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Proton magnetic resonance in iron (II) chloride tetrahydrate.*

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The X-ray studies of Penfold & Grigor (1959) gives the space group of $FeCl_2.4H_2O$ as $P2_1/c$ with $Z=4$. The hydrogen bonding scheme suggested by these authors was used to determine the *p–p* (proton–proton) directions shown as small circles in the stereographic projection in Fig. 1. Each vector was calculated from the bonds which they suggest by assuming it to be perendicular to the bisector of the angle *X*–O–*X*′ where *X* and *X*′ are the atoms to which the protons of the water molecules are hydrogen bonded. The O–H distance was taken as 0·97 Å. In the notation of Penfold & Grigor the *p–p* vectors we designated *A*, *B*, *C* and *D* correspond to the arrangements

A Cl–O(1)–Cl
B Cl(*a*)–O(2)–Cl(*b*)
C Cl(*a*)–O(2)–Cl(*c*)
D Cl(*b*)–O(2)–Cl(*c*)

The primed vectors in Fig. 1 are reflections of the unprimed vectors, the mirror plane being the *ac* plane. The fact that the angles of type Cl–O(2)–Cl are closely similar led Penfold & Grigor to suggest a possible disordered arrangement of hydrogen bonds about O(2),' two hydrogen atoms being used to form three bonds O(2)–Cl(*a*), O(2)–Cl(*b*) and O(2)–Cl(*c*).

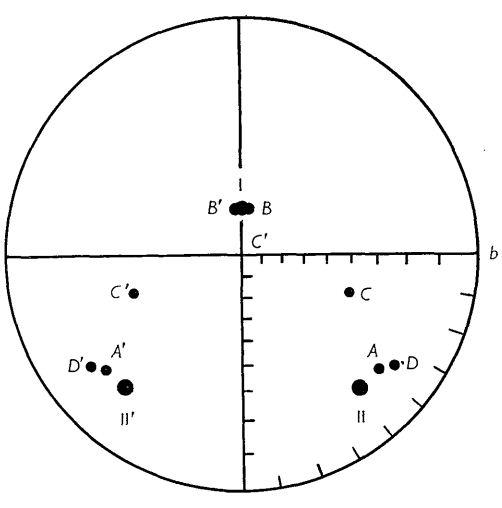

Fig. 1. Stereographic projection showing the directions of the *p–p* vectors; the small circles represent the calculated directions and the large circles represent the observed directions.

In the present investigation, resonance diagrams obtained by rotating the crystal about four different axes of rotation were used to determine the magnitude and orientation of the *p–p* vectors. The observed *p–p* directions are designated I, II, and II′ in Fig. 1. The axes of rotation were *a*′, *b*, *c* and an additional axis which was so chosen that both vectors I and II were in its plane of rotation. The observed *p–p* vectors are to be compared with those obtained from the Penfold–Grigor scheme. The comparison is shown in greater detail in Table 1 where the calculated *X*–O–*X*′ angle and the observed H–O–H angle are also given. Here α_0, β_0 and γ_0 are the angles between the *p–p* vectors and the positive *a*, *b* and *c* axes respectively.

Table 1.

	Calculated				Observed	
Angle	*A*	*B*	*C*	*D*	II	I
α_0	52·5°	111°	75°	54°	44°	111°
β_0	41·5°	87°	42·5°	39·5°	51°	90°
γ_0	89·5°	3·5°	62°	89°	90°	1°
X–O–*X*′	103°	85°	91°	94·5°		
H–O–H					110°	114°

It appears from Fig. 1 that vector I belongs to *B* while vector II belongs either to *A* or to both *A* and *D*. Our measurements do not confirm the existence of vector *C*. If this is taken to rule out the existence of the bond O(2)–Cl(*c*) then vector *D* is also eliminated. It is to be noted that the bond length O(2)–Cl(*c*) (3·40 Å) is long compared to O(2)–Cl(*a*) (3·07 Å) and O(2)–Cl(*b*) (3·18 Å). The existence of vector *B* does indicate that water molecules of type (2) have their positions determined more by the packing requirement of the large Cl^- ions than by a strong attachment to Fe^{++} (Penfold & Grigor, 1959).

The magnitudes of the *p–p* vectors are given in the form of H–O–H angle in Table 1, the O–H distance being 0·97 Å. The fact that the H–O–H angle is larger than the *X*–O–*X*′ angle may be due to bending of the bonds; this has been observed in many other hydrates (cf. McGrath & Silvidi (1961)).

The measurements reported above were made at room temperature. Pierce & Friedberg (1961) have reported that susceptibility measurements indicate a possible paramagnetic-antiferromagnetic transition in $FeCl_2.4H_2O$ at 1·6 °K. Our n.m.r. studies in the temperature range 1·15–4·2 °K. reveal no such transition. This result is in agreement with specific heat studies by Dr H. Forstat of this laboratory.

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References

McGrath, J. W. & Silvidi, A. A. (1961). *J. Chem. Phys.* **34**, 322.
Penfold, B. R. & Grigor, J. A. (1959). *Acta Cryst.* **12**, 850.
Pierce, R. D. & Friedberg, S. A. (1961). *J. Appl. Phys.* **32**, 66S.