

but, by itself, this offers no conclusive evidence for an anomalous fluorocarbon-hydrocarbon interaction, since the effect of the polar nitro group cannot be assessed.

For the naphthalene solutions, the situation is much clearer. To fit the solubility data, we must assign  $\delta_1$ -values around 5.0, in substantial agreement with our own measurements on phenanthrene solutions. While it is true that the thermodynamic solubility parameters will account for the greater part of the non-ideality (expressed as excess free energy, *i.e.*,  $\log \gamma$ , it accounts for 60–80% of the total), the remaining discrepancy is clearly beyond any reasonable estimate of errors. The source of this discrepancy remains to be elucidated.

The conclusion that the generally poor solvent power of the fluorochemicals is primarily due to their low cohesive energy density remains valid. Only for mixtures of fluorochemicals with compounds containing hydrocarbon groups does any further interpretation seem necessary. Moreover, we must

emphasize that the fact that the solubility of a substance is very low or differs very greatly from the ideal solubility is no criterion by which to measure the abnormality. Witness our data for stannic iodide in  $(C_4F_9)_3N$  in which the solubility is only 0.00001 mole fraction at 25° and for which the activity coefficient exceeds 12,000. Yet, on the basis of entirely reasonable "thermodynamic" solubility parameters, these numbers can be successfully explained.

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[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, UNIVERSITY OF CHICAGO]

## The Crystal Structure of $MnF_2$ , $FeF_2$ , $CoF_2$ , $NiF_2$ and $ZnF_2$

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The crystal structures of the five anhydrous fluorides have been checked by X-ray diffraction, using samples prepared from the melt, and precise lattice constants have been determined. All five fluorides have the rutile structure  $D^{14}_4h - P4/mnm$ . The parameters, at 25°C., are:  $MnF_2$ ,  $a = 4.8734 \pm 0.0002 \text{ \AA}$ ,  $c = 3.3099 \pm 0.0005 \text{ \AA}$ ,  $u = 0.310 \pm 0.003$ ;  $FeF_2$ ,  $a = 4.6966 \pm 0.0002 \text{ \AA}$ ,  $c = 3.3091 \pm 0.0001 \text{ \AA}$ ,  $u = 0.305 \pm 0.01$ ;  $CoF_2$ ,  $a = 4.6951 \pm 0.0002 \text{ \AA}$ ,  $c = 3.1796 \pm 0.0003 \text{ \AA}$ ,  $u = 0.308 \pm 0.003$ ;  $NiF_2$ ,  $a = 4.6506 \pm 0.0002 \text{ \AA}$ ,  $c = 3.0836 \pm 0.0004 \text{ \AA}$ ,  $u = 0.310 \pm 0.003$ ;  $ZnF_2$ ,  $a = 4.7034 \pm 0.0002 \text{ \AA}$ ,  $c = 3.1335 \pm 0.0003 \text{ \AA}$ ,  $u = 0.307 \pm 0.003$ .

In connection with a program of investigation of the magnetic and thermal properties of the anhydrous fluorides of divalent manganese, iron, cobalt, nickel and zinc, accurate values for the lattice constants of these compounds are needed. Data on  $MnF_2$  have been reported previously.<sup>1</sup> Early work<sup>2</sup> on the structure of  $FeF_2$ ,  $CoF_2$ ,  $NiF_2$  and  $ZnF_2$  shows that these compounds all have the rutile structure, space group  $D^{14}_4h - P4/mnm$ . Since the present work was begun Haendler, Patterson and Bernard<sup>3</sup> have reported precise lattice constants of  $NiF_2$  and  $ZnF_2$ .

**Preparation of Specimens.**—One of the objects of this research was to obtain lattice constants of crystals of the metal fluorides which had been grown from the melt, as had the specimens used for our magnetic and thermal measurements. All previous crystal structure determinations of the iron-group fluorides have been upon powders prepared below the melting point and it is necessary to verify that the structure of material which has been melted is the same. For this reason we made measurements on  $NiF_2$  and  $ZnF_2$  to compare with

the results of Haendler, Patterson and Bernard.<sup>3</sup> The ferrous fluoride and cobaltous fluoride samples were taken from boules which had supplied the single crystals used by Stout and Matarrese<sup>4</sup> for magnetic anisotropy measurements. Spectrochemical analysis showed 0.03% impurity in the  $FeF_2$  and 0.02% in the  $CoF_2$ . The  $FeF_2$  also contained 0.1% of ferric ion. Measurements also were made on some sublimed  $FeF_2$  which had condensed in the crystal growing furnace. This material contained no detectable ferric ion and gave X-ray pictures identical with the other sample. Two samples of  $NiF_2$  were used. One consisted of material which had been melted and the other was sintered material, taken from a sample used<sup>5</sup> in heat capacity measurements. Both samples gave identical X-ray patterns. Spectrochemical analysis of the sintered material, which was used for the back reflection photographs, showed 0.01% impurities. The  $ZnF_2$  was from a melted sample used<sup>5b</sup> in heat capacity measurements. It contained 0.01% impurities. All samples were crushed in a mortar and material sieved through a 200-mesh cloth was used for the X-ray specimens.

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TABLE I  
 SUMMARY OF BACK REFLECTION PHOTOGRAPHS

Substance	Radiation	$t$ , °C.	No. of lines	$a$ , Å.	$c$ , Å.	Av. dev. of $\sin^2\theta$
FeF <sub>2</sub>	Chromium	25.5	14	4.6965 ± 0.0001	3.3090 ± 0.0002	0.00008
FeF <sub>2</sub>	Cobalt	24.8	18	4.6967 ± .0001	3.3091 ± .0001	.00013
CoF <sub>2</sub>	Chromium	23.5	12	4.6949 ± .0002	3.1797 ± .0003	.00014
CoF <sub>2</sub>	Cobalt	23.5	18	4.6951 ± .0001	3.1793 ± .0002	.00011
NiF <sub>2</sub>	Chromium	25	13	4.6505 ± .0001	3.0839 ± .0003	.00010
NiF <sub>2</sub>	Copper	24	12	4.6506 ± .0002	3.0832 ± .0003	.00013
ZnF <sub>2</sub>	Chromium	25	13	4.7033 ± .0001	3.1337 ± .0003	.00007
ZnF <sub>2</sub>	Copper	23	14	4.7033 ± .0002	3.1331 ± .0002	.00010

**Experimental.**—Powder diffraction photographs were made in a 9-cm. diameter Debye camera with rotating specimen. The observed patterns were in agreement with those calculated for the rutile structure and preliminary values of the lattice constants were determined from the Debye photographs. To obtain precision values of the lattice constants diffraction photographs were taken in a 10-cm. diameter symmetrical back reflection focussing camera, using unfiltered radiation.

**Data and Discussion.**—The lattice constants obtained from analysis of the back reflection photographs of FeF<sub>2</sub>, CoF<sub>2</sub>, NiF<sub>2</sub> and ZnF<sub>2</sub> are listed in Table I. The observed positions of the lines on each film were fitted by least squares analysis to an equation of the form<sup>6</sup>

$$\sin^2 \theta = \lambda^2(h^2 + k^2)/4a^2 + \lambda^2l^2/4c^2 + K(\varphi/2) \sin(\varphi/2),$$

where  $\varphi = \pi - 2\theta$  and  $\theta$  is the Bragg angle. The weighting procedure used is that suggested by Hess.<sup>7</sup> For each substance two films with different wave length radiation were selected for analysis. The error given for each value of  $a$  and  $c$  is the standard error obtained from the least squares treatment. The difference between lattice constants obtained from films using different radiation is comparable to the standard error of each measurement and is evidence that no appreciable systematic error dependent on the radiation used is present. The following wave lengths were used,<sup>8</sup> all in Ångström units (1 Å. =  $10^{-8}$  cm.): chromium  $K\alpha_1$ , 2.28962;  $K\alpha_2$ , 2.29351;  $K\beta_1$ , 2.08480; cobalt  $K\alpha_1$ , 1.78892;  $K\alpha_2$ , 1.79278;  $K\beta_1$ , 1.62075; copper  $K\alpha_1$ , 1.54050;  $K\alpha_2$ , 1.54433;  $K\beta_1$ , 1.39217.

In the rutile structure each unit cell contains two metal ions at the positions (0, 0, 0) and ( $1/2$ ,  $1/2$ ,  $1/2$ ) and four fluoride ions at  $\pm(u, u, 0)$  and  $\pm(1/2 + u, 1/2 - u, 1/2)$ . To obtain values of the parameter  $u$  observed intensities in the Debye powder photographs were compared with those calculated for various values of  $u$ . The observed intensities of the lines were estimated visually by comparison with a series of standard lines of different exposure times. The atomic scattering factors and corrections for Lorentz and polarization factors, absorption, multiplicity and temperature factors were taken from the "Internationale Tabellen."<sup>9</sup> The atomic scattering factors for the metallic ion were corrected for anomalous dispersion.<sup>10</sup> For chro-

mium radiation this decreased the atomic scattering factor by: Fe, 1.9; Co, 1.8; Ni, 1.7; Zn, 1.5. In the analysis of the pattern of FeF<sub>2</sub> obtained with cobalt radiation a correction of  $-4$  was applied to the atomic scattering factor of ferrous ion. As was the case<sup>1</sup> with MnF<sub>2</sub> the ratio of intensity of the lines (202) and (311) was particularly sensitive to the choice of the parameter  $u$ . The values of  $u$  listed in Table III for CoF<sub>2</sub>, NiF<sub>2</sub>, and ZnF<sub>2</sub> are based on this ratio which was observed to be: CoF<sub>2</sub>, 2.4; NiF<sub>2</sub>, 4.3; ZnF<sub>2</sub>, 4.6. A change of 0.003 in  $u$  produces a change of about 30% in the calculated intensity ratio, and the error ascribed to the  $u$  values is based on this. In CoF<sub>2</sub>, NiF<sub>2</sub> and ZnF<sub>2</sub> the observed intensities, listed in Table II, of all lines on films taken with chromium radiation agreed, with an average deviation of 15%, with those calculated using the  $u$  values in Table III. In the case of FeF<sub>2</sub>,  $(c/a)^2 = 0.49642$ , which is sufficiently close to  $1/2$  so that many coincidences occur between lines of different indices but having the same value of  $h^2 + k^2 + 2l^2$ . Thus the separation between lines (202) and (311) is comparable to the  $\alpha_1 - \alpha_2$  separation and is not resolvable at the position on the film where these lines fall using chromium radiation. Such coincidences occurred with several lines whose

 TABLE II  
 OBSERVED INTENSITIES OF REFLECTIONS, DEBYE PHOTOGRAPHS

Only chromium  $K\alpha$  lines are listed. Intensity scale is arbitrary for each substance.

Indices	Observed intensity			
	FeF <sub>2</sub>	CoF <sub>2</sub>	NiF <sub>2</sub>	ZnF <sub>2</sub>
110	425	475	450	300
101	320	200	300	180
200	} 210	20	40	30
111		90	90	50
210	55	30	40	20
211	500	360	525	325
220	} 200	100	130	90
002		53	90	50
310	} 245	60	85	78
221		5	..	..
112	} 90	90	160	73
301		160	300	140
311	} 43	12	15	11
202		28	65	} 50
320	} 35	3	..	
212		16	..	15
321	140	100	235	130
400 $\alpha_1$	} 50	60	150	} 120
400 $\alpha_2$		30	70	
222 $\alpha_1$	} 350	30	70	
222 $\alpha_2$		65		

(6) In reference 1 the  $\varphi/2$  appearing in this equation is erroneously written as  $\varphi$ .

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(8) C. S. Barrett, "Structure of Metals," McGraw-Hill Book Co., Inc., New York, N. Y., 1952, p. 644.

(9) "Int. Tab. Bestimmung Kristallstrukturen," Vol. II, Borntraeger, Berlin, 1935, Chap. XI.

(10) See A. H. Compton and S. K. Allison, "X-Rays," D. Van Nostrand Co., New York, N. Y., 1935, p. 315.

TABLE III  
 CRYSTAL STRUCTURE PARAMETERS, 25°C.

Substance	MnF <sub>2</sub>	FeF <sub>2</sub>	CoF <sub>2</sub>	NiF <sub>2</sub>	ZnF <sub>2</sub>
$a$ , Å.	4.8734 ± 0.0002	4.6966 ± 0.0002	4.6951 ± 0.0002	4.6506 ± 0.0002	4.7034 ± 0.0002
$c$ , Å.	3.3099 ± .0005	3.3091 ± .0001	3.1796 ± .0003	3.0836 ± .0004	3.1335 ± .0003
$a_{111}$ , Å.	3.8228 ± .0002	3.7103 ± .0001	3.6810 ± .0002	3.6320 ± .0002	3.6764 ± .0002
Density, g. cm. <sup>-3</sup>	3.925	4.269	4.592	4.814	4.952
$u$	0.310 ± 0.003	0.305 ± 0.01	0.308 ± 0.003	0.310 ± 0.003	0.307 ± 0.003
$d_1$ (M-F), Å.	2.14 ± 0.02	2.03 ± 0.07	2.05 ± 0.02	2.04 ± 0.02	2.04 ± 0.02
$d_2$ (M-F), Å.	2.11 ± .01	2.10 ± .04	2.04 ± .01	1.98 ± .01	2.03 ± .01
$d$ (F-F), Å.	2.62 ± .04	2.59 ± .13	2.55 ± .04	2.50 ± .04	2.57 ± .04

intensities are particularly sensitive to the value of  $u$ . By comparison of calculated intensities with those (listed in Table II) observed on a film taken with chromium radiation, it was determined that  $u$  lies in the range 0.30-0.31. An additional comparison was made with a film taken with cobalt radiation and again the best fit to the observed intensities was obtained with  $u = 0.30$  to 0.31. We have chosen as the most probable value  $u = 0.305 \pm 0.01$ . Using this value the average deviation of observed intensities from those calculated was 15% for the film with chromium radiation and 25% for that with cobalt radiation.

The values of the lattice constants,  $a$  and  $c$ , corrected to 25°, are listed in Table III. In making the correction for temperature, an isotropic coefficient of expansion of  $2 \times 10^{-5}$  deg.<sup>-1</sup> was assumed. The maximum correction was 0.0002 Å. An error was discovered in the weighting procedure that had been used<sup>1</sup> in the calculation of the lattice constants of MnF<sub>2</sub> and the result of the corrected calculation is included in Table III. The only change in the lattice constants is a decrease of  $c$  by 0.0004 Å. which is within the experimental error. The lattice constants obtained by Haendler, Patterson and Bernard<sup>3</sup> for NiF<sub>2</sub> agree within 0.0001 Å. with ours. In the case of ZnF<sub>2</sub> their values are lower than ours by 0.0013 Å. for  $a$  and 0.0007 Å. for  $c$ . The discrepancy in  $a$  is more than twice the sum of the standard errors (0.0010 Å.) and may indicate a real difference in the samples prepared by different methods. Haendler, Patterson and Bernard<sup>3</sup> did not state the temperature corresponding to their values of the lattice constants and we have assumed it could be taken as 25°. Detailed comparison with the less accurate older work<sup>2</sup> will not be made.

Of importance in the phenomenon of antiferromagnetism is the magnetic interaction between a central positive ion and the neighboring positive

ions. In MnF<sub>2</sub>, FeF<sub>2</sub>, CoF<sub>2</sub>, NiF<sub>2</sub> and ZnF<sub>2</sub> each positive ion is surrounded by two nearest neighbor positive ions at (0, 0, ±1) at a distance  $c$ , by eight next nearest neighbors at (±1/2, ±1/2, ±1/2) at a distance  $d_{111} = \frac{1}{2}(c^2 + 2a^2)^{1/2}$ , and by four-third nearest neighbors at (±1, 0, 0) and (0, ±1, 0) at a distance  $a$ . The values of  $d_{111}$  calculated from our lattice constants are listed in Table III. Also included are values of the density calculated from the lattice constants. In making the density calculations, the natural constants used were those recommended by Rossini, *et al.*<sup>11</sup> The 1951 atomic weights<sup>12</sup> were used.

Each metal ion, M<sup>++</sup>, is surrounded by a distorted octahedron of six fluoride ions. Two of these, at ± ( $u, u, 0$ ), are at a distance  $d_1$  (M-F) and the remaining four are at the distance  $d_2$  (M-F). The structure may be thought of as a distortion of a structure with the fluoride ions arranged in a regular octahedron by compression of the  $a$ -axes. Such a distortion is favored by considerations of electrostatic energy and the observed structure is a balance between this energy and the repulsion of the fluoride ions which are squeezed together by the distortion. Such an explanation has been suggested by Pauling<sup>13</sup> for substances with the rutile structure. The observed values of the closest distance of approach of the fluoride ions,  $d$  (F-F), together with values of  $d_1$  (M-F) and  $d_2$  (M-F) are listed in Table III. The listed uncertainties are calculated from the corresponding ones in the values of  $u$ . In agreement with Pauling's explanation, the values of  $d$  (F-F) are all appreciably less than the crystal radius sum of 2.72 Å.

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