

Hydrogen Ordering Effects in $\text{DUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$

By LIONEL BERNARD,^a ANDREW N. FITCH,^a ARTHUR T. HOWE,^b ALBERT F. WRIGHT,^a and BRIAN E. F. FENDER^{a*}

(^a *Institut Laue-Langevin, 156X Centre de Tri, 38042 Grenoble, France* and ^b *Department of Inorganic & Structural Chemistry, University of Leeds LS2 9JT*)

Summary A powder neutron diffraction study of the good proton conductor $\text{DUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ at 305 K shows the presence of $[\text{D}_2\text{O}_5]^+$ ions and indicates hydrogen ordering effects in the plane of the water molecules.

THE isostructural layered hydrates $\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ (HUP) and $\text{HUO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$ (HUAs) display high proton conductivities near room temperature.^{1,2} Conductivity and n.m.r.³ measurements have shown that these compounds undergo a transition, the former at 274 K and the latter at 301 K, to a poorly-conducting low temperature phase.

X-Ray powder measurements⁴ show an accompanying change from tetragonal to orthorhombic symmetry, which for HUAs coincides with the previously reported paraelectric-antiferroelectric transition.⁵

We have performed neutron powder diffraction studies on deuteriated samples of HUAs ($\text{DUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$) at 305 K, *i.e.* above the transition temperature, on the high resolution powder diffractometer DIA at the high flux reactor at ILL (Grenoble). The diffraction pattern was analysed by the method of profile analysis,⁶ including anisotropic temperature factors,⁷ in space group $P4/ncc$.

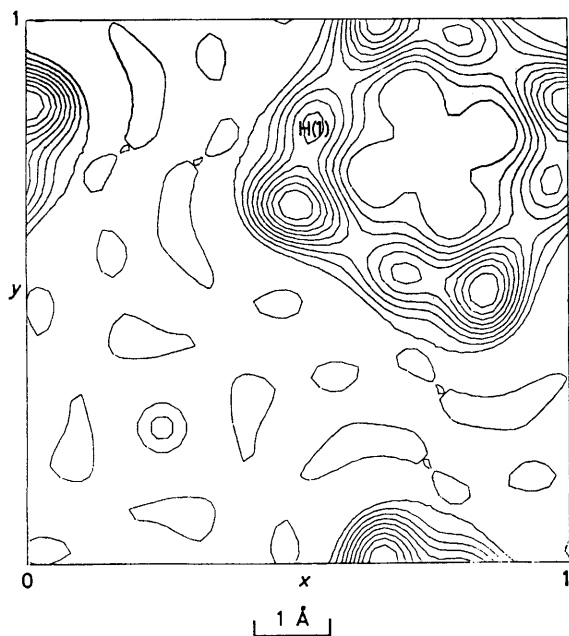


FIGURE 1. Fourier section based on observed intensities and calculated phases parallel to the x,y plane at $z = 0.19$ through the plane of the water layer. The occupancy of a single hydrogen bonding site H(1) is clearly visible.

The structure of DUAs is very similar to that obtained for HUP,⁸ in which there are planar networks of water molecules, also containing the remaining H^+ ions, alternating with layers consisting of $[UO_2PO_4]_n^{2-}$. In these

planar networks the water molecules are grouped in squares and each water molecule may participate in four hydrogen bonds so that there are more hydrogen bond sites than available hydrogen ions.⁹ The present experiment determines how these hydrogens are distributed over the available sites.

Least squares refinement of atomic parameters and Fourier synthesis based on observed intensities and calculated phases indicate the following. (i) Only one of the two crystallographically distinct sites between adjacent water molecules within a square is occupied by hydrogen atoms H(1), although, because the sites have similar chemical environments, one might have expected them both to be occupied.⁹ The hydrogen occupation within a square of 4 water molecules (see Figure 1) is therefore ordered. (ii) The occupancy of these in square sites with hydrogen atoms is only 3/4, *i.e.* 12 hydrogen atoms are statistically distributed over the 16 sites available in the unit cell. (iii) The hydrogen atoms H(2) directed towards the oxygen of an AsO_4^{3-} group are (as expected from *i.r.* data)⁴ linked to the oxygen of a water molecule. This site is fully occupied with 16 hydrogen atoms in the unit cell. (iv) The remaining 8 hydrogen atoms in the unit cell (making a total of 36 in all) are associated with a single maximum in scattering density equidistant from (though not collinear with) two oxygen atoms of water molecules in neighbouring water layers (see Figure 2). This site is the special crystallographic position $8f (\bar{x}, x, 0.25)$, which lies on a two-fold axis of symmetry. Constraining these hydrogens H(3) to this special position reduces the $R(I)$ index on intensities,^{6,7} decreases the number of structural parameters and reduces the e.s.d.'s on the atomic co-ordinates and thermal parameters of H(3) by, on average, factors of 3 and 2 respectively,

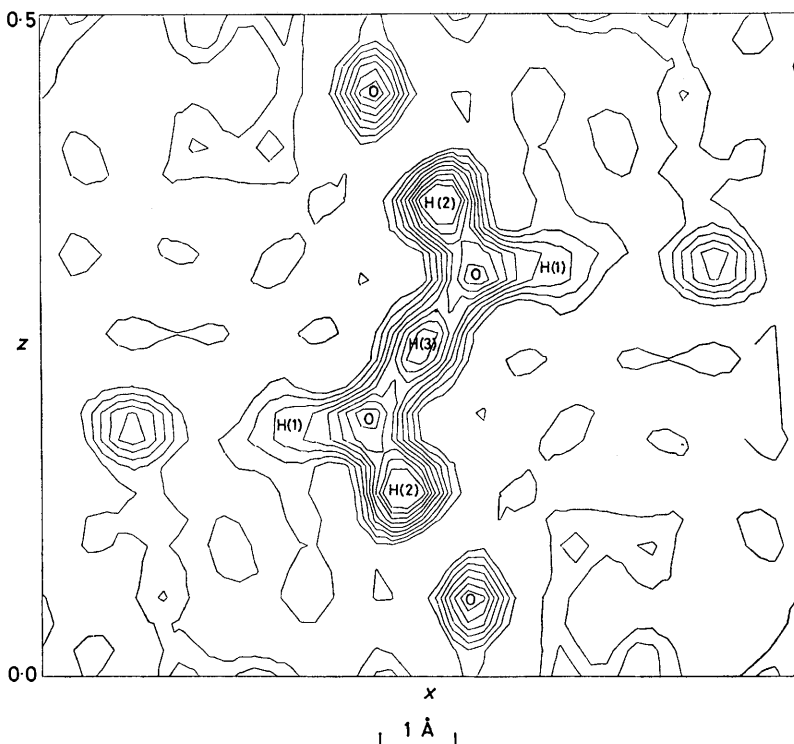


FIGURE 2. Fourier section based on observed intensities and calculated phases. x is parallel to 1,1,0 in the tetragonal unit cell. The maximum in scattering H(3) between the water layers is at $z = 0.25$.

in comparison with the refinement of a model with $\frac{1}{2}$ occupied equivalent sites on either side of this symmetry axis.

We can understand the above results for the average unit cell if we assume there to be a mixture of H_5O_2^+ and H_4O_2 dimers, implying a formula H_5O_2^+ ($\text{UO}_2\text{AsO}_4^-$) H_4O_2 . An equal proportion of $[\text{H}(1)\text{H}(2)\text{O}\dots\text{H}(3)\dots\text{OH}(2)\text{H}(1)]^+$ and $[\text{H}(1)\text{H}(2)\text{O}\dots\text{H}(3)\text{—OH}(2)]$ formula units gives the required proton to water ratio of 1:4 and an occupancy of $\text{H}(1)$ of $\frac{3}{4}$ as observed.

The average oxygen separation of $2.585(5)$ Å observed for the dimers is shorter than the average oxygen separation within a square, which justifies our description in terms of dimers. The average separation, however, probably hides a considerable variation in O—O distance between the H_5O_2^+ and H_4O_2 species because the observed temperature factors for the oxygen atoms are abnormally large. We cannot, therefore, assess whether the hydrogen bond H_5O_2^+ is centred and symmetric or consists of two equally populated asymmetric hydrogen bonds. We would not expect the former case unless the actual O—O separation in H_5O_2^+ is close to 2.4 Å.¹⁰ In the H_4O_2 dimers there must be a displacement of the linking hydrogen $\text{H}(3)$ towards the oxygen atom which has no $\text{H}(1)$ hydrogen.

We consider our single maximum in nuclear scattering density to be best described as the statistical superposition of two pairs of dimeric units of the type $[\text{H}_2\text{O—H—OH}_2]^+$ and $[\text{H}_2\text{O—H—OH}_2]^+$, and HO—H—OH_2 and $\text{H}_2\text{O—H—OH}$ with the two units of a pair being symmetrically related by the two-fold axis passing through their mid-point. Both types of species are constrained to very similar orientations owing to a strong interaction between $\text{H}(2)$ and the charged arsenate group.

The powder neutron diffraction evidence is sufficient to show that proton migration between $\text{H}(1)$ sites within a layer of water molecules involves an overall hydrogen jump distance of $2.19(1)$ Å. This migration, moreover, allows the interchange between the H_5O_2^+ and H_4O_2 species owing to

the partial occupancy of these sites. Transport of hydrogen atoms between neighbouring layers can then be easily effected by the coupled rotation through *ca.* 120° of the two water molecules of an H_4O_2 species about their respective O— $\text{H}(2)$ axes (see Figure 3).

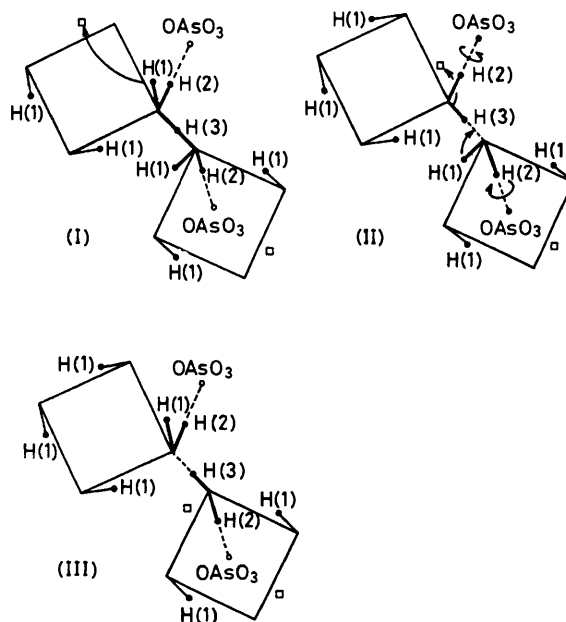


FIGURE 3. Each square of water molecules contains on average one vacant $\text{H}(1)$ hydrogen bonding site. Proton hops between filled and vacant sites convert H_5O_2^+ units into H_4O_2 dimers, sequence (I) \rightarrow (II). The H_4O_2 dimer may reverse configuration by means of two coupled rotations about the $\text{O}_{\text{water}}\text{—H}(2)\text{—O}_{\text{arsenate}}$ axes, thus transferring a proton from one layer to the next, sequence (II) \rightarrow (III).

(Received, 13th March 1981; Com. 281.)

¹ M. G. Shilton and A. T. Howe, *Mater. Res. Bull.*, 1977, **12**, 701.

² A. T. Howe and M. G. Shilton, *J. Solid State Chem.*, 1980, **34**, 149.

³ P. E. Childs, T. K. Halstead, A. T. Howe, and M. G. Shilton, *Mater. Res. Bull.*, 1978, **13**, 609.

⁴ M. G. Shilton and A. T. Howe, *J. Solid State Chem.*, 1980, **34**, 137.

⁵ M. A. R. de Benyacar and H. L. de Dussel, *Ferroelectrics*, 1975, **9**, 241.

⁶ H. M. Rietveld, *Acta Crystallogr.*, 1967, **22**, 151.

⁷ A. W. Hewat, *J. Phys. C*, 1973, **6**, 2559.

⁸ B. Morosin, *Acta Crystallogr., Sect. B*, 1978, **34**, 3732.

⁹ A. T. Howe and M. G. Shilton, *J. Solid State Chem.*, 1979, **28**, 345.

¹⁰ J. O. Thomas and R. Liminga, *Acta Crystallogr., Sect. B*, 1978, **34**, 3686.