

## Neutron-diffraction studies of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{D}_2\text{O}$

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### Auszug

Die Strukturanalyse von Kupfersulfat-Pentahydrat und -Pentadeuterat mittels Neutronenbeugung ergab aus dreidimensionalen Interferenzdaten  $R = 3,7\%$  bzw.  $5,9\%$ . Die vom Hydrat bekannten, individuell unterschiedlichen Gestalten der fünf Wassermoleküle erscheinen im Deuterat getreulich wieder. Während die Winkel H—O—H im Hydrat zwischen  $106,7$  und  $112,9^\circ$  bei Standardabweichungen um  $0,5^\circ$  für die einzelnen Werte liegen, betragen sie beim Deuterat  $104,7$  bis  $112,6^\circ$  mit  $\pm 0,3^\circ$  als Fehlergrenze.

### Abstract

Three-dimensional analysis of crystals containing hydrogen and deuterium have produced  $R$  values of  $3.7\%$  and  $5.9\%$  respectively and the distinctive individual geometry of the five water molecules previously known in the hydrate is faithfully reproduced in the deuterate. In the hydrate the H—O—H angle ranges from  $106.7$  to  $112.9^\circ$ , with a standard deviation of about  $0.5^\circ$  on the individual values, compared with a range from  $104.7$  to  $112.6^\circ$ , with a standard deviation of  $0.3^\circ$ , for the deuterate.

### Introduction

The main reason for the two-dimensional neutron-diffraction analysis of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  by BACON and CURRY (1962) was to study the geometry of the hydrogen bonds to the five water molecules. In contrast to the normal H—O—H angle of about  $109^\circ$  within the water molecule, the O—O—O angles were  $122$ ,  $129$ ,  $122$ ,  $108$  and  $121^\circ$ . Thus considerable bending of the bonds was to be expected if the preferred angle within the water molecule was to be maintained. The results did indeed show considerable bending of the bonds, with O—H $\cdots$ O angles as small as  $154^\circ$ , but there were nevertheless some departures

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of the H—O—H angles from the tetrahedral value, ranging from  $106^\circ$  to  $114^\circ$ , and it was believed that these departures were significant.

The above measurements were the last structural analysis to be carried out with the Harwell low-flux reactor BEPO and the subsequent ten years were to yield substantial increases in the flux of neutron beams from reactors and corresponding improvements in the techniques of neutron diffraction. It has subsequently been possible to carry out a three-dimensional analysis at the Harwell reactors DIDO and PLUTO using smaller crystals, for which the corrections for absorption and extinction are much reduced. In some cases spherical crystals have been used and these have permitted much higher accuracy in the calculation of the residual corrections. Moreover the intervening years have seen the development of ZACHARIASEN's (1967) new treatment of extinction and its further extension, particularly for the case of neutron diffraction, by COOPER and ROUSE (1970) and more recently, in a much more general way, by BECKER and COPPENS (1974*a,b*).

Advantage has been taken of the quite different coherent scattering lengths of hydrogen and deuterium, which are equal to  $-0.374$  and  $0.667 \times 10^{-12}$  cm respectively, to carry out a parallel analysis of the deuterated salt  $\text{CuSO}_4 \cdot 5\text{D}_2\text{O}$ . This has provided results which have given increased confidence in the accuracy of the experimental conclusions concerning the geometry of the hydrogen bonds and the coordinates for the individual water molecules. It is recalled that the 1962 measurements of BACON and CURRY contributed the data for 10 of the 28 different hydrogen atoms in water molecules which were surveyed by BAUR (1965). This survey was the basis of BAUR's conclusion that the coordinates of the hydrogen atoms in these hydrates were determined by the condition that water molecules of standard size and shape should set themselves in those positions, amid the surrounding cations and anions, which would give minimum electrostatic energy. We shall examine this postulate further in the light of our new results.

### Experimental

Hydrated copper sulphate crystallizes with a well-developed [001] zone in the triclinic system, possessing a centre of symmetry and space group  $P\bar{1}$ . There are two formula groups in each unit cell, for which  $a = 6.141$ ,  $b = 10.736$ ,  $c = 5.986$  Å,  $\alpha = 82^\circ 16'$ ,  $\beta = 107^\circ 26'$  and  $\gamma = 102^\circ 40'$ . There are copper atoms at 0,0,0 and  $\frac{1}{2}, \frac{1}{2}, 0$ , *i.e.* the centres of symmetry, and all the other atoms are in general positions.

The positions of the atoms other than hydrogen were first given by BEEVERS and LIPSON (1934) and all the atomic positions were refined by BACON and CURRY (1962).

For the hydrated salt,  $5\text{H}_2\text{O}$ , two collections of intensity data for neutrons were made and refined separately. The first used a plate-shaped crystal measuring roughly  $2.7 \times 2.7 \times 1.2$  mm and was examined with a neutron wavelength of  $1.172 \text{ \AA}$  at the reactor DIDO. 501 independent reflections were measured and there were significant variations of the absorption correction (computed by the ORABS programme of BUSING and LEVY, 1957), ranging from  $A_{\text{max}} = 1.7516$  to  $A_{\text{min}} = 1.1729$ , because of the shape of the crystal. Successive refinements in which increasing numbers of the high-intensity reflections were eliminated suggested that the extinction correction for the most intense reflections was about 45%. These data were refined only to the stage of isotropic temperature factors, since it was judged that the total of 501 reflections was not adequate for an anisotropic refinement which would demand 193 parameters. A further crystal was ground to a sphere, with a diameter of 2.5 mm, and 725 reflections were measured with a neutron wavelength of  $1.144 \text{ \AA}$  at the reactor PLUTO. The absorption factor varied only from 1.4526 to 1.4693 and could therefore be neglected. Preliminary comparison of observed  $F_o$  and calculated  $F_c$  values of structure factors showed a systematic tendency for  $|F_o|$  to be less than  $|F_c|$  for the intense reflections, suggesting extinction. More than 400 of the more intense reflections were remeasured at a shorter wavelength,  $0.870 \text{ \AA}$ , in an attempt to make a direct assessment of the extinction but no suitable computing programme was available to handle all the refinable parameters which were necessary. Accordingly the extinction was corrected in the manner described by BACON and JUDE (1973) in which the function  $\left(y^* - \frac{1}{y^*}\right)$  is plotted against  $TF_{\text{obs}}^2/\sin 2\theta$  for a representative sample of reflections. Here  $y^*$  is the ratio  $F_{\text{obs}}^2/F_{\text{calc}}^2$  where  $F_{\text{calc}}^2$  has been arrived at from the results of a refinement in which the extinction-affected data are weighted out.  $T$  is the average path length through the crystal, which, for a spherical crystal, is equal to one-and-a-half times the radius. From the slope of this plot, which is shown in Fig. 1, the best values of  $y^*$ , and hence of the extinction correction, was determined for each reflection. The final refinement, using anisotropic temperature factors, employed a weighting scheme of the form  $\omega_i = b/\{1 + (|F_o|_i - a)^2\}^{1/2}$  where  $a$  and  $b$  are constants selected to equalize the average value of

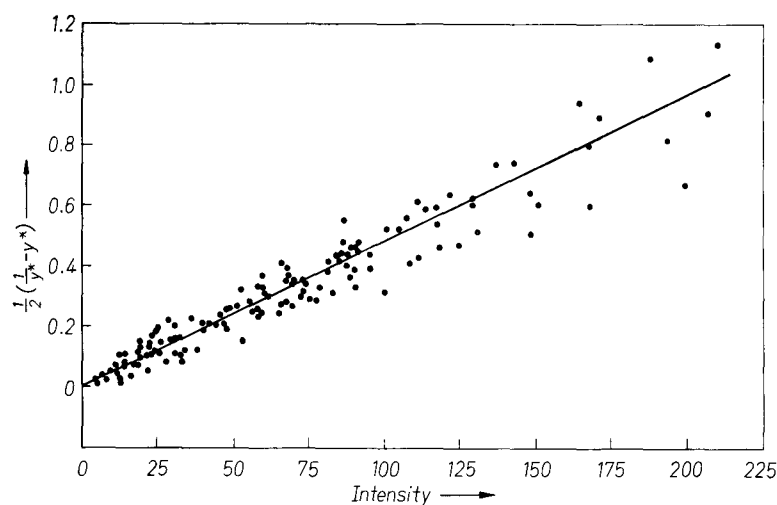


Fig. 1. Linear variation of the function  $\frac{1}{2} [(1/y^*) - y^*]$  with intensity of reflection

$\omega_i |F_o - F_c|^2$  over equal ranges of  $|F_o|$ . This weighting scheme will of course downgrade both the very weak reflections and also those which are most affected by extinction. The  $R$  value (amplitude) at the end of the refinement was 3.7%.<sup>0</sup>

Crystals grown from heavy water were accepted in their original plate-like form (in order to avoid exchange of deuterium with hydrogen during a grinding process) and sealed in silica tubes. 1103 independent reflections were measured at  $\lambda = 1.172 \text{ \AA}$  for a crystal measuring  $5.7 \times 2.9 \times 1.1 \text{ mm}$ , with a twice-daily check of the intensity of the 100 reflection, which is sensitive to the retention of the initial degree of deuteration. The linear absorption coefficient for the deuterated crystal was  $0.12 \text{ cm}^{-1}$ , compared with 2.00 for the hydrated crystal, with the result that the absorption correction had a practically constant value for all the reflections: the values deduced from the ORABS programme varied only from 1.0132 to 1.0292. These corrections were included in the subsequent computations but are not really significant. A refinement of the axial lengths of the unit cell was carried out from the  $\theta$  values of the 100 high-angle reflections and yielded values identical with those given by BACON and CURRY for the hydrated salt.

After three cycles of least-squares refinement it was evident that the intensities were severely extinguished, and indeed more so than for the hydrated crystals. The most intense reflections were systematically less than their respective calculated values and the isotropic

temperature factors all refined to negative values. On an arbitrary scale the intensities ranged from 0.6, for a just-observable reflection, to 700 units for the most intense value. Data were weighted out of the refinement until there was no longer any tendency for  $|F_o|$  to be less than  $|F_c|$ : in fact, intensities lower than 50 units (corresponding to about 550 of the reflections) appeared to be negligibly extinguished. A correction was then made by using the function  $(y^* - \frac{1}{y^*})$ , as described for the hydrated sphere with the proviso that the abscissa for the plot was  $TI_o$  in which  $T$  the average path-length through the crystal has a different value for each reflection and which was computed by the ORABS programme. It was found that beyond a certain value of  $TI_o$  the points diverged from a straight-line plot, thus indicating that the extinction corrections for these intense reflections were greater than predicted by the Zachariasen theory. In fact it was found that about 8% of the total number of reflections were inadequately corrected and for these the extinction was more than 50%. This finding is consistent with the results for  $\text{CaF}_2$ , reported by COOPER and ROUSE (1970) who concluded that the Zachariasen correction was adequate up to levels of extinction of about 40%. The influence of this 8% of reflections on the final refinement was removed by weighting them down by a factor of 100. The  $R$  value achieved finally, with an overall weighting scheme of the type mentioned earlier, was 5.9%. One concluding cycle of refinement was carried out in which the scattering length of the deuterium atom was allowed to vary, in order to take account of incomplete deuteration. This resulted in a value of  $0.610 \times 10^{-12}$  cm for the scattering length. This corresponds, in terms of 0.667 for pure deuterium (DILG, KOESTER and NISTLER, 1971) and  $-0.374$  for pure hydrogen (KOESTER and NISTLER, 1971) to a deuteration of 95%.

### Results

The final fractional atomic coordinates derived from the hydrated sphere and the deuterated plate are given in Tables 1, 2 respectively and Tables 3, 4 list the thermal parameters. From the thermal parameters we have calculated the root-mean-square displacements of the atoms along the principal axes of the thermal ellipsoids and Table 5 compares these for the hydrated and deuterated crystals. The atomic motions are illustrated in Fig. 2 which shows a view along the normal to the (001) plane constructed with the programme ORTEP

Table 1  
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  fractional coordinates and their estimated standard deviations

	$x/a$	$y/b$	$z/c$		$x/a$	$y/b$	$z/c$
Cu(1)	0	0	0				
Cu(2)	$\frac{1}{2}$	$\frac{1}{2}$	0				
S	0.0133(5)	0.2871(5)	0.6253(5)	H(54)	0.8980(6)	0.1412(6)	0.2547(8)
O(1)	0.9072(3)	0.1520(3)	0.6734(3)	H(59)	0.7185(7)	0.0126(6)	0.2283(7)
O(2)	0.2442(3)	0.3172(3)	0.7960(3)	H(62)	0.3010(6)	0.2016(7)	0.0667(9)
O(3)	0.8601(3)	0.3724(3)	0.6363(3)	H(69)	0.3341(5)	0.1270(5)	0.3188(7)
O(4)	0.0444(3)	0.3022(3)	0.3849(3)	H(74)	0.3231(6)	0.3785(5)	0.3406(6)
O(5)	0.8176(3)	0.0737(3)	0.1519(4)	H(73)	0.6016(5)	0.3937(5)	0.4256(5)
O(6)	0.2887(3)	0.1177(4)	0.1490(4)	H(83)	0.8012(5)	0.4011(5)	0.8847(9)
O(7)	0.4654(3)	0.4063(3)	0.2975(3)	H(84)	0.8570(5)	0.3845(5)	0.1620(6)
O(8)	0.7560(3)	0.4161(3)	0.0191(5)	H(91)	0.6033(5)	0.1321(5)	0.6671(7)
O(9)	0.4350(4)	0.1263(5)	0.6289(5)	H(92)	0.4108(9)	0.1932(10)	0.6922(12)

Table 2  
 $\text{CuSO}_4 \cdot 5\text{D}_2\text{O}$  fractional coordinates and their estimated standard deviations

	$x/a$	$y/b$	$z/c$		$x/a$	$y/b$	$z/c$
Cu(1)	0	0	0				
Cu(2)	$\frac{1}{2}$	$\frac{1}{2}$	0				
S	0.0142(6)	0.2861(3)	0.6254(5)	D(54)	0.8974(4)	0.1430(3)	0.2525(5)
O(1)	0.9084(3)	0.1517(2)	0.6735(3)	D(59)	0.7171(5)	0.0123(2)	0.2292(4)
O(2)	0.2443(3)	0.3175(2)	0.7956(3)	D(62)	0.3012(4)	0.2013(2)	0.0668(5)
O(3)	0.8601(3)	0.3723(2)	0.6369(3)	D(69)	0.3339(4)	0.1264(2)	0.3184(4)
O(4)	0.0443(3)	0.3013(2)	0.3849(3)	D(74)	0.3234(4)	0.3790(2)	0.3398(3)
O(5)	0.8180(4)	0.0735(2)	0.1516(4)	D(73)	0.6003(4)	0.3929(2)	0.4251(4)
O(6)	0.2898(3)	0.1172(2)	0.1488(4)	D(83)	0.8012(4)	0.4014(2)	0.8854(4)
O(7)	0.4659(4)	0.4065(2)	0.2972(4)	D(84)	0.8574(4)	0.3842(2)	0.1614(4)
O(8)	0.7542(4)	0.4159(2)	0.0190(4)	D(91)	0.6003(5)	0.1316(2)	0.6671(4)
O(9)	0.4332(4)	0.1240(2)	0.6275(3)	D(92)	0.4108(4)	0.1952(3)	0.6962(5)

described by JOHNSON (1965). It is likely that the thermal parameters given in the tables are underestimated because the intensity values have not been corrected for thermal diffuse scattering. There is a tendency for the displacements of the Cu, S and O atoms in the deuterated crystal to be smaller than those in the hydrated crystal in most cases, but all the corresponding hydrogen and deuterium displacements are very similar. This tendency may be a result of incomplete correction for extinction in the deuterated crystal.

Figure 3 shows projections of the hydrated and deuterated structures on the 001 plane, constructed by Fourier synthesis from the

Table 3.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ : anisotropic temperature factors and their estimated standard deviations ( $\times 10^4$ )

	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$
Cu(1)	89(4)	24(5)	93(6)	11(2)	24(3)	-17(3)
Cu(2)	90(4)	26(5)	89(5)	20(2)	17(3)	-4(3)
S	86(8)	35(9)	29(10)	16(4)	-5(5)	-1(5)
O(1)	116(5)	37(5)	142(6)	1(3)	6(3)	2(3)
O(2)	107(4)	44(5)	140(6)	9(2)	-33(3)	-17(3)
O(3)	155(5)	51(6)	115(6)	55(3)	25(3)	-13(3)
O(4)	137(4)	46(5)	108(6)	32(2)	53(3)	5(3)
O(5)	157(6)	43(6)	164(7)	14(3)	67(4)	-33(4)
O(6)	126(5)	35(7)	131(9)	5(3)	13(4)	-23(4)
O(7)	116(6)	66(6)	110(6)	13(3)	29(4)	29(3)
O(8)	170(6)	85(6)	108(8)	80(3)	27(5)	-5(4)
O(9)	92(7)	61(9)	150(9)	13(4)	26(4)	5(5)
H(54)	241(11)	96(11)	310(16)	23(7)	73(9)	-96(9)
H(59)	249(11)	98(10)	276(13)	7(7)	147(9)	-30(7)
H(62)	292(12)	49(13)	270(17)	-3(7)	85(9)	-16(10)
H(69)	245(9)	60(9)	167(13)	20(5)	9(8)	-33(6)
H(74)	177(11)	95(10)	189(11)	37(5)	68(7)	3(6)
H(73)	198(9)	68(9)	148(10)	29(4)	13(6)	18(6)
H(83)	203(9)	70(9)	177(15)	45(5)	70(8)	-12(6)
H(84)	199(9)	109(10)	180(12)	74(5)	33(7)	-17(6)
H(91)	130(10)	116(10)	302(13)	38(5)	12(7)	-10(7)
H(92)	254(13)	47(16)	346(23)	26(8)	65(12)	-19(11)

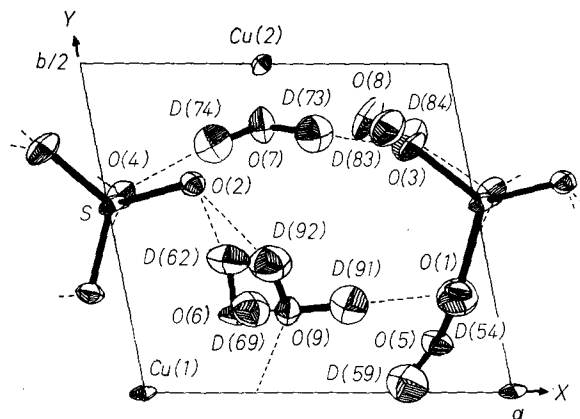
Fig. 2. A view along the normal to the 001 plane of the thermal ellipsoids for  $\text{CuSO}_4 \cdot 5\text{D}_2\text{O}$ , constructed with the programme ORTEP, for half of the unit cell

Table 4.  $\text{CuSO}_4 \cdot 5\text{D}_2\text{O}$ : anisotropic temperature factors and their estimated standard deviations ( $\times 10^4$ )

	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$
Cu(1)	116(5)	11(2)	69(5)	10(2)	19(4)	-16(2)
Cu(2)	88(5)	23(2)	58(5)	19(2)	30(4)	-5(2)
S	117(10)	16(3)	50(9)	22(4)	32(8)	-8(4)
O(1)	131(5)	19(2)	137(6)	-3(2)	20(5)	1(2)
O(2)	111(5)	24(2)	136(6)	8(2)	-25(5)	-20(2)
O(3)	166(6)	38(2)	105(5)	52(2)	33(5)	-18(2)
O(4)	155(6)	40(2)	75(5)	32(2)	51(5)	-0(2)
O(5)	162(6)	31(2)	149(6)	1(3)	85(6)	-35(3)
O(6)	161(6)	17(2)	112(6)	2(2)	35(5)	-10(2)
O(7)	107(6)	66(2)	90(6)	16(3)	33(7)	32(3)
O(8)	199(7)	89(3)	65(6)	97(3)	31(6)	-1(3)
O(9)	108(7)	41(2)	150(6)	16(2)	32(5)	-10(3)
D(54)	265(8)	68(3)	271(8)	23(3)	91(7)	-60(4)
D(59)	273(7)	66(2)	270(8)	13(3)	148(7)	-31(3)
D(62)	293(8)	45(3)	278(9)	4(3)	100(7)	-16(4)
D(69)	232(7)	58(2)	179(8)	11(3)	24(6)	-27(3)
D(74)	218(8)	61(2)	161(7)	26(3)	74(6)	-0(3)
D(73)	214(8)	61(2)	142(7)	27(3)	31(7)	-2(3)
D(83)	213(7)	62(2)	173(7)	51(3)	56(6)	-17(3)
D(84)	226(7)	80(3)	179(7)	66(3)	50(7)	-3(3)
D(91)	201(9)	64(3)	273(8)	27(3)	40(7)	-14(3)
D(92)	278(9)	62(3)	306(9)	25(3)	104(7)	-26(4)

intensities of the  $hk0$  reflections. Figure 4 shows corresponding projections of the hydrogen and deuterium atoms only, constructed by synthesis of  $(F_o - F_{\text{CuSO}})$  where  $F_o$  is the observed value of the structure amplitude and  $F_{\text{CuSO}}$  is the calculated contribution from the copper, sulphur and oxygen atoms using the parameters determined from the least-squares analyses. The hydrogen bonds which unite the five water molecules to the remainder of the structure are marked in Fig. 4. The oxygen atoms of four of the water molecules, *i.e.*  $\text{O}_5$ ,  $\text{O}_6$ ,  $\text{O}_7$  and  $\text{O}_8$ , are each linked (via a hydrogen bond) to two other oxygen atoms and they are also linked to a copper atom. The oxygen atom,  $\text{O}_9$ , of the fifth water molecule forms four bonds, two of them to the oxygen atoms  $\text{O}_1$ ,  $\text{O}_2$  in sulphate groups and also to the oxygen atoms of the water molecules  $\text{O}_5$ ,  $\text{O}_6$ .

From a structural point of view, the most interesting information is probably the comparison of bond lengths and bond angles for the hydrated and deuterated crystals which is given in Tables 6 and 7.



Table 5. *Root-mean-square displacements along principal axes of thermal ellipsoids*  
 For each parameter the upper and lower values are for the hydrated and deuterated salts respectively

	$U_1$	$U_2$	$U_3$		$U_1$	$U_2$	$U_3$
Cu(1)	0.093 Å	0.122 Å	0.135 Å	H(54)	0.151 Å	0.201 Å	0.274 Å
	0.053	0.116	0.142		0.146	0.209	0.236
Cu(2)	0.103	0.121	0.134	H(59)	0.161	0.215	0.250
	0.079	0.106	0.129		0.158	0.190	0.239
S	0.065	0.128	0.141	H(62)	0.159	0.209	0.231
	0.055	0.101	0.143		0.156	0.207	0.229
O(1)	0.129	0.140	0.181	H(69)	0.145	0.190	0.219
	0.098	0.142	0.171		0.154	0.190	0.210
O(2)	0.106	0.157	0.191	H(74)	0.161	0.177	0.231
	0.100	0.125	0.185		0.155	0.181	0.193
O(3)	0.106	0.137	0.195	H(73)	0.139	0.191	0.211
	0.074	0.137	0.189		0.151	0.185	0.195
O(4)	0.121	0.135	0.172	H(83)	0.149	0.178	0.206
	0.098	0.133	0.170		0.141	0.173	0.207
O(5)	0.116	0.160	0.184	H(84)	0.156	0.172	0.254
	0.087	0.141	0.189		0.160	0.172	0.228
O(6)	0.118	0.153	0.164	H(91)	0.142	0.235	0.254
	0.094	0.136	0.169		0.179	0.188	0.219
O(7)	0.118	0.140	0.212	H(92)	0.158	0.206	0.243
	0.101	0.133	0.209		0.177	0.209	0.230
O(8)	0.118	0.133	0.234				
	0.097	0.115	0.247				
O(9)	0.124	0.155	0.191				
	0.132	0.148	0.160				

In the former table we believe that the standard deviations of the bond lengths are realistic, for only in very few cases are the differences in value of corresponding bonds greater than the sum of the two standard deviations. The one unsatisfactory exception is the value of 0.936 for the O—H bond specified as O(9)—H(92)···O(2). This seems likely to

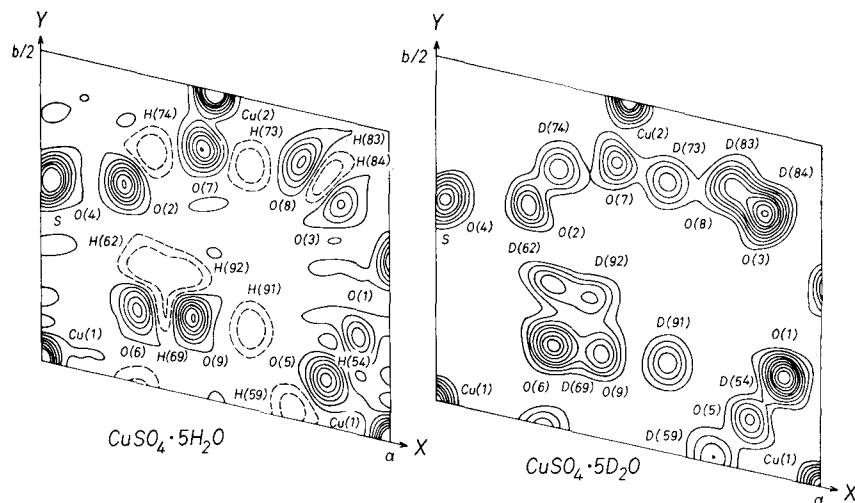


Fig. 3. A comparison of the scattering density for  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{D}_2\text{O}$  projected on the 001 plane by Fourier synthesis of the  $hk0$  reflections. Negative contours due to hydrogen are shown by broken lines

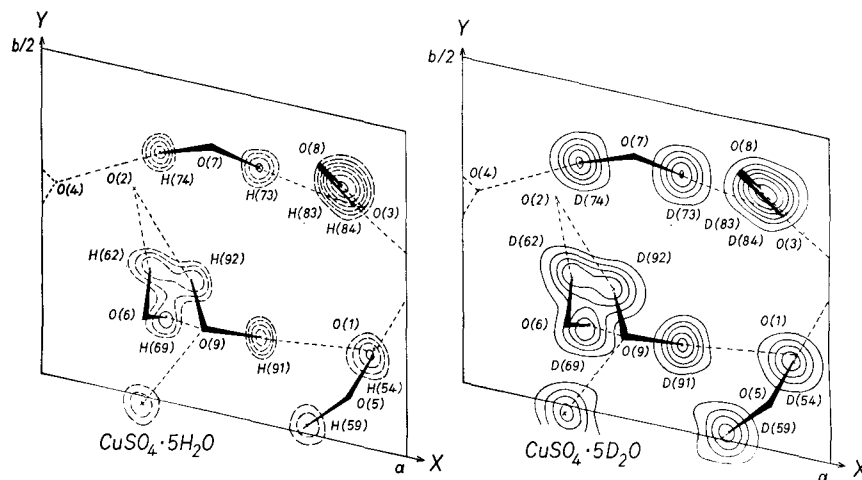


Fig. 4. Difference projections of the scattering density on the 001 plane showing, respectively, the hydrogen atoms in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and the deuterium atoms in  $\text{CuSO}_4 \cdot 5\text{D}_2\text{O}$

be associated with some error in the coordinates of O(9) for the hydrated salt.

Comparison of the bond lengths leads to the conclusion that any so-called "isotope effect" between hydrogen and deuterium is negli-

Table 6. *Dimensions in hydrogen bonds*

CuSO <sub>4</sub> · 5H <sub>2</sub> O					
Bond	Bond lengths			Angle	Distance of H from O···O line
	O···O	O—H	H···O	O—H···O	
O <sub>5</sub> —H <sub>54</sub> ···O <sub>4</sub>	2.854(5) Å	0.961(6) Å	1.913(7) Å	165.6(5)°	0.160(5) Å
O <sub>5</sub> —H <sub>59</sub> ···O <sub>9</sub>	2.781(5)	0.960(5)	1.834(7)	168.3(6)	0.129(4)
O <sub>6</sub> —H <sub>62</sub> ···O <sub>2</sub>	2.795(5)	0.971(8)	1.893(7)	153.5(5)	0.294(6)
O <sub>6</sub> —H <sub>69</sub> ···O <sub>9</sub>	2.747(5)	0.982(5)	1.771(5)	172.0(6)	0.088(3)
O <sub>7</sub> —H <sub>74</sub> ···O <sub>4</sub>	2.756(4)	0.960(5)	1.807(5)	169.3(5)	0.117(4)
O <sub>7</sub> —H <sub>73</sub> ···O <sub>3</sub>	2.715(4)	0.971(5)	1.747(4)	174.7(4)	0.058(3)
O <sub>8</sub> —H <sub>83</sub> ···O <sub>3</sub>	2.678(4)	0.968(6)	1.712(6)	176.0(3)	0.044(3)
O <sub>8</sub> —H <sub>84</sub> ···O <sub>4</sub>	2.707(5)	0.963(5)	1.761(5)	167.0(5)	0.141(4)
O <sub>9</sub> —H <sub>91</sub> ···O <sub>1</sub>	2.784(4)	0.978(5)	1.820(5)	168.1(4)	0.132(4)
O <sub>9</sub> —H <sub>92</sub> ···O <sub>2</sub>	2.985(6)	0.936(11)	2.084(10)	161.4(5)	0.208(6)

CuSO <sub>4</sub> · 5D <sub>2</sub> O					
Bond	Bond lengths			Angle	Distance of D from O···O line
	O···O	O—D	D···O	O—D···O	
O <sub>5</sub> —D <sub>54</sub> ···O <sub>4</sub>	2.851(4) Å	0.971(4) Å	1.896(4) Å	167.1(3)°	0.144(5) Å
O <sub>5</sub> —D <sub>59</sub> ···O <sub>9</sub>	2.767(4)	0.971(4)	1.809(4)	168.3(3)	0.129(4)
O <sub>6</sub> —D <sub>62</sub> ···O <sub>2</sub>	2.803(4)	0.968(3)	1.902(4)	153.9(3)	0.290(6)
O <sub>6</sub> —D <sub>69</sub> ···O <sub>9</sub>	2.740(4)	0.982(3)	1.765(3)	171.7(3)	0.091(3)
O <sub>7</sub> —D <sub>74</sub> ···O <sub>4</sub>	2.761(4)	0.959(4)	1.815(4)	168.8(3)	0.123(4)
O <sub>7</sub> —D <sub>73</sub> ···O <sub>3</sub>	2.715(5)	0.966(3)	1.752(4)	174.3(3)	0.062(3)
O <sub>8</sub> —D <sub>83</sub> ···O <sub>3</sub>	2.681(4)	0.969(4)	1.714(4)	175.2(2)	0.052(3)
O <sub>8</sub> —D <sub>84</sub> ···O <sub>4</sub>	2.717(4)	0.968(3)	1.763(4)	168.1(3)	0.130(4)
O <sub>9</sub> —D <sub>91</sub> ···O <sub>1</sub>	2.800(4)	0.969(4)	1.846(4)	167.7(3)	0.137(4)
O <sub>9</sub> —D <sub>92</sub> ···O <sub>2</sub>	2.999(4)	0.968(4)	2.070(4)	160.1(2)	0.228(6)

Table 7. *Angles at oxygen atoms of water-molecules*

	CuSO <sub>4</sub> · 5H <sub>2</sub> O		CuSO <sub>4</sub> · 5D <sub>2</sub> O		
	O···O···O	H—O—H		O···O···O	
H <sub>54</sub> —O <sub>5</sub> —H <sub>59</sub>	120.0(1) Å	108.3(5)°	D <sub>54</sub> —O <sub>5</sub> —D <sub>59</sub>	119.5(1)°	108.7(3)°
H <sub>62</sub> —O <sub>6</sub> —H <sub>69</sub>	130.0(2)	108.7(6)	D <sub>62</sub> —O <sub>6</sub> —D <sub>69</sub>	130.2(1)	109.0(3)
H <sub>74</sub> —O <sub>7</sub> —H <sub>73</sub>	118.3(1)	112.9(3)	D <sub>74</sub> —O <sub>7</sub> —D <sub>73</sub>	118.1(1)	112.6(3)
H <sub>83</sub> —O <sub>8</sub> —H <sub>84</sub>	105.4(1)	110.8(5)	D <sub>83</sub> —O <sub>8</sub> —D <sub>84</sub>	105.0(1)	109.1(3)
H <sub>91</sub> —O <sub>9</sub> —H <sub>92</sub>	122.4(2)	106.7(6)	D <sub>91</sub> —O <sub>9</sub> —D <sub>92</sub>	121.7(1)	104.7(3)

gible. In particular if we compute the mean value of first eight O—H lengths shown in Table 6 we obtain 0.967 Å for the hydrogen salt and 0.969 Å for the deuterium salt. The corresponding lengths of the H···O portion of the bond are 1.805, 1.802 Å respectively.

Table 7, which gives the O—O—O and H—O—H angles at the water molecules, seems equally convincing and we conclude that the angular differences which it shows for the five crystallographically different water molecules are significant, seeing how the individual angles are quite faithfully reproduced in the deuterated crystal. We believe that these values will justify an extension of BAUR'S (1965) calculation to cover the range of H—O—H angles within the water molecules which is measured experimentally.

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