Hydrogen-bond Ordering in the Proton Conductors Hydrogen Uranyl Phosphate and Arsenate Tetrahydrates

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Summary An H-bond ordering scheme is proposed for hydrogen uranyl arsenate $HUO_2AsO_4{\cdot}4H_2O$ which explains the observed transition from high to low values of conductivity, the antiferroelectric ordering, and the twinning behaviour, and is consistent with recent *X*-ray and i.r. data; evidence implies that $HUO_2PO_4{\cdot}4H_2O$ also orders in the same way.

MANY solids which display fast ion conductivity undergo an ordering transition from a high-temperature highly conducting phase to a low-temperature poorly conducting phase. Recent conductivity[1,2] and n.m.r.[3] data on the new proton conductors hydrogen uranyl phosphate and arsenate tetrahydrates (HUP and HUAs, respectively) have shown that these also undergo such a transition, at 274 and 301 K, respectively, the origin of which has until now been uncertain.

de Benyacar *et al.*[4] have shown that HUAs is antiferroelectric below the transition, but did not detect any change from a tetragonal unit cell from *X*-ray data. However, optical data,[5] and the observation of both domains (parallel to {110} and {110}) and subdomains (parallel to {100} and {010}), led de Benyacar *et al.*[6] to define the possible point groups, having lower symmetry, as either 222, 2, 1, or 1. This implied a slight distortion, which has recently been found in both HUP and HUAs by Shilton and Howe.[7]

The observed orthorhombic unit cell[7] now permits only 222 out of these four possible groups. Moreover, the only sub-group of the original tetragonal space group *P*4/*ncc* which is consistent with 222 is $P2_12_12$. There are only a limited number of ordered structures which could give this space group. In view of the great difficulty in refining either *X*-ray or neutron diffraction data on this invariably twinned phase, especially to give hydrogen or deuterium positions, we have considered, by a process of elimination, which ordered structures might be consistent with the space group $P2_12_12$. That the ordering occurs in the H-bond network and not in the uranyl–arsenate layers is indicated by the presence of the conductivity transition.

Structures were considered by ordering all or some of the H-bonds, H-bond vacancies,[8] H_3O^+ ions,[8] or combinations of these, and then allowing the structures to relax as suggested by either the new space groups, or by electrostatic arguments. Only two acceptable structures were found. For these the expected relaxation maintained the $P2_12_12$ space group, and the unit cells matched that of the tetragonal phase. Figure 1 illustrates the preferred head-to-tail ordering of most of the dipoles for the two layers in the unit cell, in one of the two structures. The second structure is obtained by rotating one water layer by 90°. The H-bond vacancies and H_3O^+ ions are not shown, but can be satisfactorily distributed in an unordered fashion. Structures having ordered H-bonds, vacancies, and charges were found either to be inconsistent with the twinning data, or to have lower symmetries than $P2_12_12$. I.r. studies[7] have shown that the hydrogens in the water–arsenate bonds remain attached to the water molecules below the transition, and we have not represented these in the Figures.

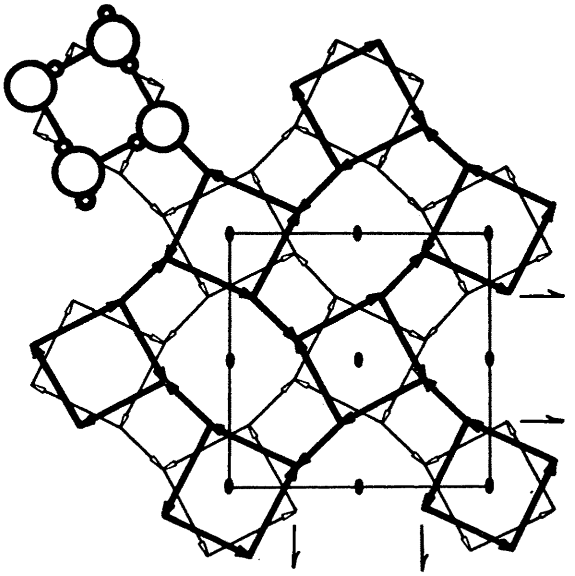

FIGURE 1. Proposed ordered structure in the two water layers (heavy and light lines), which has been derived from the tetragonal unit cell (shown) found for HUP (B. Morosin, *Phys. Letters*, 1978, **65A**, 53) and HUAs.[8] Large circles represent oxygens; small circles, hydrogens. Sheets of $(UO_2P/AsO_4)_n^{n-}$ are interspaced between the illustrated water layers. The symmetry elements corresponding to $P2_12_12$ are indicated for the unit cell. (Half arrows, 2-fold screw axes; ellipses, 2 fold rotation axes).

The presence of the domain boundaries, which are caused by the orthorhombic distortion, is explained because the dipole ordering has destroyed the four-fold symmetry axes, resulting in a unit cell in which the *a* and *b* axes are inequivalent. This can be seen from Figure 1. Across the glide plane of a domain boundary, as illustrated in Figure 2, the directions of all the dipoles are reversed, causing the *a* and *b* axes to be interchanged.

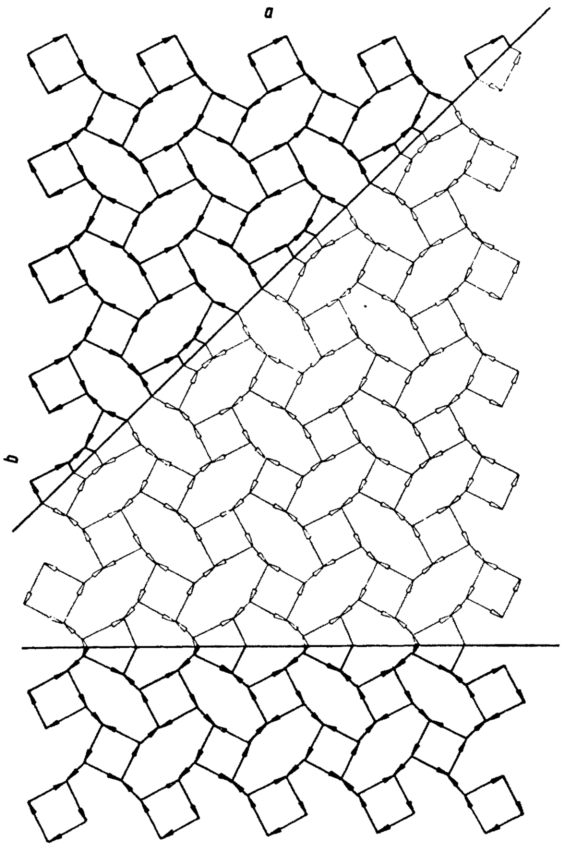

FIGURE 2. Domain and subdomain boundaries (long and short lines, respectively) in which consecutive water layers (heavy and light lines) show mirror symmetry after translation by half a unit cell in the *c* direction, perpendicular to the layers.

The subdomains are explained by a reversal, across the boundary, of only those dipoles constituting the squares (Figure 2), thus leaving the *a* and *b* axes unchanged. The subdomain boundaries can therefore cut across the domain boundaries as observed.[5] Furthermore, the observed transitory nature of the subdomains[5] may be explained by their ease of annealing out, or alternatively by further dipole reversals between alternate water layers which may change the structure to a symmetry, such as *Pccn*, which is now inconsistent with subdomain formation.

Although it has not yet been established that HUP becomes antiferroelectric below the transition, as found for HUAs, the observed similarity of the orthorhombic distortion,[7] twinning,[7] and i.r.[7] behaviour of the two compounds strongly suggests that the proposed antiferroelectric ordered structures would apply to HUP as well. The ordered structures, in inhibiting the dipole reversals necessary for H^+ conduction, provide a natural explanation for the conductivity transition found in both HUP[1] and HUAs.[7]

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