NEUTRON-DIFFRACTION LOCALIZATION OF HYDROGEN ATOMS IN THE STRUCTURE OF LITHIUM SULFATE MONOHYDRATE $\mathrm{Li_2SO_4 \cdot H_2O}$

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Abstract

Full Text

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R. P. OZEROV, L. E. FYKIN, N. V. RANNEV, G. S. ZHDANOV

NEUTRON-DIFFRACTION LOCALIZATION OF HYDROGEN ATOMS IN THE STRUCTURE OF LITHIUM SULFATE MONOHYDRATE $Li_2SO_4 \cdot H_2O$

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The motif of the crystal structure of $Li_2SO_4 \cdot H_2O$* was determined by x-ray diffraction by Ziegler (^{1}). A later refinement of the structure with respect to the positions of the heavy atoms was carried out by x-ray diffraction by Larson and Helmgoltz (^{2}); the orientation and magnitude of the interproton vector were studied by the method of nuclear magnetic resonance (NMR) by many authors ($^{3-6}$).

Fig. 1. Projection $\sigma(xz)$ of the nuclear density of the structure of lithium sulfate monohydrate

We undertook a neutron-diffraction study of a single crystal of $Li_2SO_4 \cdot H_2O$ for the purpose of directly localizing the hydrogen atoms in the structure**. Single crystals of irregular shape were used with linear dimensions of ~ 7 mm. The crystals had small natural faces, which made it possible to orient them optically directly on the diffractometer (^{7}). A total of 180 nonzero-intensity reflections of the type $\pm h0l$ and 90 reflections of the type $0kl$ were measured ($\lambda = 1.05$ Å). In measuring the intensities of reflections of the type $0kl$ (the center of symmetry is absent in the projection)

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* Monoclinic unit cell $a = 5.43$ Å, $b = 4.83$ Å, $c = 8.14$ Å, $\beta = 107°35'$; space group $C_2^2 - P2_1$, number of "molecules" 2.

** The single crystals were provided to us by I. V. Gavrilova, to whom the authors express their gratitude.

Fig. 3. Projection of the nuclear density of the structure of α-resorcinol σ (xy). G_1, G_3, J_2 and J_4 are oxygen atoms, H are hydrogen atoms, A, B, C, D, E, F are carbon atoms.

Figure 2: Fig. 3. Projection of the nuclear density of the structure of α-resorcinol σ (xy). G_1, G_3, J_2 and J_4 are oxygen atoms, H are hydrogen atoms, A, B, C, D, E, F are carbon atoms.

Fig. 2. Projection $\sigma(yz)$ of the nuclear density of the structure of lithium sulfate monohydrate

we encountered the possible influence of anomalous neutron dispersion in scattering by Li^6 nuclei (^{8}); however, it was established that for a crystal with the natural mixture of lithium isotopes this effect is small. At this stage no extinction correction was introduced either. The usual absorption correction was introduced (for a cylindrical specimen), the value of μ being obtained by calculation from the known cross sections of lithium and hydrogen and experimentally (from the absorption of a very thin neutron beam by the central part of the specimen); in both cases values $\mu = 2.2$ cm^{-1} were obtained. After this the relative values of the structure amplitudes F were determined in the usual way.

In the first approximation the projections of the nuclear density $\sigma(xz)$ and $\sigma(yz)$ were calculated* from the experimental values of F, the signs of which were determined taking into account the positions only of the heavy atoms (S, O, Li) according to the coordinates of Ziegler (^{1}). The parameters of the heavy atoms determined from these projections did not change in any appreciable way; they correspond better to the values of Ziegler (^{1}) than to those of Larson (^{2}). In both projections, minima corresponding to hydrogen atoms were clearly revealed. The results obtained were used in calculating the projections in the following approximations (Figs. 1 and 2) and in refining the coordinates by the method of differential synthesis. The parameters determining the positions of the hydrogen atoms in the structure are given in Table 1.

From the projections, the configuration of the H_2O "molecule" and the system of hydrogen bonds in the structure have been determined. The atoms H_1 and H_2 are located near the atom O_5 (the oxygen atom of the H_2O "molecule") in such a way that the hydrogen bonds O_5—$H_2 \cdots O_5'$ and O_5—$H_1 \cdots O_2$ are formed (O_2 is an oxygen atom of the SO_4 tetrahedron). The orientation of the interproton vectors is $\alpha = 96°54'$, $\beta = 43°12'$ and $\gamma = 47°36'$ (α, β, γ are the angles between the direction of the interproton vector and the positive direction of the axes)

Fig. 3. Projection of the nuclear density of the structure of α-resorcinol $\sigma(xy)$.

* All calculations were carried out on the "Kristall" machines of the L. Ya. Karpov Physicochemical Institute and the "Strela" machine of the Computing Center of Moscow State University named after M. V. Lomonosov.

G_1, G_3, J_2 and J_4 are oxygen atoms, H are hydrogen atoms, A, B, C, D, E, F are carbon atoms.

is in good agreement with the results obtained by the NMR method (^{6}).

Table 1

Position of hydrogen atoms
(xyz and $x,\ y+\frac{1}{2},\ \bar{z}$)

	x	y	z
H_1	0.480	0.122	0.297
H_2	0.517	0.788	0.488

The result obtained by us is of interest from two points of view: the interatomic distances in the H_2O "molecule" (O_5–H_1 and O_5–H_2), and especially the angle H_1–O_5–H_2, are substantially greater than those in a free water molecule, in true crystal hydrates, and in the structure of ice (the O–H distances are 1.1 Å and the H–O–H angle is 145°; the most frequently encountered values are 0.99-1.00 Å and 109°). Attention is also drawn to the shortened distance Li_1–O_5 (1.98 Å). These atoms, together with the hydrogen atoms, form a characteristic chain

$$\cdots Li_1 - O_5\begin{matrix}/H_1\\ \backslash H_2\end{matrix}\cdots Li_1 -$$

(Fig. 1), extending through the whole crystal in the direction of the x axis.

The indicated features of the crystal structure of $Li_2SO_4 \cdot H_2O$ may be explained on the basis of ideas about the nature of the Li–O bond,

being developed at present by D. N. Shigorin et al. (9,10). According to these ideas, the unshared pair of p-electrons of the oxygen atom occupies certain vacant orbitals of the valence shell of the lithium atom. As a result, the electrostatic equilibrium in the H_2O "molecule" is disturbed and the protons diverge through a larger angle. The Li—O bond becomes stronger, and in character covalent, which leads to a decrease in the corresponding interatomic distance.

The system of hydrogen bonds in the structure is characterized by the presence of a zigzag infinite chain O_5—$H_2 \cdots O_5'$—$H_2' \cdots$, with an angle of 109° at the O_5 atom, extending along the y axis (Fig. 2). To this chain, also by means of hydrogen bonds, SO_4 tetrahedra are attached. Such a system is characterized by a step (period b) of 4.83 Å. The presence of an infinite chain of bonds, similar in character but helical, O—H ⋯ O—H ⋯, was established by Bacon (11) in the structure of α-resorcinol (Fig. 3). In this case the pitch of the helix (period c) is 5.66 Å.

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named after L. Ya. Karpov

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Note: Figure translations are in progress. See original paper for figures.