culated, are compared with the values predicted by Eqs. 5 and 7 in the last three columns of Table II.

We see that Eqs. 5 and 7 agree more closely the nearer v_2/v_1 is to unity. In the cases with isoöctane and with heptane, the two values are practically identical but they differ by 0.3 with chloroform, where the volume discrepancy is largest.

There is a very large discrepancy, however, between both of these equations and experiment for solutions of perfluoroheptane with isoöctane and with normal heptane, which behave as if the δ-values of these substances were much higher than the values derived from heats of vaporization. The same can be inferred from the data for iodine solutions,[1e] which give δ_2-values for iodine considerably less in its solutions with isoöctane, *n*-hexane and *n*-heptane than in the other solvents. These paraffins are poorer solvents for fluorocarbons and better solvents for iodine and phosphorus[8] than would be concluded from their heats of vaporization. For practical purposes, one might adjust their values empirically, but curiosity is naturally aroused about the reasons for discrepancies of this magnitude. We are at present engaged in measuring volume changes of mixing of appropriate binary systems to see if these inconsistencies can be attributed to changes of packing during the mixing process. We expect to publish our findings together with a more detailed analysis of liquid–liquid solubilities in a forthcoming publication.

We gratefully acknowledge support of the Atomic Energy Commission for this research.

Summary

Liquid–liquid solubility curves have been determined for binary mixtures of perfluoro-*n*-heptane with benzene, carbon tetrachloride, chloroform, *n*-heptane and 2,2,4-trimethylpentane. The critical temperatures obtained from these curves were 113.5°, 58.7°, 78.5°, 50.0° and 23.7°, respectively.

Solubility parameter differences calculated from experimental results were in close agreement with values predicted by solubility theory for all but the two paraffin hydrocarbons listed above.

BERKELEY, CALIF. RECEIVED APRIL 11, 1950

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[8] C. Groot and J. H. Hildebrand, THIS JOURNAL, **70**, 3815 (1948).

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

Preparation of Single Crystals of Manganous Fluoride. The Crystal Structure from X-Ray Diffraction. The Melting Point and Density

BY MAURICE GRIFFEL[1] AND J. W. STOUT

In connection with the determination of the magnetic anisotropy of MnF_2 reported elsewhere[2] single crystals were grown from the melt. The method of growing the crystals will be briefly described here, together with measurements that were made of the melting point, the density and the crystal parameters as determined from X-ray diffraction.

Preparation of Single Crystals.—Powdered MnF_2 was prepared by the method of Kurtenacker, Finger and Hey.[3] $MnCO_3$ was precipitated from a solution of analytical reagent $MnSO_4 \cdot H_2O$. In order to avoid precipitation of $MgCO_3$ an excess of the $MnSO_4$ solution was used. The $MnCO_3$ was converted to MnF_2 by adding it to a 20% aqueous HF solution contained in a plastic dish. The precipitated MnF_2 was washed several times with water and a water–ethanol mixture and then dried under vacuum. When the MnF_2 so prepared was melted under a vacuum of about 10^{-4} mm. the resulting product was greenish. The original powder could be dried for a day at 300° under a vacuum of 10^{-5} mm. with no change in appearance, but further heating under vacuum to 600 to 800° would cause a darkening of the light pink color. The darkening and development of green color were presumably due to the reaction of the MnF_2 with traces of water that were not completely removed by the drying procedure. To avoid this the drying of the powder and the growing of the crystals from the melt were carried out in a stream of anhydrous HF. Under these conditions no discoloration was observed.

The apparatus for growing the crystals was similar to that described by Stockbarger.[4] Because of the necessity of maintaining an atmosphere of HF the central tube was made of nickel pipe, 6.67 cm. o. d. and 6.27 cm. i. d. The crucible was supported inside this tube on top of a capped nickel pipe, 1.11 cm. o. d., which could be raised and lowered at different rates by an electric motor and a train of gears. The outer nickel pipe was provided with entrance and exit tubes for the HF gas and the seals at the top and bottom were made with polytetrafluorethylene ("teflon") gaskets. Because of corrosion by the HF the nickel pipe had to be replaced after about 500 hours operation at 950°. The outer nickel pipe was surrounded by a heating unit of nichrome wire wound on an alundum form. Chromel–alumel thermocouples were used for temperature measurements and the temperature was controlled by a thermocouple and a proportioning temperature regulator.[5] The crucibles used were made of high purity graphite. Preliminary experiments showed that, after melting, the MnF_2 adhered tightly to platinum but could be easily removed from graphite. A typical crucible was of cylindrical form, 1.91 cm. o. d., wall thickness 0.17 cm. and depth 6 cm. The inner diameter was slightly tapered toward the bottom and ended in a cone of thirty degree half-angle.

Finely divided MnF_2, precipitated and dried at room temperature, was placed in a platinum boat in a furnace

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[1] Atomic Energy Commission Fellow 1948-1949. Present address: Iowa State College, Ames, Iowa.

[2] J. W. Stout and Maurice Griffel, *Phys. Rev.*, **76**, 144 (1949). A more detailed account will be published in the *Journal of Chemical Physics*.

[3] A. Kurtenacker, W. Finger and F. Hey, *Z. anorg. Chem.*, **211**, 883 (1933).

[4] D. C. Stockbarger, *Rev. Sci. Inst.*, **10**, 205 (1939).

[5] D. Lazarus and A. W. Lawson, *ibid.*, **18**, 730 (1947).

and dried in a stream of HF while the temperature was raised over a three hour period to 700°. The MnF_2 sintered slightly during this process. It was powdered in a mortar and transferred to a graphite crucible which was mounted in the single crystal furnace. The stream of HF was then started through the furnace and the latter heated to and controlled at a temperature so that the crucible was above the melting point of MnF_2. The crucible was then lowered at a rate of 0.25 cm. per hour until the top of the crucible was well below the point in the furnace corresponding to the melting temperature.

The crystals grown by this procedure were pink and transparent. On one occasion the entire contents of the crucible grew as one crystal but usually there would be several single crystals, of linear dimensions of the order of five mm. Since these were sufficiently large for our purposes we did not investigate in detail the conditions necessary to prevent the nucleation of several crystals. A spectrochemical analysis of the MnF_2 crystallized from the melt showed the presence of 0.001% Ca and 0.002% Fe. No other impurities could be detected.

The Melting Point of MnF_2.—The melting point of macro-crystalline MnF_2, prepared as above, was determined under vacuum using essentially the procedure described by Roeser and Wentzel.[6] No discoloration of the crystals was observed during the melting point determination. The chromel–alumel thermocouple used for the temperature measurement was calibrated in the same apparatus with 99.99% silver. Taking the melting point of silver[7] as 960.8°, the melting point of MnF_2 was determined as 929.5 ± 0.5°. Moissan and Venturi[8] have reported a melting point of 856°.

The Density of MnF_2.—The density of MnF_2 was determined by a pycnometric method using some of the single crystals described above. The density of the sample of benzene which was used as the pycnometric liquid was determined by comparison with gas-free distilled water. All density determinations were made in a thermostat at 25°. We found the density of MnF_2 at 25° to be 3.922 ± 0.004 g. cm.$^{-3}$. Moissan and Venturi[8] have reported a density of 3.98 g. cm.$^{-3}$.

The Crystal Structure of MnF_2.—Measurements of the crystal structure of MnF_2 by X-ray diffraction have been reported by Goldschmidt,[9] van Arkel,[10] and Ferrari.[11] These authors agree that the structure is of the rutile type, space group D^{14}_{4h}. However, the accuracy of the determination of the unit cell dimensions was not sufficient for the calculation of an accurate density for comparison with our measured value. In order to obtain more accurate lattice parameters and also to determine whether the crystal structure of MnF_2 crystallized from the melt was the same as that of the very fine powder precipitated from aqueous solution which had been used for the previous X-ray measurements, we have measured X-ray diffraction patterns of MnF_2. A powder was made by crushing the crystals obtained from the melt and selecting as a sample material that passed through a 200-mesh cloth.

Diffraction photographs were first made with a 9-cm. diameter Debye camera with a rotating specimen. Chromium radiation was used with a vanadic oxide filter to decrease the intensity of the beta lines. The observed pattern was in agreement with that calculated for the space group D^{14}_{4h} with the parameter $u = 0.310$ and the lattice parameters whose accurate determination will be described later. The calculated and observed intensities are listed in Table I for the $K\alpha$ lines. The observed intensities are based on visual estimates made by comparison with a series of lines of different exposure times and may be in error by as much as a factor of two for the weaker lines. The intensities of the strongest lines were also checked with a photometer and it is believed the values are accurate to about 20%. The calculated intensities are based on atomic structure factors for fluoride ion[12] and manganese.[13] The atomic structure factor of manganese has been decreased by 2.2 because of the anomalous dispersion of the chromium radiation.[14] The calculated intensities have been corrected for the Lorentz and polarization factors, the multiplicity factor, and the absorption factor.[15]

TABLE I

INTENSITIES OF DIFFRACTION LINES OF MnF_2, DEBYE CAMERA

	Intensity on arbitrary scale			Intensity on arbitrary scale	
hkl	Obs.	Calcd. $u = 0.310$	*hkl*	Obs.	Calcd. $u = 0.310$
110	150	150	112	40	48
101	90	92	301	70	110
200	6	7	311	4	7
111	50	53	202	6	9
210	12	22	320	..	2
211	125	150	212	6	20
220	30	44	321	20	33
002	25	34	400	15	33
310	15	22	222	30	115
221	...	5	222	15	59

Each unit cell contains two Mn^{++} ions at the positions (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and four F^- ions at positions $\pm (u,u,0)$ and $\pm (\frac{1}{2} + u, \frac{1}{2} - u, \frac{1}{2})$. The calculated ratio of the intensities of lines 202 and 311 is 0.46 at $u = 0.30$, 1.3 at $u = 0.31$ and 5.0 at $u = 0.32$. The intensity ratios of other close lines are much less sensitive to the value of u. Since lines 202 and 311 are quite weak, a long exposure was made in which half of the film was masked by an aluminum foil so as to decrease the intensities on part of the film by a calculable factor. From this film it was estimated that the ratio of the intensity of line 202 to that of 311 was 1.5 ± 0.4 corresponding to $u = 0.311$. In calculating the intensities no correction has been applied for the thermal vibration of the atoms because of the uncertainty of this correction for an anisotropic crystal containing two different kinds of atoms. The effect of the thermal motion is to lower the intensities at the larger angles. Furthermore the lighter fluorine atoms will have a larger amplitude of motion than the manganese and this will slightly lower the value of u obtained from lines 202 and 311. The intensities of the remaining lines limit u to a value between 0.30 and 0.32 and we have chosen as the best value $u = 0.310 \pm 0.005$.

To obtain more accurate values of the unit cell dimensions, diffraction photographs were taken in a 10-cm. diameter symmetrical back reflection

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(6) W. F. Roeser and H. T. Wentzel, "Temperature, Its Measurement and Control in Science and Industry," Reinhold Publ. Co., New York, N. Y., 1941, p. 293.

(7) *Chem. Eng. News*, **27**, 702 (1949).

(8) Moissan and Venturi, *Compt. rend.*, **130**, 1158 (1900).

(9) V. M. Goldschmidt, "Geochem. Verteilungsgesetze," v. VI, Oslo, 1926 (measurements of W. Zachariasen).

(10) A. E. van Arkel, *Rec. Trav. Chim. Pays-Bas*, **45**, 437 (1926).

(11) A. Ferrari, *Atti Acad. Lincei*, [6] **3**, 224 (1926).

(12) "Int. Tab. Bestimmung Kristallstrukturen," v. II, Borntraeger, Berlin, 1935, p. 571.

(13) H. Viervoll and O. Ögrim, *Acta Crystallographica*, **2**, 277 (1949).

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

(15) See C. S. Barrett, "Structure of Metals," McGraw-Hill Book Co., Inc., New York, N. Y., 1943, p. 541.

focussing camera (manufactured by Geo. C. Wyland; Ramsay, N. J.). Unfiltered chromium radiation was used. Two films, one having 15 lines and the other 17 were used. The observed values for each film were fitted by least squares to an equation of the form

$$\sin^2\theta = \lambda^2(h^2 + k^2)/4a^2 + \lambda^2 l^2/4c^2 + K\varphi\sin\varphi \quad (1)$$

where $\varphi = \pi - 2\theta$. The wave lengths for chromium radiation were taken as $K\alpha_1$, 2.28962; $K\alpha_2$, 2.29352; $K\beta_1$, 2.08479, all in units of 10^{-8} cm. The weighting procedure used, due to Hess[16] is a modification of that proposed by Cohen.[17] The essential change is that the points are weighted according to the error in the actual film measurements rather than by giving equal weight to each $\sin^2\theta$. The intensities of the observed lines are in qualitative agreement with those calculated from the assumed structure and value of u, but because of the possibility of preferred orientation in the back reflection camera we have not made quantitative estimates of intensities. The average deviation of $\sin^2\theta$ from that given by Eq. (1) was 0.00039.

The values of the parameters obtained from the least squares solution, taking both films into account, are $a = (4.8734 \pm 0.0005) \times 10^{-8}$ cm.; $c = (3.3103 \pm 0.0010) \times 10^{-8}$ cm. The ± represents the standard error. The values of a and c are for a temperature of 25°.

From the values of a and c and the molecular weight of 92.93 the calculated density is 3.925 ± 0.003 g. cm.$^{-3}$ at 25°. This is in good agreement with the measured density of 3.922 ± 0.004.

In the MnF_2 structure each manganese ion is surrounded by six fluoride ions. Using the observed parameters two of these are at a distance 2.14 Å. and four at 2.11 Å. The value of u necessary to make all six manganese–fluorine distances equal (2.120 Å.) is 0.3077. The six fluoride ions are arranged at the corners of a distorted octahedron. The two fluoride ions lying above (in the direction of the c-axis) or below the central manganese are closer to each other and farther from the remaining four than would be the case for a regular octahedron. The distance of these two closest fluoride ions is 2.62 Å. From Pauling's table of ionic radii[18] one computes a manganese–fluoride distance of 2.16 Å. and F–F distance of 2.72 Å. The observed distances are smaller than the radius sums as is found for other crystals with the rutile structure.[19]

Acknowledgment.—We are indebted to Mr. Larry Howell for performing the spectrochemical analysis and to Professor C. S. Barrett and Mr. J. B. Hess for assistance and advice regarding the X-ray measurements.

Summary

The preparation of single crystals of MnF_2 from the melt in an atmosphere of HF is described. From X-ray diffraction measurements the parameters of the tetragonal unit cell, each containing two molecules of MnF_2, are $a = (4.8734 \pm 0.0005) \times 10^{-8}$ cm. and $c = (3.3103 \pm 0.0010) \times 10^{-8}$ cm. at 25°. The parameter u that determines the position of the fluorine atoms in the space group $D^{14}{}_{4h}$ is 0.310 ± 0.005. The density calculated from the X-ray parameters is 3.925 ± 0.003 g. cm.$^{-3}$. The measured density is 3.922 ± 0.004 at 25°. The melting point of MnF_2 is 929.5 ± 0.5°.

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(16) J. B. Hess, *Acta Cryst.*, in press.

(17) M. U. Cohen, *Rev. Sci. Inst.*, **6**, 68 (1935); **7**, 155 (1936).

(18) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 350.

(19) *Ibid.*, p. 365.

CHICAGO, ILLINOIS RECEIVED FEBRUARY 4, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

The Reaction of Chromyl Chloride with Olefins[1]

BY STANLEY J. CRISTOL AND KENDRICK R. EILAR

The first significant study of the action of chromyl chloride on organic compounds was made by Étard.[2] He discovered that chromyl chloride reacts with toluene to form a brown solid which when hydrolyzed produces benzaldehyde. This reaction, which now bears his name, has been extended to numerous nuclear-substituted toluenes.

Later, Étard reported[3] that an aldehyde was produced by the action of chromyl chloride on the olefin, camphene. Henderson and co-workers used this reaction to a considerable extent, but without great success, in their studies of the terpenes[4]; from reactions of chromyl chloride with several of the terpenes, they obtained mixtures of ketones, aldehydes, and chlorinated compounds; the constituents of these mixtures were usually not identified. Similar results were reported by Bredt.[5]

In view of the confusion arising from these terpene reactions,[6] it seemed desirable to study the

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[1] This paper was presented before the Division of Organic Chemistry at the March, 1949, meeting of the American Chemical Society, San Francisco, California.

(2) Étard, *Ann. chim. phys.*, **22**, 218 (1881).

(3) Étard and Moissan, *Compt. rend.*, **116**, 434 (1893).

(4) Henderson and Smith, *J. Chem. Soc.*, **55**, 45 (1889); Henderson and Gray, *ibid.*, **83**, 1299 (1903); Henderson and Heilbron, *ibid.*, **93**, 288 (1908); **99**, 1887 (1911); Henderson, Robertson and Brown, *ibid.*, **121**, 2717 (1922); Henderson and Chisholm, *ibid.*, **125**, 107 (1924).

(5) Bredt and Jagelki, *Ann.*, **310**, 112 (1899).

(6) Sword, *Chem. News*, **133**, 1 (1926).