A New Structure for the Lowest-temperature Phase of Solid Hydrogen Sulphide

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Powder neutron diffraction studies of the lowest-temperature phase (III) of deuteriated solid hydrogen sulphide show the previously reported structure to be erroneous; in the new structure hydrogen bonding appears to be unimportant in determining the ordering of the hydrogen atoms.

Hydrogen sulphide is a well-known molecule of great importance to the understanding of basic chemical interactions such as dipole–dipole interactions and hydrogen bonding. It is therefore surprising that the packing of the molecules is poorly characterized in the solid state phases, although the molecular structure has been determined by microwave spectroscopy.[1]

Both solid H_2S and D_2S undergo a transition from a cubic orientationally disordered phase (II) to a low temperature ordered phase (III) at 103.5 and 107.8 K, respectively.[2—5] *X*-Ray and electron diffraction studies[6] suggest a tetragonal arrangement of the sulphur atoms in phase (III). An earlier

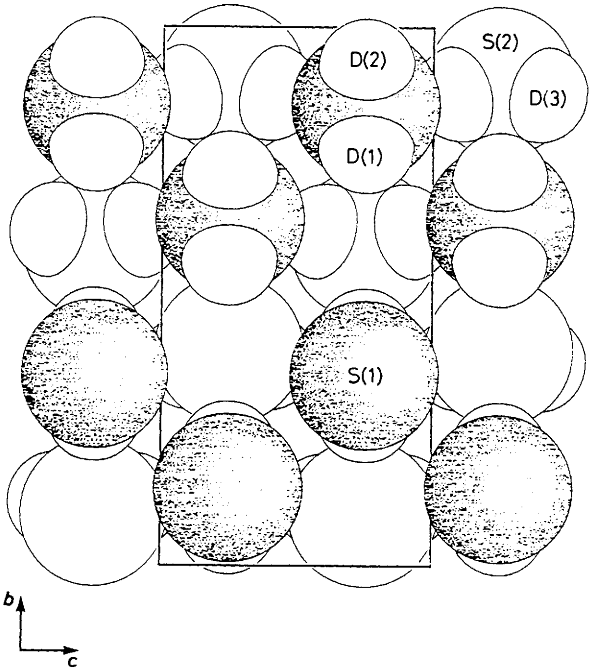

Figure 1. View of the structure of D_2S showing the arrangement of the molecules in the *bc*-plane.

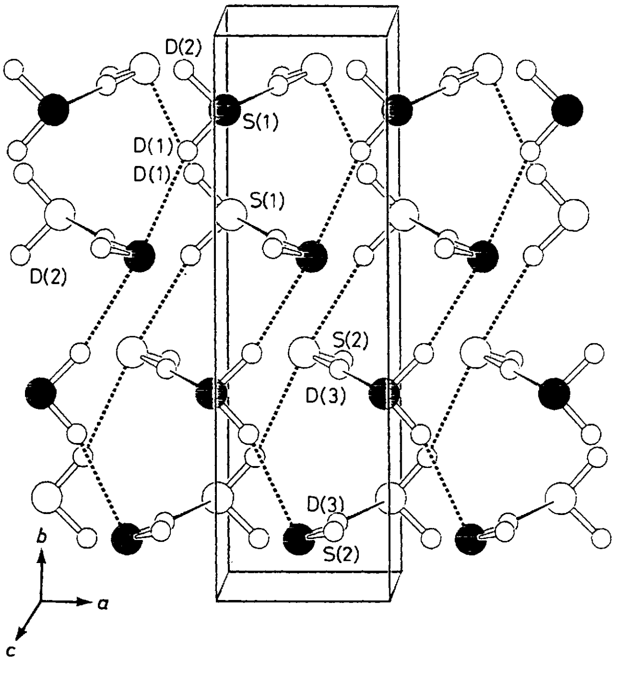

Figure 2. The hexagonally close-packed structure of D_2S viewed from above the *ab*-plane. Shaded sulphur atoms are at z = 3/4, open sulphur atoms are at z = 1/4. Shortest D ··· S non-bonded interactions are shown as dotted lines.

powder neutron diffraction study on D_2S adopted a similar arrangement of sulphur atoms, and in addition reported the positions of the hydrogen atoms.[7] This arrangement of hydrogen atoms, however, in which the molecules form hydrogen-bonded zigzag chains parallel to the [100] and [010] axes, is completely incompatible with our recent powder neutron diffraction studies on D_2S. We wish to report some key aspects of our new structure for phase (III) of hydrogen sulphide refined by the Rietveld method[8,9] using high-resolution data collected on the diffractometer D1A at the Institut Laue Langevin, Grenoble.

Our new structure is orthorhombic, space group *Pbcm* (No. 57), with $a = 4.0760(1)$, $b = 13.3801(5)$, and $c = 6.7215(3)$ Å at 1.5 K. The slight deviation from unity in the ratio $b:2c$ is insufficient to cause resolvable splitting of the lines in the diffraction pattern and explains the previously reported tetragonal unit cells. Figure 1 shows the near-tetragonal arrangement of the sulphur atoms and the doubling of the unit cell along *b* due to the ordering of the hydrogen atoms.

The structure can be described in terms of a hexagonally close-packed arrangement of molecules (Figure 2), with distortions to accommodate the hydrogen atoms. The close-packed layers lie perpendicular to the *c*-axis, with the dipoles of the molecules aligned along *a* in an antiferroelectric arrangement. Molecules which lie in the range $1/2 < y < 1$ have their dipoles along the positive *a* direction, whereas those in the range $0 < y < 1/2$ have dipoles in the opposite sense. The structure contains two crystallographically distinct D_2S molecules with S(1)–D distances of 1.301(8) and 1.354(8) Å, an S(2)–D distance of 1.332(8) Å, and D(1)–S(1)–D(2) and D(3)–S(2)–D(3) angles of 92.4(4) and 93.4(4)°, respectively. There are three S–D · · · S interactions which resemble hydrogen bonding. They have sulphur–sulphur distances between 3.985(5) and 4.027(9) Å. This is much longer than the sum of the van der Waals radii for sulphur (1.85 Å[10]) and longer than the shortest sulphur–sulphur distance in the structure of 3.672(9) Å where there is direct contact between the sulphur atoms. If the principle is accepted that X–H · · · Y are hydrogen bonded when the separation between X and Y is close to the sum of the van der Waals radii of X and Y,[11] then the ordering of the hydrogen atoms in D_2S is not dominated by hydrogen bond formation.

Full crystallographic details of all three solid-state phases of D_2S will be reported elsewhere, including characterization of the orientationally disordered phases.[12]

Received, 14th November 1989; Com. 9/04875H

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