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THE TETRAFLUORIDES OF IRIDIUM, RHODIUM AND PALLADIUM.

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Abstract :

The noble-metal tetrafluorides IrF_4 , RhF_4 and PdF_4 have been synthesized. All three fluorides are isostructural with PtF_4 the unit cells being face centred orthorhombic, $Z = 8$, (probable space $Fdd2$) with the following parameters :

	a_0 (Å)	b_0 (Å)	c_0 (Å)	V (Å ³)
IrF_4	9.64(2)	9.25(2)	5.67(1)	505.8
RhF_4	9.71(2)	9.05(2)	5.63(1)	494.7
PdF_4	9.37(2)	9.24(2)	5.84(1)	505.6

PdF_4 is diamagnetic (low spin d^6) whereas RhF_4 and IrF_4 are paramagnetic. The magnetic susceptibility of the latter obeys a Curie-Weiss law over the temperature range 100-300°K ($\theta = -60^\circ\text{K}$) with $\mu_{\text{eff}} = 1.89$ B.M. Below 100°K significant deviation from the Curie-Weiss relationship occurs. This and the large negative value of the Weiss temperature are consistent with antiferromagnetic coupling between adjacent iridium atoms. This is in harmony with a proposed structural model.

INTRODUCTION

Within recent years our knowledge of the binary fluorides of the platinum metals has been extensively revised.

In 1958, the fluoride long known (1) as OsF_8 was shown by Weinstock and Malm(2) to be OsF_6 and, in 1965, the fluoride of iridium, reported (3,4) on two occasions to be a tetrafluoride was shown (5) by Bartlett and Rao to be a pentafluoride. New hexafluorides and pentafluorides (9, 10, 11) (in addition to RuF_5 which had long been known) have now established hexafluorides and pentafluorides for all of the platinum metals other than palladium. Moreover, the trifluorides, RuF_3 , RhF_3 , PdF_3 and IrF_3 have been established by X-ray crystal structure analysis (12) although that of palladium has been shown (13) to be the mixed oxidation state compound Pd(II)Pd(IV)F_6 . So far only one binary fluoride of the platinum metals, PdF_2 , has been reported (14, 15, 16)

The establishment of pentafluorides of rhodium and iridium (5) as well as the trifluorides raised the possibility of each element also making a tetrafluoride (17). On the other hand the mixed oxidation state character (13) of " PdF_3 " (Pd(II)Pd(IV)F_6) raised the possibility of the tetrafluorides RhF_4 and IrF_4 being M(III)M(V)F_8 compounds. At the same time the existence of Pd(IV) in the compound Pd(II)Pd(IV)F_6 indicated the probable existence of PdF_4 .

The tetrafluorides were also, however, of considerable interest for their structural features. Octahedral coordination was already the established platinum-metal atom coordination in the hexafluorides(18), pentafluorides(19,20), trifluorides (12) and PdF_2 (16) but the preliminary structural findings of Bartlett and Lohmann (21) on PtF_4 had indicated the possibility (22) of that fluoride being a structural relative of UCl_4 (in which the uranium atom is eight-coordinated in chlorine atoms in two flattened-tetrahedral four-fold sets, one close and the other more distant from the metal atom (23). Of course such a structure in a tetrafluoride

renders all of the fluorine ligands equivalent whereas adoption of octahedral metal-atom coordination immediately requires F-ligand inequivalence. Such inequivalence had already been established (19, 20) for the platinum metal pentafluorides, in which somewhat distorted MF_6 groups are linked by a sharing of two of the F-ligands (in cis relationship to each other) with 2 other octahedra to form cyclic tetrameric units $(MF_5)_4$.

The tetrafluorides of iridium, rhodium and palladium (13) have been established by the work reported in this paper and together with PtF_4 constitute a structurally related set.

EXPERIMENTAL

Materials. Finely divided or sponge platinum metals of high purity were obtained from Johnson, Matthey and Mallory Ltd., (Rh, Pd) and Engelhardt Industries Inc., (Ir), and the iridium and rhodium were used as obtained. The palladium was always converted to the dibromide prior to fluorination. $PdBr_2$ was prepared by dissolving palladium sponge in concentrated hydrobromic acid containing bromine. The solution was passed through a sintered glass filter and was then evaporated to dryness. The final drying was achieved by placing the powder in a glass ampoule which was then pumped down to a hard vacuum for several hours. The ampoule was subsequently opened only in the dry atmosphere of a VAC Corporation "Drilab". Bromine trifluoride obtained from Matheson Company, East Rutherford N.J., U.S.A., was vacuum distilled and the more volatile impurities were rejected. Fluorine was used as supplied by the Matheson Co.

Apparatus. Fluorine and bromine trifluoride were used in systems similar to those previously described (24). A nickel or Monel container was used in the synthesis of each tetrafluoride as detailed below.

Iridium Tetrafluoride

Preparation. Although it was possible to prepare IrF_4 by direct fluorination of iridium sponge with a slight excess of fluorine (31 psi) at 310° the best synthetic approach proved to be

from the interaction of IrF_5 (in excess) with iridium metal sponge. Iridium pentafluoride was prepared by heating iridium sponge with the stoichiometrically required quantity of fluorine. A typical synthesis involved 2 to 3g metal contained in a Monel vessel of ~ 100 ml capacity, the pressure of F_2 gas being ~ 2 to 3 atmospheres. The base of the vessel (25) was heated to 300° (10 hrs) and the lid (which was provided with a Teflon gasket) was kept cold with a stream of cold air. The pentafluoride was removed in the "Drilab", as a yellow crystalline solid, from the lid and upper walls of the reactor.

In a typical iridium tetrafluoride synthesis, sponge iridium (~ 0.1 g) was heated with a large excess of the pentafluoride (~ 1 g) in a small nickel vessel. This vessel was made by welding a cap to a 3 in. length of $1/2$ in. diam. nickel tubing. The tube was provided with a Swagelock stopper, the fitting and gaskets being of Monel metal. The materials were loaded, in a small nickel bucket into the vessel in the dry nitrogen atmosphere (1 atmos.) of the "Drilab" and the vessel was sealed before its removal. The entire vessel was immersed in a sand bath and the upper region was maintained at a slightly higher temperature (400°) than the base (350°). The vessel was maintained at this temperature for ~ 12 hours and was then allowed to cool slowly to 180° at which temperature it was held for 10 hours. This last step was to facilitate recrystallization of IrF_4 from liquid iridium pentafluoride. The excess IrF_5 was removed from the IrF_4 by heating the opened small container within a large container (similar to that used in the IrF_5 synthesis) under vacuum at 260° .

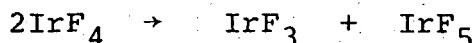
On occasions traces of Ir metal remained with the IrF_4 (as revealed by X-ray powder photography and the magnetic behaviour). It was then necessary to mix the material with IrF_5 and repeat the above procedure.

The solid was light brown and hydrolysed slowly in moist air to yield a violet product. Analysis by pyrohydrolysis (26) for F followed by reduction in hydrogen for Ir, yielded F, 27.8 ; Ir, 72.4 %. IrF_4 requires F, 28.2 ; Ir, 71.8 %. X-Ray Powder Data

for IrF_4 are given in Table 1. They establish the isomorphism of IrF_4 with PtF_4 (which in the original paper (21) is described in terms of a special body-centred monoclinic cell ($a = c$) which is truly face-centred orthorhombic). The observed reflexions obey the conditions : $h k l : h + k , k + l , (l + h) = 2n ;$
 $0 k l : k + l = 4n , (k, l = 2n) ; h 0 l : l + h = 4n (l, h = 2n) ;$
 $h k 0 : (h, k = 2n) ; 0 k 0 : (k = 4n) ; 0 0 l (l = 4n)$ and indicate the space group $Fdd2$ ($N^\circ. 43$ in the International Tables for X-Ray Crystallography) (27).

Magnetic Susceptibility Data for IrF_4 were obtained from a sample enclosed in a Kel F capsule, using a Princeton Applied Research Corp. vibrating-sample magnetometer. Measurements were made in the temperature range 4.2 to 300°K with applied magnetic fields up to 12.5 kOe. The variation of the magnetization of IrF_4 with the applied magnetic field was found to be linear. Figure 1 shows the dependence of the inverse of the susceptibility of IrF_4 upon the temperature and Table 2 gives the numerical data. From 100 to 300°K there is a Curie-Weiss relationship with a Weiss temperature of -60°K but below 100°K there is a marked departure from this dependence.

Thermal Stability of IrF_4 . The tetrafluoride is stable to 400° in a dynamic vacuum but above this temperature disproportionates :



A sample contained in a nickel boat and sealed in a quartz tube, quickly and quantitatively yielded IrF_5 and IrF_3 , when the sample-containing end of the tube was inserted in a furnace at 500°.

Rhodium Tetrafluoride.

Preparation. The synthetic procedure for RhF_4 is similar to that given for IrF_4 but the lower stability of RhF_4 with respect to disproportionation requires that the temperature not exceed 290°. Fluorination of rhodium trifluoride (12), at 250° for several days, with a slight excess of elemental fluorine in a Teflon gasketed Monel reactor similar to that employed in the IrF_5 synthesis yielded a sandy-brown solid. Analysis by pyrohydrolysis for F, followed by hydrogen reduction for Rh, yielded F, 43.7 ; Rh, 56.0% ; RhF_4 requires F, 42.5 ; Rh, 57.5 %.

Our material in no way resembles the RhF_4 described by Sharpe (17). Following Sharpe's procedure we obtained material similar to that described by him. It gave an X-Ray powder pattern which indexed on the basis of a face-centred cubic cell, $a = 10.31 \text{ \AA}$, $V = 1097 \text{ \AA}^3$, but satisfactory analyses for the stoichiometry RhF_4 or for any other binary fluoride composition were never obtained. We believe that this material obtained from bromine trifluoride is not RhF_4 .

The tetrafluoride as prepared by our procedure hydrolyses rapidly in moist air and liberates ozone smelling gases in the process. The solid was found to be paramagnetic but low temperature studies have not yet been carried out.

X-Ray Powder Data for RhF_4 given in Table 3 indicate that the compound is isomorphous and structurally related to IrF_4 , PdF_4 and PtF_4 . As for IrF_4 , the systematic absences indicate space group Fdd2 .

Palladium Tetrafluoride.

Preparation. Since a pentafluoride of Pd is so far unknown the synthesis of PdF_4 requires the fluorination of one of the lower fluorides. Although it is possible to oxidize " PdF_3 " with gaseous fluorine the process is slow and becomes increasingly more difficult as the "trifluoride" becomes more crystalline. The preparation is carried out in a bomb similar to that described elsewhere (25) for the synthesis of RhF_5 . Palladium (II) hexafluoropalladate (IV), Pd_2F_6 , may be conveniently prepared by Sharpe's procedure (17). This interaction of PdBr_2 with bromine trifluoride yields a material of composition $\text{BrF}_3 \cdot \text{PdF}_3$ the constitution of which is presently unknown. It is of importance to the effectiveness of the PdF_4 synthesis that this complex be decomposed at the lowest possible temperature, under vacuum. Decomposition within a quartz bulb connected to a line of Pyrex traps provides for following the loss of BrF_3 from the complex, visually. Decomposition can be effected at temperatures slightly in excess of 210° . The resulting PdPdF_6 is poorly crystalline and suitable for the moderate pressure (~ 7 atmos.) fluorination, at 300° , to yield PdF_4 . It is best to re-charge the bomb with fluorine at least

once, as fluorine is consumed. The oxidation to PdF_4 is slow and serious contamination with Pd_2F_6 may only be avoided by fluorination over a period of several days. (It should be noted that fluorination (13) of PdSnF_6 , which may be prepared from SnBr_2 and PdBr_2 in BrF_3 , yields an equimolar mixture of SnF_4 and PdF_4 which is not contaminated by PdPdF_6 and this mixture is diamagnetic).

PdF_4 is a pink solid. It is a powerful oxidizer and is rapidly hydrolysed by moisture in the air. Analysis by water-vapour hydrolysis, for F, followed by hydrogen reduction, for Pd, yielded : F, 40.7 ; Pd, 58.5 % . PdF_4 requires : F, 41.7 ; Pd 58.3 %.

X-Ray Powder Data for PdF_4 are given in Table 1. They indicate isomorphism with RhF_4 , IrF_4 and PtF_4 , and the systematic absences again indicate space group $\text{Fdd}2$.

DISCUSSION

The demonstrated existence of IrF_4 , RhF_4 and PdF_4 as true +4 oxidation state metal fluorides brings the oxidation states known for the binary fluorides of the platinum metals to those indicated in Table 4. It is of interest that the ready disproportionation of RhF_4 and IrF_4 indicates a preference (as in the Pd(II)Pd(IV)F_6 case and the disproportionation (21) of PtF_5 to PtF_6 and PtF_4) for even numbered d electron configurations (Rh(III) and Ir(III) being low spin d^6 and Rh(V) and Ir(V) low spin d^4). The observed magnetic properties of IrF_4 clearly demonstrate the +4 oxidation state (low spin d^5) the magnetic susceptibility being akin to that previously reported (28) for the isoelectronic PtF_6^- ion. The nature of the temperature dependence of the magnetic susceptibility is also in harmony with the proposed structure, as is discussed below.

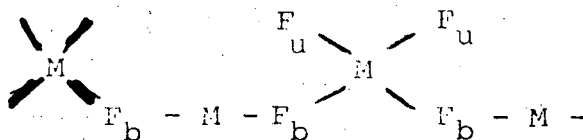
The most immediately interesting aspect of the new tetrafluorides is the structural one. The X-ray powder data show that IrF_4 , RhF_4 , PdF_4 and PtF_4 all have the same space group and are probably isostructural. Bartlett and Lohmann had noted (21) the similarity of the PtF_4 cell to that of UCl_4 (23) and Rao and Bartlett had conjectured earlier (22) on all four tetrafluorides possessing this structure. More recently we have realized that a structure, other than that of UCl_4 , which has the appealing feature of preserving the habitual "octahedral" coordination of the metal atoms, is also possible. We have already briefly described (29) this structure

for the IrF_4 case. The essence of the structural model is illustrated in figure 2.

The unit cell volume is in all cases close to 500 \AA^3 which on the basis of Zachariasen's criterion (30) that the cell volume of a fluoride structure is primarily determined by the number of fluorine atoms (of effective volume $\sim 16 \text{ \AA}^3$ in IrF_3 (12) and RhF_5 (19)) indicates 8 formula units per unit cell. Certainly the observed line intensities are consistent with eight metal atoms in the special positions $0, 0, 0$; $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; $\pm(\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$ and $0, \frac{1}{2}, \frac{1}{2}$). Thus each metal atom (as in the UCl_4 structure) is surrounded by a flattened tetrahedral set of metal atoms at a distance of $(\sqrt{a_o^2 + b_o^2 + c_o^2} / 4) \text{ \AA}$. The ideal values of important distances and angles are given in Table 5. Calculations based on this structure (for IrF_4) yield much superior agreement with the observed line intensities (with a conventional R value of $\sim 10\%$) than do refinements based on the UCl_4 structure which yielded a best R value $\sim 17\%$ which is indeed slightly inferior to that obtained from a calculation which omitted the F atoms entirely ($R \sim 16.5\%$).

The metal atom placement, just described, is generated naturally in our structural model by the particular linkage of octahedra by corner sharing. Of the six F ligands, octahedrally coordinating each metal atom, four are shared (one to one) with four other octahedra. Thus the stoichiometric requirements (MF_4) are fulfilled, in that each metal atom is coordinated uniquely to two F ligands and has (on the average) a half share in four others. The unique F ligands in this structure are in cis relationship to one another, in contrast with the NbF_4 structure (31) where the the unique F ligands are trans. All of the shared F ligands in the IrF_4 -type structure are equivalent and are in the 16 fold general positions of the space group.

In the ideal structure the octahedra are linked by corner sharing such that each shared F ligand (F_b) makes an angle M-F-M of 135° . A segment of the bridging system in one plane can be represented thus



A similar bridging system occurs in the plane at right angles. Thus each M atom is linked to two M atoms above it and, in a plane at right angles to the first, to two M atoms below it.

This structure is related to rutile and the F centred orthorhombic unit cell of MF_4 can be derived from a $2 \times 2 \times 2$ stack of rutile cells by omitting, in an ordered way, half of the metal atoms. There are, of course, important differences from the rutile structure. These differences have particular relevance to the magnetic behaviour.

In the simple magnetic rutile difluorides, magnetic coupling within the parallel sets of edge-shared chains of octahedra, which run parallel to the c axis of the body-centred tetragonal cell, is much less important than coupling between those chains (32). (This is generally true when only one transition element is involved in the structure). The antiferromagnetic coupling observed in NiF_2 and certain other transition metal difluorides is consistent with dominance of the inter-chain coupling over intra-chain coupling. Moreover in the $MnAlF_5$ structure (34), where rutile-like edge-shared octahedral chains (containing the Mn(II) atoms) also occur, but where sharing of F ligands between the chains does not occur, there is no evidence of magnetic coupling down to liquid helium temperature. In IrF_4 the edge-shared chains no longer exist, but the F ligand sharing, between the broken chains, allows for coupling. It may well be that the large value of -60° found for the Weiss temperature and the deviation of the $\frac{1}{\chi_g}$ versus $T^\circ K$ plot (figure 1) from linearity, below $100^\circ K$, is due to antiferromagnetic coupling by the agency of the shared F ligands.

Our efforts are now directed towards the growing of single crystals of RhF_4 and IrF_4 to determine, with precision, their structural parameters and to define the magnetic behaviour more certainly .

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REFERENCES

1. O. RUFF and F.W. TSCHIRCH, Ber. 46, 929 (1913).
2. B. WEINSTOCK and J.G. MALM, J. Amer. Chem. Soc., 80, 4466 (1958).
3. O. RUFF and J. FISCHER, Z. anorg. Chem., 179, 161 (1929).
4. G.J. WESTLAND and P.L. ROBINSON, J. Chem. Soc., 1956, 4481.
5. N. BARTLETT and P.R. RAO, Chem. Communications, 1965, 252.
6. B. WEINSTOCK, H.H. CLAASSEN and J.G. MALM, J. Amer. Chem. Soc., 79, 5832 (1957) and B. WEINSTOCK, J.G. MALM and WEAVER, 83, 4310 (1961).
7. H.H. CLAASSEN, H. SELIG, J.G. MALM, C. CHERNICK and B. WEINSTOCK, J. Amer. Chem. Soc., 83, 2390 (1961).
8. C. CHERNICK, H.H. CLAASSEN and B. WEINSTOCK, J. Amer. Chem. Soc., 83, 3165 (1961).
9. N. BARTLETT and D.H. LOHMANN, Proc. Chem. Soc., 1960, 14., and ref. 20.
10. G.B. HARGREAVES and R.D. PEACOCK, J. Chem. Soc., 1960, 2618.
11. J.H. HOLLOWAY, P.R. RAO and N. BARTLETT, Chem. Commun. 1965, 306.
12. M.A. HEPWORTH, K.H. JACK, R.D. PEACOCK and G.J. WESTLAND, Acta Cryst., 10, 63 (1957).
13. N. BARTLETT and P.R. RAO, Proc. Chem. Soc., 1964, 393.
14. O. RUFF and E. ASCHER, Z. anorg. Chem., 183, 193 (1929).
15. N. BARTLETT and M.A. HEPWORTH, Chemistry and Industry, 1956, 1425.
16. N. BARTLETT and R. MAITLAND, Acta Cryst., 11, 747 (1958).
17. A.G. SHARPE, J. Chem. Soc., 1950, 3444.
18. B. WEINSTOCK and G.L. GOODMAN, Advances in Chem. Physics, 9, 169 (1965).
19. S.J. MITCHELL and J.H. HOLLOWAY, J. Chem. Soc., A, 1971, 2789.
20. B.K. MORRELL, A. ZALKIN, A. TRESSAUD and N. BARTLETT, Inorg. Chem., 12, 2640 (1973).
21. N. BARTLETT and D.H. LOHMANN, J. Chem. Soc., 1964, 619.
22. Preliminary papers on IrF_4 , RhF_4 , PdF_4 and their structural relationship with PtF_4 have been presented at The Second European Symposium on Fluorine Chemistry, Abstracts Section 1 p. 4, Göttingen, 28-31 August 1968 and The 154 Annual General Meeting of The American Chemical Society, 1967, ABSTRACTS K15.
23. K. MUCKER, G.S. SMITH, Q. JOHNSON and R.E. ELSON, Acta Cryst., 25B, 2362 (1969) and R.C.L. MOONEY, *ibid*, 2, 189., (1949).
24. N. BARTLETT in "Preparative Inorganic Reactions", Vol. 2, W.L. JOLLY, Ed., Interscience, New York, London, p. 301 (1965).
25. N. BARTLETT, P.R. RAO and M. AKHTAR, "The Preparation and Some Properties of Rhodium, Iridium and Platinum Pentafluorides and ARhVF_6 Complexes (A = NO, Cs). to be published.
26. Welsh and Parker, U.K.A.E., unclassified report WSL-R-36, 1959.

27. "International Tables for X-Ray Crystallography", vol. I, Kynoch Press, Birmingham, England, 1952.
28. N. BARTLETT and S.P. BEATON, Chem. Comms., 1966, 28.
29. N. BARTLETT and A. TRESSAUD, C. R. Acad. Sc., submitted for publication.
30. W.H. ZACHARIASEN, J. Amer. Chem. Soc., 70, 2147 (1948).
31. F.M. GOETSEMA and R. DIDCHENKO, Inorg. Chem., 4, 182 (1965).
32. M. BUTLER, V. JACCARINO, N. KAPLAN and M.J. GUGGENHEIM, Phys. Rev., BI, 3058 (1970).
33. A. TRESSAUD, J.M. PARENTEAU, J.M. DANCE, J. PORTIER and P. HAGENMULLER, Mat. Res. Bull., 8, 565 (1973).

TABLE 1

X-Ray Powder Data for IrF₄ and PdF₄
 (orthorhombic unit cells at 23±2°; CuKα radiation,
 Ni filter : IrF₄ a ,9.64(1) b ,9.25(1) c ,5.67(1) (Å)
 PdF₄ a ,9.37(1) b ,9.24(1) c ,5.84(1) (Å)

hkl	IrF ₄			PdF ₄		
	1/d ² x 10 ⁴		I/I ₀ (phot.)	1/d ² x 10 ⁴		I/I ₀ (vis.)
	obs.	calc.		obs.	calc.	
111	539	535	100	523	524	vs
220	902	899	52	927	924	s
311	1400	1392	42	1453	{1436}	s
131	1474	1476	39		{1460}	
202	1681	1671	29	1642	{1634}	s
022		{1713}			{1646}	
400	1722	{1713}	48	1847	{1824}	mw
040	1871	1881	7		{1872}	
222	2143	2141	9	2112	2096	ms
420	2188	2192	vvw		{2292}	
240		{2309}		2309	{2328}	m
331	2338	{2332}	36	2387	2372	ms
113	3039	3022	20	2875	2868	ms
511	3114	3104	21	3277	3260	m
151	3341	3357	26	3349	3332	m
422	3428	3428	58		{3464}	
242	3543	3552		3501	{3500}	vvs
440	3586	3594	125	3709	3696	ms
313	3882	3877	17		{3780}	
133	3961	3961	19	3806	{3804}	ms
531	4047	4047	24		{4244}	
351	4189	4211	24	4239	{4292}	ms
620	4317	4323	20	4596	4572	m
260	4640	4640	14		4668	
333	4802	4816	14	4724	{4707}	m
004	4973	4973	14		{4688}	
602	5095	5117	38	5289	5276	m
062	5423	5455	15	5399	5384	m
622		{5586}		-	5744	-
513	5586	{5603}	10	5619	5568	ms
711	5662	5696	9.5	{6075}	6068	mw
153	5836	5827	8	-	5677	-
224		{5872}		5619	5612	ms
262	5872	{5881}	45	-	5840	
551		{5881}		{6075}	6068	mw
171	6094	6151	19.5	-	6140	
533	6483	6535	16	{6578}	6541	m
731	6567	6631	16	6956	6932	mw
353		{6686}			{6589}	
404	6664	{6697}	22	{6578}	{6515}	m
044	6830	6841	8		{6563}	m

TABLE 2

IrF₄ magnetic susceptibility temperature dependence

Temp. (°K)	$\chi \text{ gx}10^6$ (c.g.s.units)	Temp. (°K)	$\chi \text{ gx}10^6$ (c.g.s.units)
293	4.70	112	9.59 ₅
283	4.82	90	10.68
270	5.02 ₅	72	11.63
247.5	5.42	62	12.40 ₅
226	5.82 ₅	49	13.46
199	6.39	36	14.14 ₅
174	7.03	20	15.15
154	7.71 ₅	6	16.66 ₅
133.5	8.44		

TABLE 3

X-Ray Powder Data for RhF_4
 (Debye-Scherrer data, $CuK\alpha$ radiation from a
 graphite monochromator. Unit cell : orthorhombic
 $a, 9.71(2)$; $b, 9.05(2)$; $c, 5.63(1)$ (\AA) ; $V, 495$ (\AA^3),
 $Z = 8$, S.G. Fdd2)

hkl	calc. $1/d^2$	obs.	$I/I_0(\text{vis.})^*$
111	543	543	s
220	912	905	vw
311	1391	1415	w
131	1519	1519	m
202	1684	1678	m,b
400	1696		
022	1748	—	
040	1952	1950	vw
222	2172	2165	s,b
420	2184		
331	2367	2390	w
240	2376		
113	3063	3076	wm,b
511	3087		
422	3444	3470	vw
151	3471		
242	3636	3632	vs
440	3648		
313	3911	3861	vw
133	4039	4045	vw
531	4063		
620	4304	4329	vw
351	4319		
260	4816	4851	w
333	4887		
004	5040	5032	ms,b
602	5076		
711	5631	5731	vw,b
062	5652		
224	5945	—	
153	5991	—	
551	6015	6033	w,b
262	6076		
171	6399	6389	vw,b

* $vw < v < w < wm < m < ms < s < vs$; b = broad line

TABLE 4

Oxidation States of the Known Binary Fluorides
of the Platinum Metals.

Ru	Rh	Pd
6 ^a	6 ^h	
5 ^b	5 ⁱ	
4 ^c	4 ^j	4 ^j
3 ^d	3 ^d	—
		2 ^l
Os	Ir	Pt
7 ^e		
6 ^f	6 ^k	6 ^m
5 ^g	5 ^l	5 ⁿ
	4 ^j	4 ⁿ
	3 ^d	

a, ref.7; b, O. RUFF and E. VIDIC, Z. anorg. Chem., 143, 163 (1923).

c, J.H. HOLLOWAY and R.D. PEACOCK, J. Chem. Soc., 1963, 3892.

d, ref.12 ; e, O. GLEMSER, H.W. ROESKY, K-H.HELLBERG, and H.U. WERTHER, Chem. Ber., 99, 2652 (1966).

f, ref. 2 ; g, ref. 10 ; h, ref. 8 ; i, ref. 11 and 19 ;

j, present work ; k, ref. 4 ;

l, ref. 5 ; m, ref. 6 ; n, ref. 9 and 20.

TABLE 5

Comparison of Distances in IrF₄ - Type Fluorides

	IrF ₄	RhF ₄	PdF ₄	PtF ₄ [*]
Closest M-M distance (Å) †	3.63	3.60	3.60	3.63
Ideal M-F _{b_o} distance (Å) **	1.96	1.94	1.93	1.96

* Ref. 21

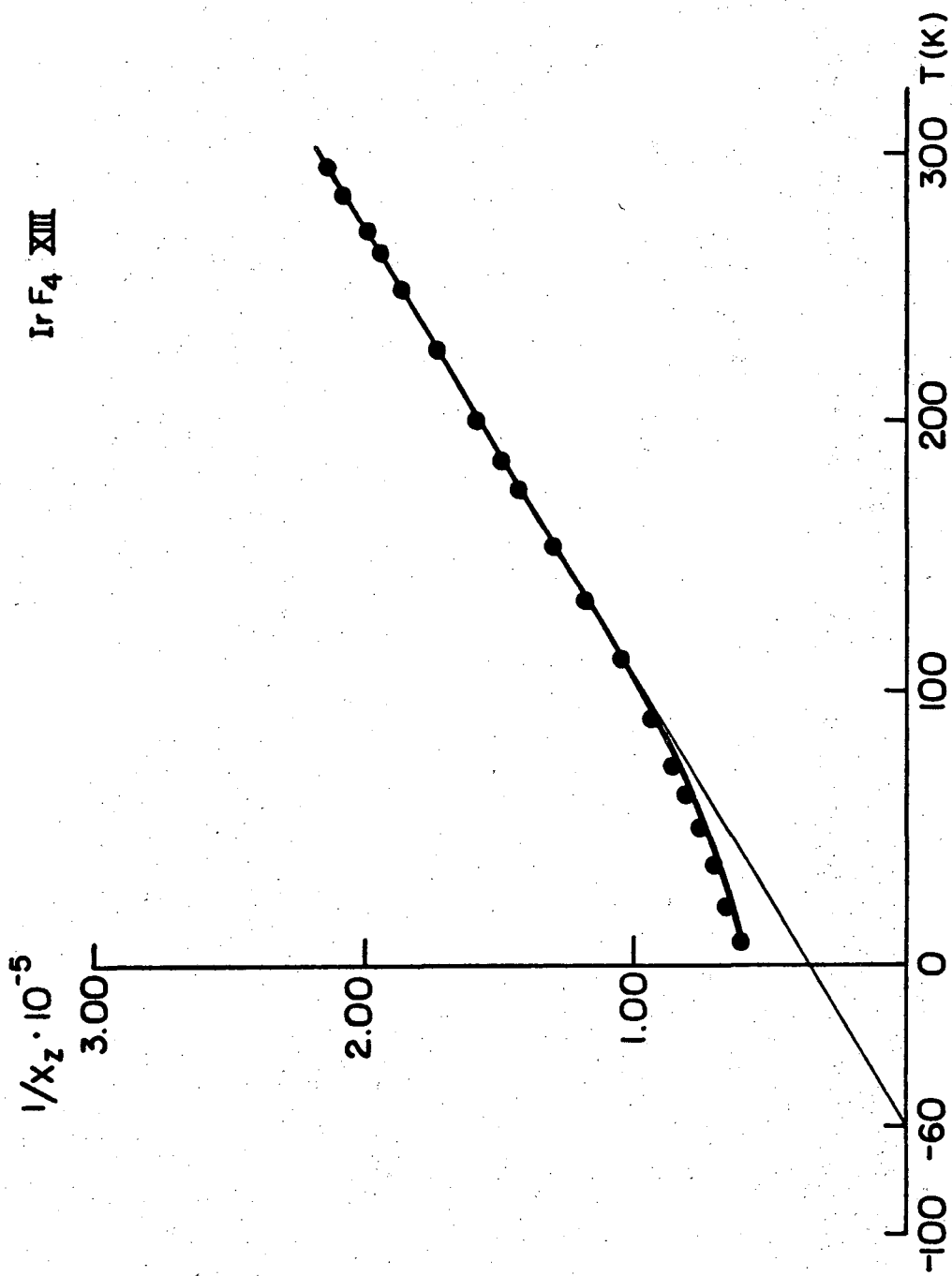
† The closest M-M distance is $\sqrt{a_o^2 + b_o^2 + c_o^2} / 4$

** If the octahedra are packed with ideal hexagonal close packing M-F_b-M = 135° (see ref. 20). If, furthermore, the bridging F ligands are equidistant from the two bridged metal atoms and have the coordinates x = y, z = 0 etc., then M-F = $\sqrt{a_o^2 + b_o^2} / 4 (1 + \cos 45)$. Other studies (see ref. 20) indicate that M-F_u will be less than M-F_b.

FIGURES CAPTIONS

Fig. 1 : Dependence of the inverse of the susceptibility of IrF_4 upon the temperature.

Fig. 2 : Projection of the IrF_4 type structure in the (001) plane showing the linkage of the MF_6 octahedra.



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Fig. 1

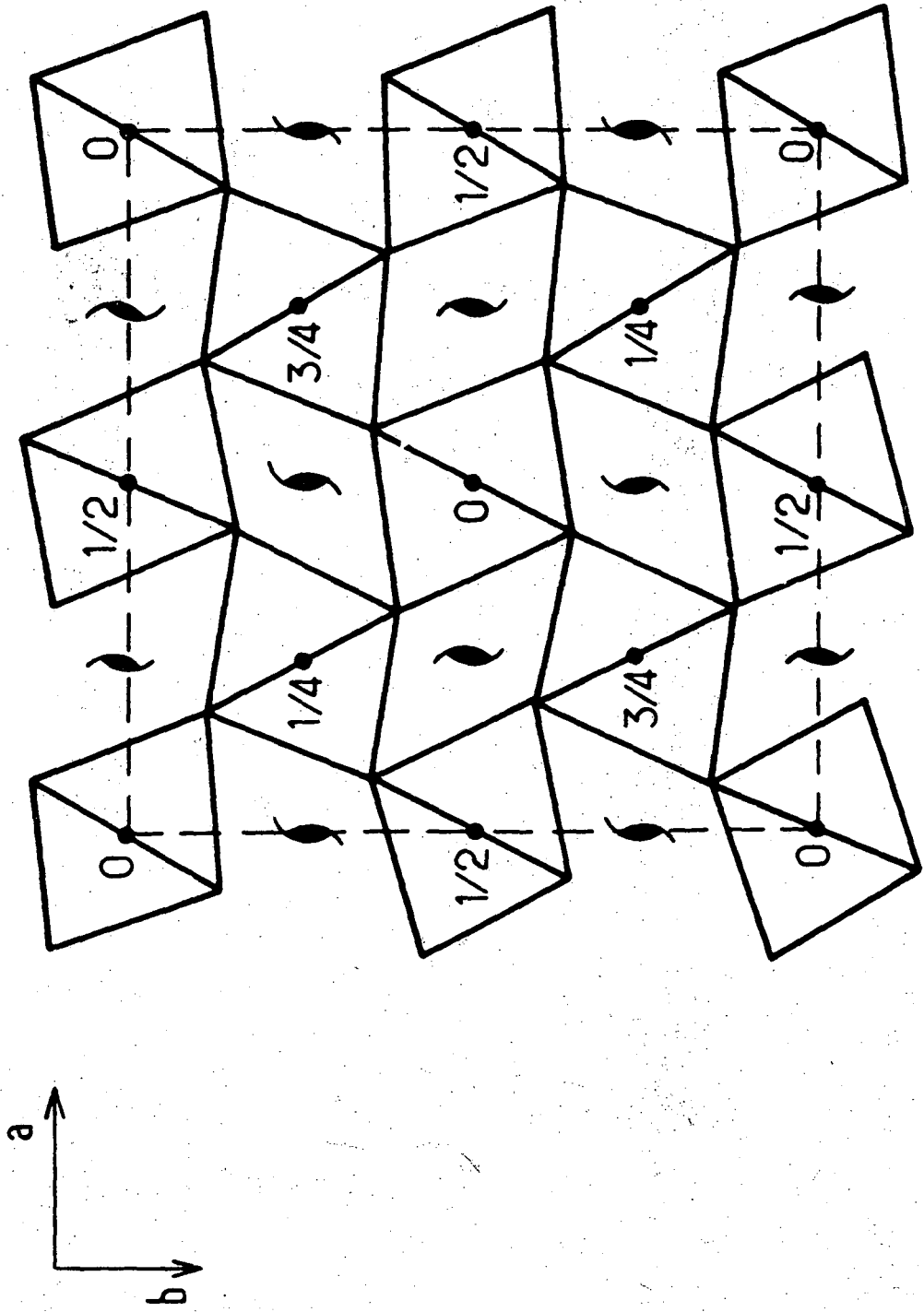


Fig. 2 XBL 744-5988

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