and to the other xanthate group by two Pb–S bonds, each of which is intermediate in length between a single bond and an ionic bond and makes an angle of approximately 90° with the Pb–S single bond. In order to collect further relevant experimental data the structure analyses of the ordered crystal of Pb nB X and the Pb isoP X crystals obtained from the acetone solution are now in progress.

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On the Water Molecules in FeSO$_4$.7H$_2$O. A Nuclear Magnetic Resonance Study*

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The angular dependence of the nuclear magnetic resonance spectrum of single crystals of monoclinic FeSO$_4$.7H$_2$O has been studied in nine planes of rotation with a view to establishing the proton–proton vectors. The experimentally determined vectors were employed to confirm the hydrogen-bonding scheme suggested by Baur, (Acta Cryst. (1964) 17, 1167) and to determine the coordinates of the hydrogen atoms.

The crystal structure of monoclinic FeSO$_4$.7H$_2$O was first studied by Leonhardt & Ness (1947) who gave the cell constants, space group and essentially correct positional parameters for iron and sulfur. More recently, Baur (1964) reported a complete determination of the structure of this compound. The X-ray studies reveal that the space group is $P2_1/c$ with $a=14\cdot072$, $b=6\cdot503$, $c=11\cdot041$ Å, $\beta=105°34'$, $Z=4$. The iron ions occupy special positions and are surrounded by six water molecules which form hydrogen bonds to SO$_4^{2-}$ and to the seventh water molecule which is not coordinated to Fe^{2+}. The hydrogen-bonding scheme suggested by Baur (1964) is, in his atomic designation, as follows:

O(1)...H(11)–O(w1)–H(12)...O(2)
O(2)...H(22)–O(w2)–H(24)...O(4)
O(1)...H(31)–O(w3)–H(32)...O(2)
O(3)...H(43)–O(w4)–H(47)...O(w7)
O(4)...H(54)–O(w5)–H(57)...O(w7)
O(1)...H(61)–O(w6)–H(63)...O(3)
O(4)...H(74)–O(w7)–H(76)...O(w6) .

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* The experimental part of this work was carried out at the Department of Chemistry, Johns Hopkins University, Baltimore, Maryland, U.S.A.

According to this scheme, the iron-coordinated water molecule O(w6) receives an 'outward' hydrogen bond from O(w7) which may account for the fact that Fe–O(w6) is significantly longer than the mean Fe–O(w). The alternative arrangement O(3)...H–O(w7)...O(4) which is geometrically feasible is ruled out by Baur.

In the present study, nuclear magnetic resonance (n.m.r.) has been employed to determine the orientations of the water molecules in FeSO$_4$.7H$_2$O. The equipment and method employed have been described in detail by the author (El Saffar, 1969). The magnetic field strength of 960 gauss employed in this study is considered low enough to render negligible any possible anisotropic shift of the resonance lines resulting from crystal paramagnetism. The measurements were made at room temperature on nine single crystals each of about 1 cm^3 in volume. Each of these crystals was mounted in a Teflon holder which was in turn attached to an indexed head that allowed rotation of the crystal about an axis normal to the external magnetic field. The axes of rotation were determined to within 1° with the aid of the crystal morphology as quoted by Groth (1908), and a precision optical goniometer. The n.m.r. spectra were recorded for each crystal over a range of 180° in steps of 5°. Readings on the oscilloscope were

also taken and were possible because of the high signal intensity. The n.m.r. measurements were employed to plot resonance diagrams such as the one shown in
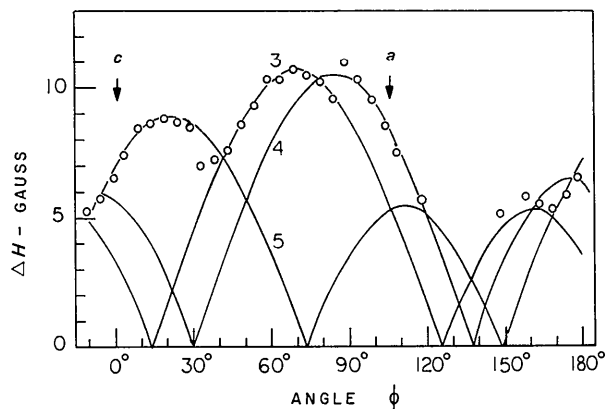

Fig. 1. Resonance diagram showing the angular dependence of ΔH in the (010) plane. This is used in partial determination of the vectors 3, 4, and 5. The smooth curves are obtained from equation (1) and the experimental vectors 3, 4 and 5 given in Table 2.
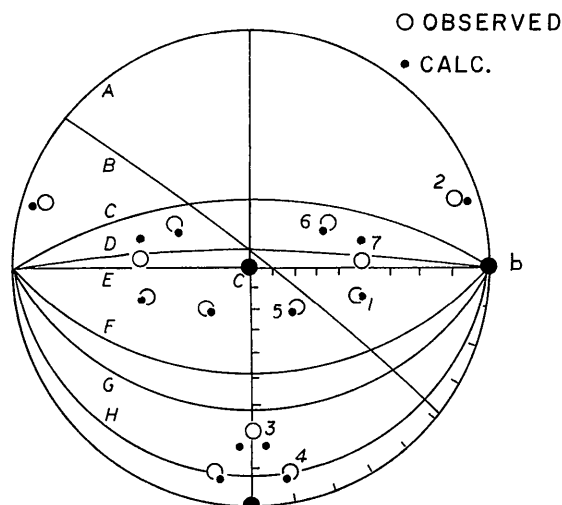

Fig. 2. Stereographic projection showing the directions of the observed and calculated proton–proton vectors. The larger filled circles indicate the crystallographic axes chosen by Baur. All directions are taken in the upper hemisphere and projected through the south pole.

Fig. 1. In all, nine such resonance diagrams were obtained corresponding to nine different planes of rotation. These planes of rotation are described in Table 1 and shown in Fig. 2.

Table 1. *Orientations of the planes of rotation in terms of α and β, the angles that the axes of rotation make with [100] and [010] respectively*

Also given are the p–p vectors determined from the resonance diagrams corresponding to these planes of rotation.

| | Axis of rotation | | p–p vectors |
Plane	α	β	determined
A	90°	90°	2, 4
B	38	128	1, 5, 6
C	29	90	2, 6
D	8	90	2, 7
E	0	90	2, 5, 7
F	132	90	1, 2, 3
G	119	90	2, 3
H	98	90	2, 3, 4
(010)	90	0	3, 4, 5

The experimental p–p (proton–proton) vectors are determined from maximum values of ΔH appearing in the resonance diagrams. Three ΔH_{max} appear in Fig. 1 corresponding to the vectors 3, 4 and 5. Each of the seven nonequivalent p–p vectors given in Table 2 is determined from the magnitudes and orientations of the related ΔH_{max} appearing in at least two different planes of rotation. Each plane of rotation indicated in Table 1 yields ΔH_{max} corresponding to the vectors given in the last column of Table 1. The direction and p–p separation, r, are finally calculated from the following relation (Pake, 1948)

$$\Delta H_{max}=\tfrac{3}{2}\mu r^{-3}\,(3\cos^2\delta-1)\,, \tag{1}$$

where μ is the proton magnetic moment and δ is the smallest angle the vector makes with the plane of rotation. The error involved in the determination of the p–p direction is estimated to be $\sim 4°$, while the error involved in the determination of r is estimated to be less than 0·02 Å.

Each of the experimental p–p vectors is assigned to one of the water molecules as indicated in Table 2 and Fig. 2. This assignment is based on the agreement between the experimental p–p direction and the corresponding H–H direction calculated from the probable H

Table 2. *The orientations and magnitudes of the experimental and calculated vectors*

The angles α and β are those that the vectors make with [100] and [010] respectively. The experimental p–p distance is given by r and is used to calculate the HOH angle on the assumption that OH is 0·987 Å. X and X' are the H-bond acceptor ions.

| Water molecule | Experimental | | | | Calculated | | |
	α	β	r(Å)	$\angle$HOH	α	β	$\angle$XOX'
1	79°	±48°	1·62	108°	79·1°	±46·0°	121·4°
2	108	±19	1·63	112	105·9	±16·3	123·3
3	21	±90	1·58	106	18·3	±86·0	114·0
4	13	±80	1·57	106	11·3	±80·8	110·5
5	72	±69	1·57	106	71·0	±69·8	102·6
6	109	±55	1·62	111	107·0	±56·5	121·2
7	93	±40	1·66	115	100·3	±41·6	145·0

coordinates given by Baur. The HOH angles given in Table 2 were calculated from the experimental p–p distance on the assumption that the O–H distance is 0·987 Å (El Saffar, 1966). The H coordinates given in Table 3 were calculated by the use of the p–p vectors determined, the X-ray structure, and a method previously described by the author (El Saffar, 1966, 1968).

Table 3. *Hydrogen coordinates calculated from the X-ray structure and the n.m.r. experimental vectors*

The H atoms are given in the designation of Baur (1964).

	x/a	y/b	z/c
H(11)	0·149	0·257	0·462
H(12)	0·126	0·425	0·352
H(22)	0·121	0·812	0·198
H(24)	0·158	0·050	0·196
H(31)	0·087	0·884	0·470
H(32)	0·978	0·884	0·381
H(43)	0·421	0·521	0·198
H(47)	0·534	0·478	0·257
H(54)	0·373	0·276	0·368
H(57)	0·409	0·361	0·506
H(61)	0·295	0·913	0·463
H(63)	0·334	0·770	0·366
H(74)	0·322	0·092	0·152
H(76)	0·328	0·896	0·058

The good agreement obtained between the experimental and calculated vectors supports the hydrogen-bonding scheme suggested by Baur. The geometrically feasible configuration O(3)...O(w7)...O(4) which was rejected by Baur is rejected here also since the calculated H–H direction for such a configuration gives $\alpha = 101°$ and $\beta = \pm 11°$ while the experimental p–p direction corresponding to O(w7) has $\alpha = 93°$ and $\beta = \pm 40°$ (Table 2). The H coordinates given by Baur are also in good agreement with those given in Table 3; the average discrepancy between his coordinates and those given in Table 3 is ~0·06 Å. This appears to support the assumptions and method employed by Baur to calculate the H coordinates as against the direct application of X-ray difference synthesis. The magnitude of the errors involved in employing difference synthesis to determine H positions is probably best illustrated by the three-dimensional X-ray and neutron-diffraction

studies of MnCl₂.4H₂O. The H positions obtained from X-ray difference maps (Zalkin, Forrester & Templeton, 1964) were found to have an average deviation of 0·21 Å and a maximum deviation of 0·73 Å from the H positions given by neutron diffraction (El Saffar & Brown, 1969).

According to the H-bonding scheme employed here, the mean O(w)–H...O distance is 2·82 Å. According to the H coordinates given in Table 3, the bond parameters relating to the H bonds are (with one exception) as follows: the angles O(w)–H...O range from 167 to 178° and have a mean of 173°; the angles H–O(w)–O range from 1 to 8° and have a mean of 4°, the distances H...O range from 1·73 to 1·96 Å with a mean of 1·83 Å. The exception is the hydrogen bond from O(w7) to O(w6) where O(w7)–H(76)...O(w6) is 151°, H(76)–O(w7)–O(w6) is 27° and H(76)...O(w6) is 2·19 Å. Of all the p–p distances given in Table 2, the one corresponding to O(w7) appears to be the longest (1·66 Å). This may be a result of the presence of a considerable amount of thermal motion, probably about the O(w7)–O(4) bond. The presence of thermal motion of any kind results in an increase in the 'apparent' p–p distance determined by means of nuclear magnetic resonance (*cf.* Pedersen, 1964).

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