockwood *et al.*, 1985) within the rather low precision of the present measurements.

Again, the preliminary data shed no light on the possibly different temperature dependence of the hydrogen occupancy and the heavy atom distortions close to T_c found in LHP, where an unusually marked increase in the heavy atom distortion found immediately below T_c is accounted for by the observation that this asymmetry persists above T_c .

Conclusions

While the precision of the parameters obtained is rather low, as expected from the limited data sets collected, the low-temperature measurements have confirmed the gradual onset of full hydrogen ordering in the structure below the paraelectric-

ferroelectric phase transition. This is paralleled by an increasing distortion of the heavy atom lattice in the same region. The measurements in the high-symmetry phase are somewhat inconclusive, but do not, within experimental error, preclude the possibility of some distortion of the heavy-atom lattice in this region. Further experiments concentrating on measurements of the weaker reflections and small intensity differences most influenced by this potential distortion would be required to yield unambiguous conclusions regarding this feature.

Thus, in conclusion, the present measurements have yielded the temperature dependence of the structure of schultenite and shown it to be similar to the widely studied LHP structure in both the high- and low-temperature regions.

Note: Tables of observed and calculated structure factors for the data sets collected at 324 K and 330 K can be obtained from the editorial office.

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