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Crystal Structure of Copper Fluoride Dihydrate,  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ 

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The crystal structure of copper fluoride dihydrate,  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ , has been determined from single crystal x-ray data. The monoclinic unit cell, space group  $C_{2h}(3)-I2/m$ , with  $a=6.416$ ,  $b=7.397$ ,  $c=3.301$ , all  $\pm 0.005$  Å,  $\beta=99.6 \pm 0.1^\circ$ , contains two formula units. The atoms are in the following positions: Cu(II) in  $2(a)$ :  $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ;  $\text{F}^-$  in  $4(i)$ :  $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x, 0, z)$  with  $x=-0.222$ ,  $z=0.311$ ; O in  $4(g)$ :  $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (0, y, 0)$  with  $y=0.261$ . The estimated parameters of the H atoms in  $8(j)$ :  $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x, y, z)$ ;  $x, y, z$  are  $x=0.107$ ,  $y=0.340$ ,  $z=-0.073$ . In this structure the Cu(II) atoms have two fluorine neighbors at 1.89 Å, two (water) oxygen neighbors at 1.93 Å, and two fluorine neighbors at 2.47 Å. These form a highly distorted octahedron about the Cu(II), and in fact, the distance of the two further fluorine atoms implies that the Cu(II) prefers square coordination. The distance 2.66 Å between an oxygen and a fluorine associated with a neighboring lattice point implies appreciable hydrogen bonding between these atoms. Comparisons are made with other Cu(II) halide compounds and the observed antiferromagnetism is discussed.

The morphology and optic axes have been investigated. The refractive indices (NaD) are  $\alpha=1.51$ ,  $\beta=?$ ,  $\gamma=1.54$ . The optic angle  $2V \cong 46^\circ$  and the optic axes lie in the (010) plane between  $+a$  and  $+c$ , one optic axis making an angle of  $16^\circ$  with the  $c$  axis.

## INTRODUCTION

RECENTLY, there has been considerable interest in  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , mainly toward an understanding of the antiferromagnetic ordering which occurs at  $4.3^\circ\text{K}$ .<sup>1</sup> The structure of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  had been determined by Harker<sup>2</sup> and by MacGillavry and Bijvoet,<sup>3</sup> but no hydrogen positions could be determined by the x-ray method. An accurate determination of the proton positions as well as a further refinement of the structure has been made by Petersen and Levy<sup>4</sup> by means of a neutron diffraction analysis, following which Rundle<sup>5</sup> reinterpreted the nuclear magnetic resonance data of Poulis and Hardeman\* and proposed a different antiferromagnetic ordering from that proposed by the original authors. Rundle has also presented arguments to indicate that the magnetic moments are not localized on the Cu(II) atoms† but are distributed partially over the chlorine atoms and practically not at all on the oxygen atoms.‡ An insight into the bonding of this compound may thus be gained by a combination of structural and nuclear magnetic resonance analyses.

In these Laboratories, nuclear magnetic resonance studies have been made by Shulman and Jaccarino on  $\text{MnF}_3$ <sup>6</sup> and  $\text{MnF}_2$ <sup>7</sup> in which cases it was found possible to evaluate the amount of covalency in the  $\text{Mn}^{2+}-\text{F}^-$  bonds. These authors had also planned a study of  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ , but the structure of the crystal

was unknown. Susceptibility vs temperature measurements made by Bozorth and Nielsen<sup>8</sup> proved that  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  is antiferromagnetic with a Néel point,  $\theta_N=26^\circ\text{K}$ . The higher Néel temperature and the simplicity of the structure of  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  make it ideal for nuclear magnetic resonance and optical studies.

Recent work on copper-fluorine compounds has been reported by Haendler and co-workers.<sup>9</sup> This work includes a structure analysis of anhydrous  $\text{CuF}_2$  and the powder data for  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ , which may now be indexed on the unit cell found in our study.

## DETERMINATION OF THE STRUCTURE

A very small cleavage piece from one of the larger crystals was mounted on a goniometer head. The crystal was aligned along a longest natural edge. Oscillation and Weissenberg photography indicated that the crystal was triclinic containing one  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  in the unit cell. Subsequently, photographs were taken with the Buerger precession camera ( $\text{MoK}\alpha$  radiation), which led to the conclusion that the diffraction symmetry of the crystal is actually  $C_{2h}-2/m$  with a centered cell. The description chosen is  $I$ , the body centered one: reflections ( $hkl$ ) with  $(h+k+l)$  odd are absent. Thus the probable space groups are  $C_{2h}(3)-I2/m$ ,  $C_2(3)-I2$  and  $C_s(3)-Im$ . The absence of piezoelectricity§ and the compatibility of the x-ray data with the centrosymmetric structure indicate the first ( $I2/m$ ) to be the most probable.

Measurements of lattice constants were made with a single-crystal goniometer leading to  $a=6.416$ ,

<sup>1</sup> N. J. Poulis and G. E. G. Hardeman, *Physica* **18**, 201 (1952).

<sup>2</sup> D. Harker, *Z. Krist.* **93**, 136 (1936).

<sup>3</sup> C. H. MacGillavry and J. M. Bijvoet, *Z. Krist.* **94**, 231 (1936).

<sup>4</sup> S. W. Petersen and H. A. Levy, *J. Chem. Phys.* **26**, 220 (1957).

<sup>5</sup> R. E. Rundle, *J. Am. Chem. Soc.* **79**, 3372 (1957).

\* The interpretation originally given their data by the authors had led to erroneous positions of the protons.

† This was corroborated by Petersen and Levy<sup>4</sup> also by examination of the magnetic resonance data from below  $4^\circ\text{K}$ .

‡ However, a private communication from R. E. Rundle now indicates revision of these conclusions. See Discussion.

<sup>6</sup> R. G. Shulman and V. Jaccarino, *Phys. Rev.* **109**, 1084 (1958).

<sup>7</sup> R. G. Shulman and V. Jaccarino, *Phys. Rev.* **108**, 1219 (1957).

<sup>8</sup> R. M. Bozorth and J. W. Nielsen, *Phys. Rev.* **110**, 879 (1958).

<sup>9</sup> C. M. Wheeler, Jr. and H. M. Haendler, *J. Am. Chem. Soc.* **76**, 263 (1954); Haendler, Towle, Bennett, and Patterson, *ibid.* **76**, 2178 (1954); C. Billy and H. M. Haendler, *ibid.* **79**, 1049 (1957).

§ The test for piezoelectricity was carried out by Dr. J. W. Nielsen.

TABLE I. Parameters obtained from  $F_o$  synthesis and after correction for series termination error.

Atom	Position	Parameters				
		From (001) projection		From (100) projection		
		$x$	$y$	$y$	$z$	
Cu(II)	2(a)	0	0	0	0	Initial
		0	0	0	0	Final
F <sup>-</sup>	4(i)	-0.239 <sup>a</sup>	0	0	0.300 <sup>a</sup>	Initial
		-0.222 <sup>a</sup>	0	0	0.311 <sup>a</sup>	Final
O	4(g)	0	0.258	0.259	0	Initial
		0	0.261	0.261	0	Final

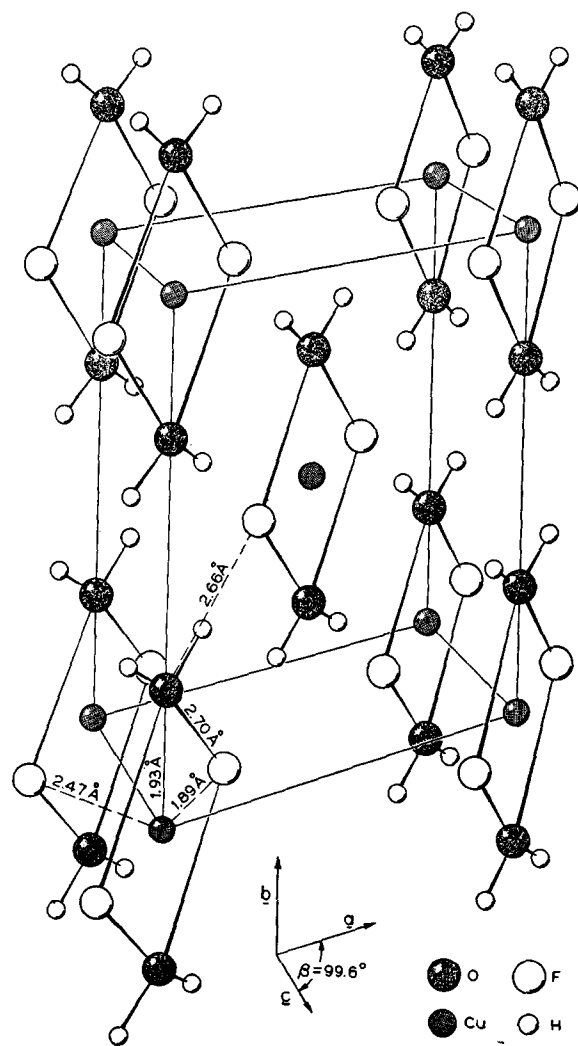
\* These projections do not give the sign of the parameter. However, the only other possibility (in which both the  $x$  and  $z$  parameters have the same sign) gives an impossibly short Cu-F distance.

$b=7.397$ ,  $c=3.301$ , all  $\pm 0.005$ ,  $\beta=99.6 \pm 0.1^\circ$ . These values were corroborated very closely by results from measurements of the precession photographs. With two formula units per cell, the x-ray density is 2.95 g/cc, in good agreement with the reported<sup>10</sup> density, 2.93 g/cc, presumably measured by another method.

The intensities of the ( $h$  $k$ 0) and (0 $kl$ ) reflections were estimated visually and relative  $|F_o|^2$  values obtained after application of the proper Lorentz-polarization factors.<sup>11</sup> No corrections were made for absorption. This structure determination is straightforward. With the Cu(II) ions at (0, 0, 0) and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , all but very small structure factors occurring in the low-angle region ( $\sin\theta/\lambda \leq 0.25$ ) are necessarily positive. Because there were no (0 $kl$ ) or ( $h$  $k$ 0) reflections of this kind, all structure amplitudes were taken as positive and projections of relative electron density on the (001) and (100) pinacoids calculated. The values of the parameters obtained from these projections are given in Table I. Using these parameters and making an estimate of the positions of the H atoms, calculations of the structure factors were carried out. In these calculations, the atomic scattering factors for Cu(II) were obtained from the paper of Thomas and Umeda;<sup>12</sup> for F<sup>-</sup> and O, the atomic scattering factors of Berghuis *et al.*<sup>13</sup> were used; and for H, those of Viervoll and Ögrim.<sup>14</sup> The Cu(II) values were corrected for dispersion.<sup>15</sup> Isotropic temperature factors were superposed on these atomic scattering factors as follows:  $B_{\text{Cu(II)}}=0.5 \text{ \AA}^2$  and  $B_{\text{F}^-}=B_{\text{O}}=B_{\text{H}}=2.0 \text{ \AA}^2$ . Initial

agreement between calculated and observed structure amplitudes was very good. However, an additional isotropic  $B=0.7 \text{ \AA}^2$  had to be applied to the calculated  $F_{0kl}$ ; thus for this zone, the temperature factor values are  $B_{\text{Cu(II)}}=1.2 \text{ \AA}^2$  and  $B_{\text{F}^-}=B_{\text{O}}=B_{\text{H}}=2.7 \text{ \AA}^2$ , and the value of the discrepancy factor for the first calculation of (0 $kl$ ) amplitudes was 8.4%. The agreement between calculated and observed ( $h$  $k$ 0) amplitudes was 13.4%, not as good as that for the (0 $kl$ ). [No additional temperature correction on the ( $h$  $k$ 0) amplitudes was indicated.] The largest percentage difference between a calculated and observed amplitude was that for the (220) reflection for which  $F_o=1.9$  and  $F_c=0.1$ .

It appeared worthwhile to calculate the  $F_c$  syntheses, which when carried out led to rather large backshift corrections on the fluorine parameters but only a small correction on the oxygen parameter. The values of the parameters obtained from the  $F_o$  synthesis (initial) and those corrected for series termination

FIG. 1. The  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  structure.

<sup>10</sup> *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Inc., Brooklyn, New York), 38th edition (primary reference unknown).

<sup>11</sup> J. Waser, *Rev. Sci. Instr.* **22**, 567 (1951); *ibid.* **23**, 420 (1952).

<sup>12</sup> L. H. Thomas and K. Umeda, *J. Chem. Phys.* **26**, 293 (1957).

<sup>13</sup> Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.* **8**, 478 (1955).

<sup>14</sup> H. Viervoll and O. Ögrim, *Acta Cryst.* **2**, 277 (1949).

<sup>15</sup> C. H. Dauben and D. H. Templeton, *Acta Cryst.* **8**, 841 (1955).

TABLE II. Calculated and observed ( $hk0$ ) structure amplitudes.

Amplitude			Amplitude			Amplitude			Amplitude		
$hk$	calc	obs	$hk$	calc	obs	$hk$	calc	obs	$hk$	calc	obs
11	53.1	62.6	31	30.1	36.4	51	37.9	42.0	71	17.3	15.5
13	53.8	50.7	33	30.1	31.2	53	35.6	38.4	73	17.8	15.5
15	31.6	26.2	35	21.8	21.0	55	27.2	31.1	75	14.9	12.6
17	30.0	29.1	37	23.1	20.3	57	25.0	26.7			
19	19.0	15.5	39	15.6	13.5						
20	46.4	53.1	40	58.4	65.8	60	28.8	27.2	80	23.5	21.0
22	1.5	1.9	42	33.2	42.5	62	16.2	11.6	82	16.9	15.8
24	33.7	30.2	44	45.1	50.7	64	24.9	21.6	84	20.8	19.5
26	12.9	11.1	46	24.4	20.2	66	15.0	9.2			
28	21.3	15.5	48	25.6	28.2						
2, 10	12.4	8.3									

error (final) are shown in Table I. It should be noted that although the backshift correction for the fluorine  $x$  parameter is large, 0.11 Å, the nearest neighbor interatomic distances are changed only by a component of this amount; that is, with the uncorrected set of parameters the shortest Cu–O distance is 1.96 Å and the final distance is 1.89 Å.

The positions of the hydrogen atoms could not be determined directly from the present study. An estimate of these positions was made as follows: The O–H distance is assumed to be 0.96 Å and the H–O–H angle 105°, the H atom is assumed to lie in the plane of the Cu(II), and O atoms at one lattice point and the nearest F<sup>−</sup> ion of a neighboring lattice point (Fig. 1). With these assumptions the H atoms which most probably lie in the general positions, 8( $h$ ), have parameters (0.107, 0.340, −0.073).

The structure amplitudes, calculated with the corrected parameters for O and F<sup>−</sup>, the deduced parameters for H, and the temperature factors previously given, agree well with the observed (Tables II and III); the discrepancy factors are 7.0% for the ( $0kl$ ) amplitudes and 12.7% for the ( $hk0$ ) amplitudes.

TABLE III. Calculated and observed ( $0kl$ ) structure amplitudes.

Amplitude			Amplitude		
$kl$	calc	obs	$kl$	calc	obs
00	124.8	...	02	36.6	37.8
20	51.8	49.7	22	11.4	14.5
40	67.4	68.8	42	26.8	24.7
60	29.4	30.6	62	12.5	13.6
80	27.3	31.9	82	15.5	16.8
10,0	14.0	14.0			
11	33.1	34.2	13	28.4	27.4
31	37.3	41.3	33	26.8	27.4
51	21.8	23.6	53	19.8	18.2
71	21.4	21.1	73	17.1	15.3
91	12.6	9.7			
			04	18.3	17.5
			24	12.7	10.9
			44	15.2	14.6

Although the improvement in the discrepancy factors is not really significant, the application of the backshift corrections improved very significantly the agreement for the (220) amplitude. It is probable that much of the discrepancy for the ( $hk0$ ) amplitudes results from omission of absorption corrections of intensities; although very small, the crystal used to obtain the data was not of optimum shape for the method employed.

#### MORPHOLOGY, CLEAVAGE, OPTICAL STUDIES

The crystals used in this study, grown from HF solution,<sup>10</sup> show forms (Fig. 2):  $m\{110\}$ ,  $q\{011\}$ , and  $r\{101\}$ . The faces were not developed well enough to allow the accurate measurements of interfacial angles. The latter were therefore calculated from the lattice constants (previously given) and are listed in Table IV.

Examination of the cleavage pieces (Fig. 2) shows that if one of these pieces were mounted in the long direction of the crystal: in two cases, where  $r$  and  $m$

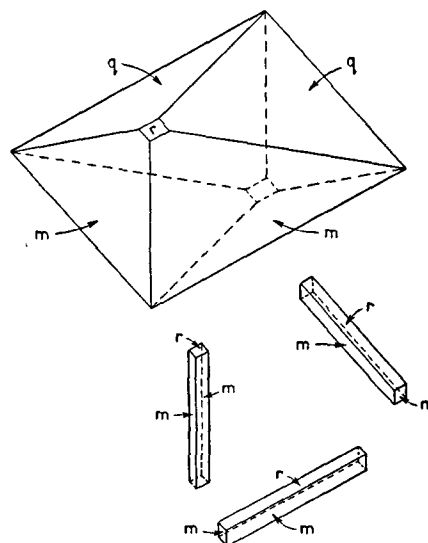
FIG. 2. The CuF<sub>2</sub>·2H<sub>2</sub>O crystal and cleavage pieces.

TABLE IV. Interfacial angles of a  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  crystal.

$m:m' = (110):(1\bar{1}0) = 81.1^\circ$
$m:q = (110):(011) = 67.8$
$m:r = (110):(101) = 64.4$
$r:q = (101):(011) = 34.4$
$q:q' = (011):(0\bar{1}1) = 47.5$

planes join, the edge shared by these planes is a  $[11\bar{1}]$  direction of the monoclinic crystal; in the third case, where  $m$  planes meet, the common edge is along the monoclinic  $c$  axis. In the former cases, the Weissenberg x-ray photographs about the  $[11\bar{1}]$  rotation axis would indicate a triclinic unit cell containing one  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ . The transformation from the primitive triclinic subcell may be the following:

$$a' = c - a,$$

$$b' = c,$$

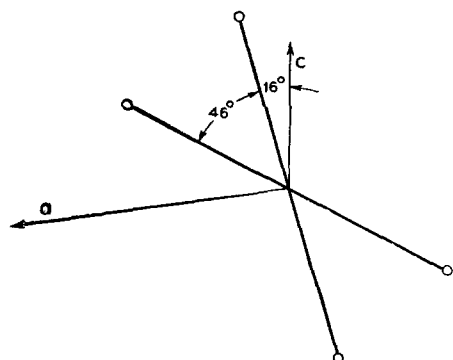
$$c' = \frac{1}{2}(a + b + c),$$

where the primes refer to the triclinic cell. This accounts for our initial observation that the cell was triclinic.

A sketch of the optic axes (Hg-5461 Å) is shown in Fig. 3; the plane of these axes is (010) with  $2V \cong 46^\circ$ . The crystals were of such nature that the refractive index  $\beta$  along the  $b$  axis could not be measured (although it is hoped that we shall eventually be able to obtain this value). It was possible, however, to measure the other two indices,  $\alpha = 1.51$ ,  $\gamma = 1.54$  (NaD).

### DISCUSSION

In  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  (Fig. 1), Cu(II) prefers square planar coordination, with two fluorine ions at 1.89 Å and two water oxygen atoms at 1.93 Å (Table V). Two very weak bonds are formed with two other fluoride ions at 2.47 Å, which if included as near neighbors of a given Cu(II) ion make the coordination polyhedron a distorted octahedron. Within a  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  grouping, the  $\text{F}^-$  ion is 2.70 Å from the oxygen, somewhat shorter than the sum of the van der Waals radii.

FIG. 3. Optic axes of  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ .

Each  $\text{F}^-$  ion of one grouping is strongly hydrogen bonded to two oxygen atoms of two neighboring groupings (Fig. 1). The planes of the grouping being nearly parallel to the (101) plane accounts for the perfect (101) cleavage; the hydrogen bonding occurs nearly in this plane and the bonding in a direction nearly perpendicular to this plane is weak. The secondary (110) cleavages which are almost perfect are also explained by the hydrogen bonding. These planes do not disrupt hydrogen bonds; they pass through Cu(II) atoms cutting through O-F interactions within the  $(\text{CuO}_2\text{F}_2)$  groupings.

With respect to packing in the  $b$ -axis direction, hydrogen atoms neighbor each other. If the estimate of the  $y$  parameter of the H is correct, the centers of the H atoms along the  $b$  axis are separated by 2.37 Å, which is about twice the van der Waals radius (1.2 Å) of the H atom.

TABLE V. Interatomic distances in  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ .

Atom	Interatomic distance, Å
Cu(II)	4 F <sup>-</sup> at 1.89 (2), 2.47 (2) 2 O at 1.93
F <sup>-</sup>	2 Cu(II) at 1.89, 2.47 2 O at 2.70 2 O-H at 2.66 2 F <sup>-</sup> at 2.89, 3.30
O	Cu(II) at 1.93 2 F <sup>-</sup> at 2.70 2 -H-F at 2.66

\* Because of the small backshift correction for oxygen, the indication is that the Cu-O distance is good to within  $\pm 0.02$  Å. As for the Cu-F distance, it is more difficult to say what the probable accuracy is. It is likely, however, that 1.89 Å is a lower limit for this distance.

The immediate surroundings of the Cu(II) ion in  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  are analogous to those in  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,<sup>2-4</sup> in which crystal the Cu(II) ion prefers four strong coplanar bonds, two of which are to oxygen atoms. The Cu-O distances in the two hydrates are the same, namely 1.93 Å. In both crystals there are two very much weaker bonds between the Cu(II) ion and the next nearest halide ions, these forming with the strongly bonded atoms a distorted coordination octahedron. The weak bonding was supposed some time ago by Wells<sup>16</sup> to be attributable to the odd electron localized in the copper  $4p$  orbital. However, Rundle has established that this description is untenable; the odd electron must reside in a molecular orbital rather than be localized in a copper orbital.

The  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  structure differs in some important respects from the corresponding chloride. In the fluoride, one grouping is associated with each lattice point, so that all the  $(\text{CuO}_2\text{F}_2)$  planes are parallel. In  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  there are two groupings in the primitive orthorhombic cell; the Cu(II) atoms are at the corners

and *C*-face centers. The plane of the groupings centered at the corners makes an angle of  $102.6^\circ$  with that of the groupings centered at  $(\frac{1}{2}, \frac{1}{2}, 0)$ . It should be noted that the H atoms lie very nearly in the planes of the  $(\text{CuO}_2\text{Cl}_2)$  groupings.<sup>4</sup> In  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ , if the estimated H positions are correct, the plane of the water molecule is  $14^\circ$  out of the  $(\text{CuO}_2\text{F}_2)$  plane. Some such displacement of the H atoms might be expected as the result of the stronger hydrogen bonding in the case of the fluoride than in that of the chloride.

If the interatomic distances in  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  are compared with those in anhydrous  $\text{CuCl}_2$ ,<sup>16</sup> it is found that the short and long Cu-Cl distances in both are 2.3 and 2.9 Å, respectively. However, in the case of the fluorides, the short Cu-F distances are 1.89 and 1.93 Å for the hydrated and anhydrous crystals, respectively, and the long ones are 2.47 and 2.27 Å, respectively. The anhydrous  $\text{CuF}_2$  has a distorted rutile structure,<sup>9</sup> whereas the structure of anhydrous  $\text{CuCl}_2$  is unrelated to the rutile structure. There is indication that when  $\text{H}_2\text{O}$  is not present, the more electronegative (than chlorine) fluorine atoms promote the formation of more nearly octahedral coordination to the Cu(II) atom. An investigation of the structures of  $\text{KCuF}_3$  and  $\text{K}_2\text{CuF}_4$  now underway in these Laboratories by K. Knox gives further substance to this observation.

As in the case of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , the  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  crystal does not have three-dimensional linkage through the halide ions. Including the weak Cu(II)—F<sup>-</sup> bonds there are  $\text{CuF}_2$  chains along the *c* axis (Fig. 4). The separation of the Cu(II) ions along the *c* axis is the length of the *c* axis, 3.30 Å; the next nearest Cu(II) atoms are at the distances from the origin to the body center: 4.99 Å ( $[111]$  direction) and 5.34 Å ( $[11\bar{1}]$  direction). The  $\text{CuF}_2$  chains are not linked directly in the *a*-axis direction; the three-dimensional linking occurs only through the hydrogen bonds (Fig. 1). One might speculate that in the antiferromagnetic  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  there are two types of superexchange linkage: that *within* the  $\text{CuF}_2$  chains (Fig. 4) through the weak Cu(II)—F<sup>-</sup> bonds, and that *between*  $\text{CuF}_2$  chains which occurs through the Cu—O—H—F—Cu linkages despite the large separation (5.34 Å) of Cu(II) atoms. Thus, the magnetic electron would be distributed to some extent over all the atoms of the structure including hydrogen.

Rundle's results on  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  would appear to establish that the Cu—O—H—Cl—Cu linkage is not important in effecting magnetic ordering. In the antiferromagnetic state, ordering of spin moments occurs in the  $\text{CuCl}_2$  chains through superexchange; whole chains interact directly resulting in three-dimensional antiferromagnetic ordering. Because of the similarity of the two structures in respect to the linkages between the groupings, the antiferromagnetic

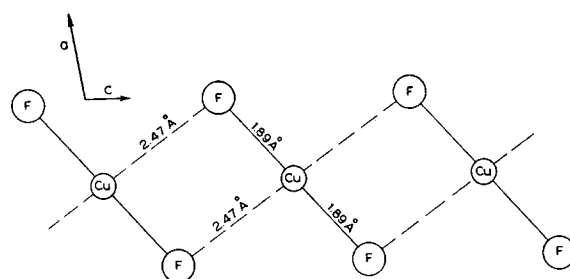


Fig. 4. The  $\text{CuF}_2$  chains. Separations of the Cu(II) ions along the *c* axis is 3.30 Å.

ordering in the fluoride should be analogous to that in the chloride.||

Of the two mechanisms (others are not precluded), that including the superexchange linkage between chains is the more likely for antiferromagnetic  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ . Neither mechanism for interaction between chains has been observed previously. However, although there has been no former speculation of involvement of hydrogen atoms in magnetic exchange interactions, there has been direct evidence that the magnetization of a magnetic ion can be felt through linkages involving more than one atom. The specific cases involve —O—P—O— linkages in iron group phosphates<sup>17</sup> some of which show antiferromagnetic ordering.

If the proposed mechanism for antiferromagnetic ordering in  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  is the correct one and if, as usual the superexchange results in negative interaction, it is possible to predict also the most likely arrangements of magnetic sublattices. A given Cu(II) ion will be magnetically linked by superexchange to six others: two through the weak Cu(II)—F<sup>-</sup> bonds (Figs. 1 and 4) and four through the hydrogen bonds (Fig. 1). These six will have spins antiparallel to that of the given Cu(II) ion to which they are linked. This results in ordering of spins in the  $(10\bar{1})$  planes, such that in a given  $(10\bar{1})$  plane of Cu(II) ions the spins are parallel and are antiparallel to those in the  $(10\bar{1})$  planes on either side. The nuclear magnetic resonance¶ and neutron diffraction\*\* studies should establish the true situation.

Of interest also is the fact that the  $\text{Cu}^{2.47\text{Å}}\text{F}^{1.89\text{Å}}\text{Cu}$  angle is  $98.0^\circ$ ; in  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  the analogous



angle is  $91.2^\circ$ . Although the Néel temperature of the fluoride is significantly higher than that of the chloride, the importance of the size of the interaction angle is in doubt. Ideas on the mechanism of superexchange are being reconsidered by both theorists

|| In a private communication from R. E. Rundle, we have learned that some additional data received from Poullis indicate that more of the magnetic electron density must be placed on the oxygen atoms and that on the chloride ion reduced.

<sup>17</sup> J. M. Mays, Phys. Rev. **108**, 1090 (1957).

¶ Being carried out by R. G. Shulman.

\*\* Being carried out by S. C. Abrahams and E. Prince.

<sup>16</sup> A. F. Wells, J. Chem. Soc. (1947), 1670.

and experimentalists as more fundamental information is obtained on crystals which show antiferromagnetic ordering.

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### Effect of Pressure on the Spectra of Certain Transition Metal Complexes\*

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The effect of pressure (to 130 000 atmospheres) has been measured on the splitting of the 3d levels of the nickel and chromium ions complexed with water and ammonia. Data have also been obtained on  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{K}_3\text{Fe}(\text{CN})_6$ . In general, the effect of pressure is to increase the effect of the ligand field and to increase the splitting of the levels. This is interpreted in terms of the change in ligand-metal distance. A phase transition was noted in  $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$  at 65 000 atmospheres.

A charge transfer band was also observed in  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ . The effect of pressure is to increase the intensity with no apparent change in the location of the maximum.

THE electronic spectra of the complexes of the first transition group metals can be thought of as arising from two separate processes. First, there are a low number of absorption bands due to essentially internal transitions of the electrons in the incomplete 3d shell of the metal ion. The number of these bands is the same for all combinations of a given geometry and metal with various ligands, and they appear in the region from the near infrared, through the visible, and into the near ultraviolet. The position of these bands is highly dependent upon the particular ligand with which the metal is coordinated. By considering the anion or dipole ligands to exhibit an electric field of symmetry corresponding to the stereochemistry of the complex, it has been shown that the energy levels of the ground and excited states of the free ion are, in general, each split into various levels. The spectra can be nicely interpreted as the electronic transition from the lowest level to the various upper levels. Although some work has been done on the extremely weak transitions between states of differing multiplicities, only those transitions between states of the same multiplicity will be considered in this work.

Although qualitative calculations of the strength of the ligand field (commonly called the crystal field) do not give the proper order of magnitude of the spectra, the use of an empirically determined value does give good results, especially when other refinements are added. The discrepancy between theory and experi-

ment is explained in part by the presence of chemical bonding. It is found that the empirically determined crystal field strength ( $E_1 - E_2$ ), historically termed 10  $Dq$ , varies with changing ligands in approximately the same manner for each transition metal.

Another way of changing the crystal field strength, but in a continuous manner, is through the use of pressure. Using high-pressure bombs with sodium chloride as both the pressure transmitting medium and the light path, absorption spectra were taken to approximately 130 000 atmospheres in the visible ultraviolet range on transition metal  $[\text{Ni}(\text{II})$  and  $\text{Cr}(\text{III})]$  complexes using  $\text{H}_2\text{O}$  and  $\text{NH}_3$  as the six ligands placed around the central atom in an essentially octahedral arrangement. In all cases the absorption maximum shifted blue indicating an increase in the crystal field strength. In two cases intensity measurements were also made, with the absorption of the peak increasing with pressure.

Less extensive measurements, mainly on band shapes, were made on two other systems. The observable band of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , which is a double band, was measured as a function of pressure. Also one "covalent" complex,  $\text{K}_3\text{Fe}(\text{CN})_6$ , was studied to determine if its behavior was of a different character than the "normal" complexes.

The second type of electronic process giving rise to spectra has been termed charge transfer and involves the transfer of an electron from the metal to the ligand or *vice versa*. These are broad, intense bands of higher energy than those previously mentioned, and usually

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