

pendent upon the nature of the substituent) we have, then, for the ground state of a reaction

$$\Delta F_g = \alpha_g \sigma_1 + \beta_g \sigma_R$$

and for the transition (or product) state

$$\Delta F_{\ddagger} = \alpha_{\ddagger} \sigma_1 + \beta_{\ddagger} \sigma_R$$

and thus the polar effect of the substituent on the free energy of activation (or reaction),  $\Delta F_{\ddagger} - \Delta F_{\ddagger_0}$ , becomes

$$\Delta F_{\ddagger} - \Delta F_{\ddagger_0} = \Delta F_{\ddagger} - \Delta F_g = \sigma_1(\alpha_{\ddagger} - \alpha_g) + \sigma_R(\beta_{\ddagger} - \beta_g)$$

It is interesting to note that special relationships are required between  $(\alpha_{\ddagger} - \alpha_g)$  and  $(\beta_{\ddagger} - \beta_g)$  for this equation to reduce to  $\Delta F_{\ddagger} - \Delta F_{\ddagger_0} / -2.303RT = \sigma\rho$ . (For example, for *p*-substituents  $\alpha_{\ddagger} -$

$\alpha_g$  must be nearly equal to  $\beta_{\ddagger} - \beta_g$ .) If these conditions are not met then  $\log(k/k_0)$  should be correlated more precisely by an equation of the form of eq. 2 than by the Hammett equation. It is also apparent that the quantities  $(\alpha_{\ddagger} - \alpha_g)$  and  $(\beta_{\ddagger} - \beta_g)$  will generally be different than  $\alpha$ - and  $\beta$ -values for a single state, a condition consistent with different susceptibilities of the magnetic shielding and Hammett parameters,  $\delta^F$  and  $\sigma$ , to inductive and resonance interactions.

The  $\delta^F$ -values for *o*-substituted derivatives of fluorobenzene do not follow eq. 2, except within similar types of substituents. The presence of large proximity effects on electron distributions is implied.

UNIVERSITY PARK, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

## The Crystal Structure of Copper(II) Fluoride

BY CLAUDINE BILLY<sup>1a</sup> AND HELMUT M. HAENDLER<sup>1b</sup>

RECEIVED OCTOBER 1, 1956

### Introduction

The structures of several simple metallic fluorides are as yet unknown. In general, fluorides of the type  $MF_2$  have been reported with either the cubic fluorite structure or the tetragonal rutile structure. The transition from 8-coördination in the fluorite type to the 6-coördination of the rutile structure has been related to a decrease in radius ratio. As the cation radius becomes still smaller, deviations from the rutile structure might be expected. At the lower extremity, beryllium fluoride has the 4-coördinated  $\beta$ -cristobalite structure.

The crystal structure of copper(II) fluoride has been reported incorrectly as cubic by Ebert and Woitinek.<sup>2</sup> This erroneous conclusion has been previously discussed<sup>3</sup> and corrected on the basis of powder pattern data. It has now been possible to complete a single crystal study of this fluoride, which agrees with our earlier conclusions that the symmetry can be no higher than monoclinic.

### Experimental

During a study of the melting of copper(II) fluoride<sup>3a</sup> in an inert atmosphere it was noted that the solidified melt from one run contained several small, apparently crystalline, fragments of colorless material imbedded in the dark red matrix. The sample was transferred immediately to the dry box and the fragments separated by hand from the residual solid. Three or four irregular pieces were obtained. These were coated with Formvar-T (from ethylene dichloride solution) and mounted on glass fibers with R-313 bonding agent.<sup>4</sup> They showed no plane surfaces and were

rather poor in quality, with considerable inhomogeneity. It was not certain that they were copper(II) fluoride.

The samples were mounted at random in the goniometer head and oscillation photographs taken at various orientations until recognizable layer lines appeared. In some cases the crystals apparently were multiple, and it was necessary to search for a clear single crystal region. It was not always possible to reorient or remount a specimen without interference by the glass support rod.

Oscillation and Weissenberg photographs were taken with both Cu  $K\alpha$  and Mo  $K\alpha$  radiation. We were able to obtain usable photographs for *hkl* and *nhl* reflections. Intensities of zero layer Weissenberg photographs were estimated by comparison with an intensity scale printed on the same film. An actual reflection was used to imprint the scale. With the traverse of the Weissenberg camera set at the equivalent of 3.5° of crystal rotation, exposure in seconds corresponds to exposure in hours of the usual Weissenberg film (crystal rotation about 200°). The camera was moved 5 mm. between each timed exposure. Both multiple film technique and controlled variation in exposure time were used simultaneously. Because of the poor crystals it was still difficult to obtain as satisfactory intensity data as desired.

It soon became obvious from correlation of powder diffraction data with the single crystal results that the samples were actually copper(II) fluoride. These powder data, from a Philips 114.6 mm. camera, were used to improve the unit cell dimensions. Diffractometer data from one of our samples have been obtained recently.<sup>5</sup> These do not alter the previous dimensions appreciably.

**Structure Determination.**—The unit cell of copper(II) fluoride is monoclinic with the symmetry of space group  $P2_1/c$ , but comparison to other  $AF_2$  type fluorides is simplified if a different monoclinic cell is chosen. The structure is then very nearly the rutile type. The space group designation is transformed to  $P2_1/n$ . This designation has also been used to elucidate the structure of the styrene-palladium chloride complex,<sup>6</sup> and we have followed the terminology suggested in that article.

The dimensions of the new cell are:  $a = 3.32 \text{ \AA.}$ ,  $b = 4.54 \text{ \AA.}$ ,  $c = 4.59 \text{ \AA.}$ ,  $\beta = 83^\circ 20'$ ,  $Z = 2$ ,  $V = 68.64 \text{ \AA.}^3$ ,  $D_x = 4.91 \text{ g./cc.}$ ,  $D_{\text{obs}} = 4.85 \text{ g./cc.}$  The two copper atoms are in the special positions 000 and  $1/2, 1/2, 1/2$ . The fluorine atoms are in the four general positions  $x, y, z$ ;  $\bar{x}, \bar{y}, \bar{z}$ ;  $1/2 + x, 1/2 - y, 1/2 + z$ ;  $1/2 - x, 1/2 + y, 1/2 - z$ .

(1) (a) Laboratoires des Services Chimiques de l'Etat, Paris. (b) To whom communications should be addressed. This work was supported in part by the Research Corporation and the Atomic Energy Commission.

(2) F. Ebert and H. Woitinek, *Z. anorg. Chem.*, **210**, 269 (1933).

(3) (a) H. M. Haendler, L. H. Towle, E. F. Bennett and W. L. Patterson, Jr., *THIS JOURNAL*, **76**, 2178 (1954); (b) J. M. Crabtree, C. S. Lees and K. Little, *J. Inorg. Nuclear Chem.*, **1**, 213 (1955); (c) H. M. Haendler, *Science*, **123**, 459 (1956).

(4) R. Pepinsky, *Rev. Sci. Instr.*, **24**, 403 (1953); obtainable from Carl H. Biggs, 2255 Barry Ave., Los Angeles.

(5) H. E. Swanson, X-Ray Diffraction Standards Group, National Bureau of Standards, Washington, D. C., personal communication.

(6) J. R. Holden and N. C. Baenziger, *THIS JOURNAL*, **77**, 4987 (1955).

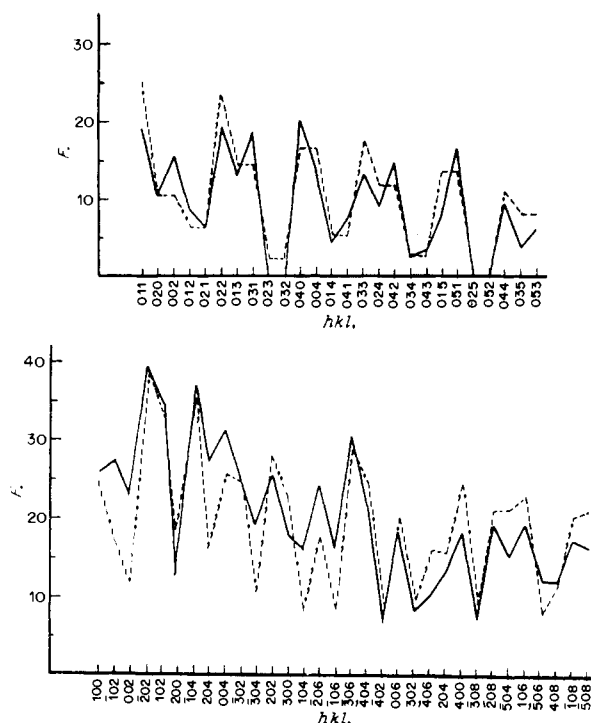


Fig. 1.—Comparison of observed and calculated structure factors:  $F_o$ , —;  $F_c$ , - - -.

The  $x$ ,  $y$  and  $z$  coordinates were determined by two Fourier projections on the (010) and (100) planes;  $x = -0.033$ ;  $y = 0.300$ ;  $z = 0.300$ . As stated above, intensity data were not as precise as desired for exact calculation of interatomic

TABLE I  
INTERPLANAR SPACINGS OF  $\text{CuF}_2$

Obsd. $d$ , Å. This work	Relative intensity	Obsd. $d$ , Å. Bur. of Stand.	Calcd. $d$ , Å.	$hkl^a$
3.219	100	3.221	3.218	011
2.822	26	2.825	2.832	101
2.661	36	2.663	2.669	110
2.533	10	2.532	2.535	$\bar{1}01$
2.394	15	2.406	2.404	111
<sup>b</sup>	..	2.286	2.284	002
2.277	6	2.275	2.278	020
2.210	7	<sup>c</sup>	2.213	$\bar{1}11$
<sup>b</sup>	..	2.043	2.041	012
2.036	4	2.037	2.034	021
1.819	20	1.820	1.819	112
1.769	14	1.771	1.772	121
1.690	19	1.692	1.692	$\bar{1}21$
1.659	15	1.660	1.658	$\bar{1}12$
1.641	13	1.642	1.648	200
1.610	20	1.612	1.609	022
1.512	4	1.514	1.519	003
1.443	11	1.445	..	013, 103
1.439	1	1.439	1.438	031
1.416	6	1.417	..	..
1.375	11	1.376	..	..
<sup>b</sup>	..	1.331	..	..
1.325	6	1.325	..	..
1.266	1.5	1.268	..	..
1.219	2.5	1.220	..	..
1.200	5.5	1.200	..	..

<sup>a</sup> Based on  $P2_1/n$ . <sup>b</sup> Too faint for film record. <sup>c</sup> Tungsten line interference.

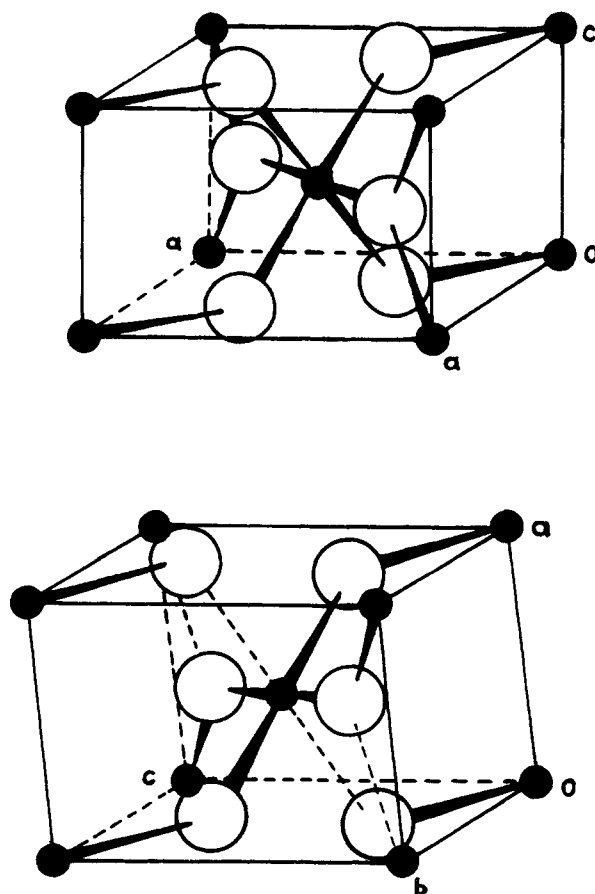


Fig. 2.—Comparison of rutile structure (top) with  $\text{CuF}_2$  structure; open circles are fluorine atoms.

distances and radii. A comparison of the observed and calculated structure factors is shown in Fig. 1.

**Powder Pattern.**—The powder pattern of copper(II) fluoride has been indexed and is given in Table I. The Bureau of Standards values<sup>6</sup> were run on one of our preparations to correct an error in a previously published compilation.<sup>7</sup> Intensities are the average of several visual estimations, using calibrated films, and densitometer measurements of the same films.

### Discussion

The structure of copper(II) fluoride can be compared to that of the other fluorides, of formula  $\text{MF}_2$ ,

TABLE II  
CRYSTAL STRUCTURE PARAMETERS

	$\text{NiF}_2$	$\text{CuF}_2$
$a$ , Å.	3.08	3.32
$b$ , Å.	4.65	4.54
$c$ , Å.	4.65	4.59
$\beta$	$90^\circ$	$83^\circ 20'$
$x$	0.00	-0.033
$y$	0.31	0.30
$z$	0.31	0.30
$d_1$ (M-F), Å.	$2.04 \pm 0.02$	$2.27 \pm 0.03$
$d_2$ (M-F), Å.	$1.98 \pm 0.01$	$1.93 \pm 0.03$
$d_1$ (F-F), Å.	$2.50 \pm 0.04$	$2.61 \pm 0.03$
$d_2$ (F-F), Å.	.....	$2.73 \pm 0.03$

(7) "Standard X-Ray Diffraction Powder Patterns," National Bureau of Standards Circular 539, Volume V. The pattern given for  $\text{CuF}_2$  is that of  $\text{CuCl}$ , and has been withdrawn pending correction.

which have the rutile structure,<sup>8</sup> as shown in Fig. 2. Using nickel fluoride as a specific example, comparable cell dimensions are listed in Table II, with the customary tetragonal symbolism for nickel fluoride changed to the same basis as that used for the copper(II) fluoride.

In each case, the metal ion,  $M^{++}$ , is surrounded by a distorted octahedron of six fluoride ions. In copper(II) fluoride two of these are at a distance  $d_1(M-F)$  and the other four, in planar coordination, are at a distance  $d_2(M-F)$ , as shown in Table II. The structure can be perceived as "CuF<sub>4</sub>" group-

(8) (a) H. M. Haendler, W. L. Patterson, Jr., and W. J. Bernard, *THIS JOURNAL*, **74**, 3167 (1952); (b) J. W. Stout and S. A. Reed, *ibid.*, **76**, 5279 (1954).

ings, with successive copper atoms in the  $[111]$  direction having their surrounding squares of fluorine atoms sharing corners. The closest distance of approach of two fluoride ions is  $d_1(F-F)$ , and the distance in the "CuF<sub>4</sub>" grouping is  $d_2(F-F)$ . The angle F-Cu-F is  $90^\circ$ ; the angle Cu-F-Cu is  $130^\circ$ .

If an ionic structure is assumed the ionic radius of the copper(II) ion is about 0.57 Å. It is interesting to note that the covalent radius sum ( $1.27 + 0.64 = 1.91$  Å.) is close to the observed distance, 1.93 Å. The calculated radius ratio is 0.42, close to the theoretical limit (0.414) for octahedral coordination.

DURHAM, NEW HAMPSHIRE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ARGONNE NATIONAL LABORATORY]

## Graphite Compounds<sup>1,2</sup>

BY MARCELINE L. DZURUS AND GERHART R. HENNIG

RECEIVED OCTOBER 11, 1956

Most lamellar compounds of graphite are definitely ionic. Some conceivable exceptions to this rule appeared to be the lamellar graphite compounds with aluminum chloride. Therefore, these have been investigated in detail. It has been found that, besides aluminum chloride and graphite, a third substance capable of forming negative ions had to be present for reaction to occur. Hence these compounds are also ionic. Electrical measurements have shown that all the compounds examined are P-type and have the approximate compositions  $C_n^+Cl^- \cdot 3AlCl_3$ ,  $C_n^+Br^- \cdot 3AlCl_3$ ,  $C_n^+I^- \cdot 3AlCl_3$ ,  $C_n^+Cl^- \cdot FeCl_2 \cdot 3AlCl_3$  and  $C_n^+Cl^- \cdot FeCl_2 \cdot 3FeCl_3$ , where  $n$  can vary between about 30 and infinity.

### Introduction

Graphite reacts with a large number of substances, such as bromine, ferric chloride and potassium to form interstitial compounds of graphite called lamellar compounds. In these lamellar compounds, planes of carbon atoms alternate in a definite periodic sequence with planes of the reactant. Experiments have shown that the lamellar reactions always cause an electron transfer between graphite and the reactant. It is our belief that the formation of lamellar compounds depends upon this electron transfer. If electrons are transferred to the graphite, donor or N-type compounds such as potassium graphite and rubidium graphite are formed. If electrons are removed from the graphite, acceptor or P-type compounds such as graphite bromide are formed.

One of the reasons why the electron transfer stabilizes the compounds is that an electrostatic interaction is set up in the resulting ionic compound. The electrostatic energy of the compounds will be most favorable, if the charges of equal sign are separated as much as possible, preferably by molecules of high polarizability. The stability of the lamellar compounds will, therefore, be increased if ions carrying the same charge are not in close proximity. Electrical properties, such as the resistance and Hall coefficient show that only a definite fraction, usually one-third of the reactant, is ionized.<sup>3</sup> The remainder apparently serves as a spacer to keep the ions separated. This require-

ment of a spacer between the ions of the reactant permits the introduction of many substances into graphite which do not enter spontaneously. Sodium, for instance, does not react with graphite, but forms a compound in the presence of ammonia because the ammonia serves as an effective spacer between the sodium ions.

This ionic model of the lamellar graphite compounds appears to fit all but one of the lamellar compounds which have been investigated in detail. The apparent exception is a reported compound containing only aluminum chloride and graphite and no species capable of forming free ions. Croft<sup>4</sup> has reported that pure aluminum chloride can be introduced into graphite in substantial quantities, but does not state clearly whether the reaction mixture in his experiments had been free of excess chlorine. Rüdorff<sup>5</sup> states that free chlorine must be present to permit aluminum chloride to react with graphite; nevertheless, he was not able to detect even a trace of excess chlorine in the compounds. Therefore, catalytic activity was attributed to the excess chlorine. Because of these reports and the apparent discrepancy with our model, we investigated in detail the system graphite-aluminum chloride.

A series of qualitative tests was carried out to determine whether chlorine actually was consumed during the reaction of graphite and aluminum chloride and whether this reaction ceased after the chlorine had been consumed. The presence of excess chlorine in the compounds was then established by a quantitative analysis of the com-

(1) Presented at the 129th Annual Meeting of the American Chemical Society, Dallas, April, 1956.

(2) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(3) G. Hennig, *J. Chem. Phys.*, **19**, 922 (1951); **20**, 1443 (1952).

(4) R. C. Croft, *J. Appl. Chem. (London)*, **2**, 557 (1952).

(5) W. Rüdorff and R. Zeller, *Z. anorg. allgem. Chem.*, **279**, 182 (1955).