SOME PROPERTIES OF PLATINUM PENTAFLUORIDE

AND

SOME PROPERTIES OF GERMANIUM DIFLUORIDE

by

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in the Department

of

CHEMISTRY

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

December, 1965.
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Date __________________________
Platinum pentafluoride has been prepared, by a new preparative method, in a more stable, pure and crystalline form than the material already described. It has been shown, by x-ray powder photography, to be isomorphous with other noble metal pentafluorides and almost isodimensional with rhodium pentafluoride. A tetrameric structural unit like that observed in ruthenium pentafluoride is also assumed for platinum pentafluoride. Its magnetic properties have been shown to be representative of a third transition series $d^5$ ion in a distorted octahedral environment.

The nature of the bonding in germanium difluoride is discussed in the light of the crystal structure, which has been deduced from data obtained from single crystals prepared in this work. The products of interaction of chlorine or bromine with the difluoride are consistent with the structural findings. The $^{19}F$ n.m.r. spectra of the mixed chlorofluorides ($\text{GeFCI}_3$, $\text{GeF}_2\text{Cl}_2$, $\text{GeF}_3\text{Cl}$, $\text{GeF}_4$) and bromofluorides, indicate that intermolecular exchange between these compounds must be extremely slow, at least in the absence of a catalyst. It has been shown that germanium difluoride is so strong a reducing agent that it reduces iodine pentafluoride to iodine below room temperature. The powerful reducing properties of the difluoride were also illustrated by the reduction of platinum tetrafluoride to the metal at room temperature. Attempts to reduce tungsten hexafluoride at 300° led to the formation of $\text{Ge}_2\text{WF}_8$. In glass the germanium difluoride reacted with tungsten hexafluoride and the container to yield $\text{WO}_2\text{F}$. 
I would like to thank Professor Neil Bartlett for encouragement, guidance and valuable suggestions during this work. I am also grateful to Professor James Trotter for the determination of the crystal structure of germanium difluoride. Finally, I would like to thank Mr. P. T. Inglefield for recording the $^{19}\text{F}$ n.m.r. spectra of the mixed halides of germanium.
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SECTION 1

THE PREPARATION AND SOME PROPERTIES
OF PLATINUM PENTAFLUORIDE
CHAPTER 1

INTRODUCTION

Bartlett and Lohmann were the first to prepare platinum pentafluoride. They obtained material of empirical formula PtF$_5$ by the following methods:

1. By photolysis of platinum hexafluoride.
2. By fluorination of platinum compounds at temperatures higher than 350°.
3. By fluorination of platinum dichloride contained in a nickel boat in a silica apparatus at 350°.

Highest yields were obtained by the last method. In no case however did they prepare a stable pure sample of the pentafluoride. At no time did they obtain a sufficiently crystalline sample for X-ray photography, nor was a large enough sample of high purity material ever obtained for magnetic susceptibility measurements by the Gouy technique.

Thorough structural, magnetic and chemical characterization recently became desirable. Peacock and his coworkers recently described the crystal structures of the pentafluorides of niobium, tantalum, molybdenum and ruthenium. They gave preliminary structural data on the pentafluorides of technium, rhenium and osmium. Their results have shown that there are three structural types characterized in Table 1, as monoclinic I, orthorhombic and monoclinic II. The niobium, tantalum and molybdenum fluorides are the first type. The structural unit in this type is a tetrameric unit in which all of the metal atoms are in the same plane and at the corners of a square. Fluorine atoms situated in the mid-point of each edge of this square link


**TABLE I.**

**Known Pentafluorides of the Second and Third Transition Metals.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\text{NbF}_5$</th>
<th>$\text{MoF}_5$</th>
<th>$\text{TcF}_5$</th>
<th>$\text{RuF}_5$</th>
<th>$\text{RhF}_5$</th>
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<tbody>
<tr>
<td>Colour</td>
<td>white</td>
<td>yellow</td>
<td>white</td>
<td>green</td>
<td>dark red</td>
</tr>
<tr>
<td>m.p. (°C)</td>
<td>80</td>
<td>67</td>
<td>50</td>
<td>86.5</td>
<td>95.5</td>
</tr>
<tr>
<td>Crystal Class</td>
<td>monoclinic(I)</td>
<td>monoclinic(I)</td>
<td>orthorhombic</td>
<td>monoclinic(II)</td>
<td>monoclinic(II)</td>
</tr>
<tr>
<td>$\mathbf{a};\mathbf{b};\mathbf{c}; \ (\mathbf{\AA})$</td>
<td>9.62;14.43;5.12</td>
<td>9.61;14.22;5.16</td>
<td>5.8;7.6;16.7</td>
<td>12.47;10.01;5.42</td>
<td>12.38;9.85;5.48</td>
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<tr>
<td>$\beta \ (°)$</td>
<td>96.1</td>
<td>94.3</td>
<td>99.82</td>
<td>99.2</td>
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<table>
<thead>
<tr>
<th>Compound</th>
<th>$\text{TaF}_5$</th>
<th>$\text{ReF}_5$</th>
<th>$\text{OsF}_5$</th>
<th>$\text{IrF}_5$</th>
<th>$\text{PtF}_5$*</th>
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</thead>
<tbody>
<tr>
<td>Colour</td>
<td>white</td>
<td>yellow</td>
<td>grey green</td>
<td>yellow</td>
<td>dark red</td>
</tr>
<tr>
<td>m.p. (°C)</td>
<td>95</td>
<td>48</td>
<td>70</td>
<td>105</td>
<td>98.5</td>
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<td>Crystal Class</td>
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<td>orthorhombic</td>
<td>monoclinic(II)</td>
<td>monoclinic(II)</td>
<td>monoclinic(II)</td>
</tr>
<tr>
<td>$\mathbf{a};\mathbf{b};\mathbf{c}; \ (\mathbf{\AA})$</td>
<td>9.64;14.45;5.12</td>
<td>12.5;10.0;5.4</td>
<td>12.37;9.84;5.47</td>
<td>99.8</td>
<td>99</td>
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<tr>
<td>$\beta \ (°)$</td>
<td>96.3</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

* Present work.
the metal atoms by linear fluorine bridges. Each metal atom is coordinated by a distorted octahedron of fluorine atoms. Ruthenium pentafluoride, on the other hand, characterizes the monoclinic II structure. The detailed structure described by Holloway, Peacock and Small, again reveals a tetrameric structural unit but in this case although each metal atom is again surrounded by a distorted octahedron of fluorine ligands, the fluorine bridges Ru-F-Ru are bent. Details of the third structure type have not been given and it is not even certain that the structural unit is a tetramer.

Edwards, in his paper on the NbF$_5$ and TaF$_5$ structures remarked on the apparent dependence of the structure on the element rather than valency state. The change in packing from the cubic close packing of fluorine atoms in Nb, Ta and MoF$_5$ to the hexagonal close packing evident in RuF$_5$ and OsF$_5$ is similar to the situation found in the trifluoride structures. In Nb, Ta and MoF$_5$ the ligand packing is again cubic whereas in RuF$_3$ it is hexagonal. It remained to determine how general this correlation was. Since RuF$_3$ is structurally related to RhF$_3$ and PdF$_3$ [Pd$^{2+}$(PdF$_6$)$^-$] the pentafluorides of rhodium, iridium, palladium and platinum appeared likely, on this basis, to be structurally akin to RuF$_5$ and OsF$_5$. With the preparation and structural characterization in these laboratories of RhF$_5$ and IrF$_5$ as monoclinic II, the probability of PtF$_5$ being isomorphous with RuF$_5$ appeared more certain.

Structural and magnetic information on the pentafluoride of platinum was also of value to the elucidation of the nature of the Xe(PtF$_6$)$_x$ adducts. It was possible that the platinum rich adducts, i.e. those approaching Xe(PtF$_6$)$_2$ were mixtures of XePtF$_6$ and PtF$_5$. Such adducts usually gave weak x-ray powder patterns. They were possibly patterns of the pentafluoride. The pure pentafluoride was in any event an essential precursor for the
synthesis of $\text{Xe}(\text{PtF}_6)_2$ from:

$$\text{XeF}_2 + 2\text{PtF}_5 \longrightarrow \text{Xe}(\text{PtF}_6)_2$$

The characterization of $\text{Xe}(\text{PtF}_6)_2$ is necessary to help in the characterization of $\text{XePtF}_6$.

The successful preparation of rhodium pentafluoride$^6$ and palladium tetrafluoride$^9$ by the medium temperature fluorination of the lower fluorides in monel reactors, employing pressures of fluorine of ten atmospheres or greater, encouraged the use of this procedure in the preparation of platinum pentafluoride.

It was also of interest to compare the magnetic properties of Pt(V) in $\text{PtF}_5$ with those of the $[\text{PtF}_6]^{-}$ ion, since the magnetic susceptibility of this ion in the salt NOPtF$_6$ had been determined recently in these laboratories by S. Beaton.
CHAPTER II
EXPERIMENTAL AND RESULTS

(i) Fluorine Handling

Fluorine is oxidatively the most reactive of all the elements. Indeed its great chemical reactivity has been the primary reason for the rather late development of the chemistry of the element. The last twenty years have seen marked improvements in the technology of fluorine generation and handling and with proper precautions fluorine can now be used in the laboratory with safety and assurance. The handling techniques will be briefly described.

A general purpose fluorine supply which may be directly connected to any form of apparatus is shown in Fig. 1. This system is assembled largely from 30,000 p.s.i. monel metal Autoclave Engineering valves, crosses, tees and seamless tubing. Such an assembly may be easily taken down and cleaned and parts can be readily replaced as needed. The low pressure part of the system incorporates flexible 1/4 in. copper tubing, and valves on the low pressure part of the assembly are Hoke A431. An important part of the system is the soda lime tower which is used to remove fluorine gas from the vacuum lines, and the reaction vessels to the pumping system. Another tower filled with sodium fluoride pellets served to remove the traces of hydrogen fluoride present in fluorine.

Vacuum of better than $10^{-6}$ mm of Hg is desirable for such a system although in practice it is seldom achieved. The pumping system used in this work was a Welch DUOSEAL mechanical pump coupled to a metal oil-diffusion pump. The vacuum was checked by a combination of a thermocouple-
MV, 30,000 p.s.i. monel valve; MX, Monel cross; MT, Monel tee; G1 Monel Bourdon gauge, 400 lb.p.s.i.; G2, Monel Bourdon gauge, 1000 mm. Hg; C, 30,000 p.s.i. seamless monel tubing 3/8 in. o.d., 1/8 in. i.d., silver soldered to 3/8 in.o.d. copper tubing; F, 3/8 in. flare fitting; K, 3/8 in. 30,000 p.s.i. tubing, silver soldered to 1/4 in. monel tubing; H1 and H2 Hoke A431 and A432 valves, respectively; B, Flexible copper bellows; SL, Soda lime tower; BV, 3/8 in. bore teflon-seated ball valve; J, Connection for vacuum pumps; HP, High-pressure fluorine outlet; LP, Low-pressure fluorine outlet via "Swagelok" compression fittings; S, "Swagelok" outlet for apparatus requiring fluorine diluted with nitrogen.

Figure 1. A General Purpose Fluorine Line.
ionization control B710 gauge supplied by NRC Equipment Corporation, Newton, Massachusetts, U.S.A. Whitey valves and Hoke A431 valves were used in the vacuum lines, on the various monel pots used for volatile fluoride storage, and on the monel reactors using low pressure fluorine. For high pressures of fluorine Hoke A431 valves were used, never Whitey valves.

(a) Fluoride preparation and handling in glass or quartz apparatus.

For the preparation of fluorine compounds in glass or quartz apparatus, strictly anhydrous conditions are necessary. Even a trace of moisture is capable of initiating the etching cycle:

$$MF + H_2O \rightarrow MOH + HF$$

$$4HF + SiO_2 \rightarrow 2H_2O + SiF_4$$

Hence all the glass apparatus used was baked under vacuum three or four times with a non-luminous flame. Any monel apparatus attached to the glassware was pumped out for long periods, care being taken that such apparatus was leak tight.

(b) Monel Apparatus.

In routine preparations monel or nickel containers and reactors proved to be invaluable. In this work a particularly important vessel was a wide mouthed monel reactor. This vessel of ~100 ml capacity was a 4 in. x 2 in. diam. cylinder of 1/8 in. wall thickness, capped at one end, and provided with a 1/4 in. thick flange at the mouth. The 1/4 in. thick lid, which was provided with a 1/4 in. monel tube outlet fitted with a Hoke A431 valve, was sealed to the vessel by an aluminum gasket which was
compressed by tightening the six flange bolts. A chamber was formed above the lid by silver soldering a dome to it. This chamber was provided with inlet and exit tubes and served, with the passage of a fast stream of cold compressed air, as an effective condenser in certain preparations. The arrangement is indicated in the diagram of the vessel given in Fig. II.

In all of the work described, pieces of monel apparatus were generally joined together with the aid of Swagelock compression fittings and 1/4 in. monel or nickel tubing. Swagelock straight tee and cross unions were also employed. All monel apparatus was fluorinated prior to use.

(ii) Preparation of Platinum Pentafluoride

The compound was prepared by the high pressure fluorination of platinum tetrafluoride in an aluminum gasketed monel reactor like that described in Fig. II. The tetrafluoride was obtained as a side product in the preparation of PtF₆ by the method described by Weinstock, Malm and Weaver.¹⁰

Platinum tetrafluoride (3g) was taken in a 100 ml capacity monel can, provided with a monel lid sealed by an aluminum gasket. The can was loaded in a dry box and the lid bolted in place. Care was taken prior to fluorination to be sure that the vessel was leak tight. Fluorine at ~130 p.s.i. at room temperature was used and the base of the can was heated at 350 - 400° for 48 hours. The lid was kept cooled by a stream of compressed air. The pot was cooled at room temperature and the fluorine was disposed of by passing it through the soda lime scrubber.

Platinum pentafluoride was obtained as a dark red solid on the
Figure II. High Pressure Monel Reactor.
lid and the upper regions of the can. Analysis was by pyrohydrolysis.

Found: Pt, 66.1; F, 32.1%

PtF$_5$ requires Pt, 67.3; F, 32.7%.

(iii) General Properties

The compound melted sharply at 98.5°. As observed previously by Bartlett and Lohmann$^1$ the compound disproportionated as $2\text{PtF}_5 \rightarrow \text{PtF}_6 + \text{PtF}_4$ on heating, but this was only evident above the melting point, whereas Bartlett and Lohmann had observed disproportionation at temperatures as low as 80°.

The compound may be sublimed under vacuum, however, in the temperature range 50 - 70°. Unfortunately it did not prove possible to obtain single crystals for x-ray structural investigation either in the synthesis or by vacuum sublimation.

The pentafluoride reacted exothermally with water, some of the platinum being precipitated as the hydrated platinum dioxide, and the remainder being reduced to hexafluoroplatinic (IV) acid which remained in solution.

(iv) Analysis by Pyrohydrolysis

The apparatus used for analysis of platinum pentafluoride was the same as used by Lohmann,$^{11}$ shown in Fig. III.

It consisted of a silica tube housed in an electrically heated furnace, and having a 35/20 B.S. silica socket at one end, and a pyrex glass steam condenser joined by a B 10 ground silica cone at the other end. The carrier gases passed through a steam generator, having a copper
FIGURE 111 Apparatus used for pyrohydrolysis
steam trap, which could be joined leak tight to the 35/20 B.S. silica socket.

A small platinum boat was weighed in a small horizontal weighing bottle after reduction in hydrogen at \( \sim 300^\circ \). A known weight of the sample (\( \sim 0.2\)g) was taken into the platinum boat in a dry box, and the boat quickly transferred into the pyrohydrolysis tube. Nitrogen carrying some moisture from the steam generator was passed over the sample for five minutes, after that the temperature of water in the steam generator was raised to boiling, and that of the furnace to \( \sim 300^\circ \)C. Thus steam passed over the sample at high temperature. The distillate was collected by bubbling through 50 mls of very dilute sodium hydroxide solution. Fluoride ion concentration was determined in the distillate as lead chlorofluoride.\(^{12}\)

For platinum estimation, steam trap and steam generator were replaced by a two way silica tubing connected to nitrogen and hydrogen cylinders. The apparatus was flushed thoroughly by nitrogen, then hydrogen was passed through at \( \sim 300^\circ \), the emergent gas being burnt, until the platinum residue in the platinum boat weighed to a constant weight.

The flow of nitrogen and hydrogen passing through the pyrohydrolysis tube was controlled by passing the gases through bubblers containing concentrated sulphuric acid.

\((v)\) Magnetic Susceptibility Measurement

Magnetic susceptibility measurements were made with a Gouy balance, a detailed description of which has been given by Clark and O'Brian,\(^{13}\) over the temperature range 77 - 304\(^\circ\)K.

A finely powdered sample of the pentafluoride was packed into an 11.2 cm x 3 mm. pyrex tube, care being taken to ensure a uniformity of
packing by briskly tapping the sample between successive additions of the fine powder. All manipulations were conducted in the DRI-LAB - HE 43-2 supplied by Vacuum Atmospheres Corporation, Los Angeles, California. The tube was sealed by drawing under vacuum. The length of the sample was 6.2 cm and its weight 0.8878 g. The loaded tube was suspended from the balance pan on a thin brass chain in a thermostatically controlled Dewar flask, the temperature of which was controlled by the current passing through an electrically heated coil.

Mercury cobalt tetrathiocyanate, HgCo(CNS)$_4$ recommended by Figgis and Nyholm$^{14}$ was used as the paramagnetic standard. The weighings were corrected for the diamagnetic contributions of the glass sample tube, which were assessed for the full temperature range. The molar susceptibility, $\chi_M$, was obtained from the relationship:

$$\chi_M = \chi_g \times \frac{\Delta W + \delta W}{W} \times \frac{W}{\Delta W + \delta W} \times \frac{M.W}{M.W}$$

where:

$\chi_g$ = gram susceptibility of HgCo(CNS)$_4$, $16.44 \times 10^{-6}$ c.g.s. units at 20°.$^{14}$

$W$ and $W$ = weights of HgCo(CNS)$_4$ and PtF$_5$ respectively.

$\Delta W$ and $\Delta W$ = changes in the weights of HgCo(CNS)$_4$ and PtF$_5$.

$\delta W$ and $\delta W$ = Diamagnetic corrections for the glass containers, at each temperature, for HgCo(CNS)$_4$ and PtF$_5$.

$M.W$ = Molecular weight of PtF$_5$.

The molar susceptibility, $\chi_M$, was corrected for the diamagnetic susceptibility of fluorine ligands, to give the gram atomic susceptibility $\chi_A$ as $\chi_A = \chi_M + 55.$.$^{15}$ $\mu_{\text{eff}}$ was calculated as $\mu_{\text{eff}} = 2.83\sqrt{\chi_A} \times T$, where $T$ is the temperature in °K.

A least squares refinement of the data showed a close obedience
to Curie-Weiss behaviour, with a value of 28° for the Weiss Constant.
A program IBFTC APPROX (Appendix I) was run in the IBM 7040 computer
for this purpose.

The values for the molar susceptibilities and magnetic moment
are given in Table II. The purity of the material was checked by analysis
after the magnetic measurements. A powder photograph of a sample taken
before packing the material into the glass tube for magnetic measurements
showed only the pattern characteristic of a pentafluoride. The melting
point of the material used for the susceptibility measurements was 98.5°.
TABLE II

Magnetic Susceptibility of Platinum Pentafluoride.

<table>
<thead>
<tr>
<th>Temp. °K</th>
<th>$\chi_A^{\text{obs}} \times 10^{-6}$ c.g.s. units.</th>
<th>$\chi_A^{\text{refined}} \times 10^{-6}$ c.g.s. units.</th>
<th>$\chi_A^{\text{obs}} - \chi_A^{\text{refined}} \times 10^{-6}$ c.g.s. units.</th>
<th>$\mu = 2.83 \sqrt{\chi_A} \times (T + \theta)$</th>
<th>$\mu = 2.83 \sqrt{\chi_A} \times T$</th>
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<tr>
<td>77.2</td>
<td>5005</td>
<td>4856</td>
<td>148</td>
<td>1.75</td>
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<td>88.4</td>
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$\chi_A^{\text{xrefined}}$ was obtained by least squares refinement of $\chi_A$ assuming Curie-Weiss behaviour.

$\mu$ calculated from $\chi_A^{\text{obs}}$. 
(vi) X-ray Powder Data.

The samples for the x-ray powder photographs were prepared from the finely powdered material in 0.5 mm. diameter quartz capillaries. The capillaries were loaded in the DRI-LAB under strictly anhydrous conditions. Photographs were taken on a 14.32 cm. General Electric Camera, using nickel-filtered CuK\(\alpha\) radiation (\(\lambda = 1.5418\text{Å}\)). Photographs of different intensities were taken with different exposure times, depending upon the nature of the material.

The photographs were measured by using an accurate scale and vernier. Bragg angles, interplanar spacing \(d\), \(1/d^2\) values, \(\sin^2 \theta\) values and Nelson-Riley Extrapolation Function were obtained by using the program IBFTC INDEX (Appendix II) in an IBM 7040 computer.

X-ray powder photographs showed PtF\(_5\) to be isomorphous and nearly isodimensional with RhF\(_5\). The observed reflexions were indexed on a monoclinic lattice with the unit cell parameters \(a = 12.37\text{Å}, \ b = 9.84\text{Å}, \ c = 5.47\text{Å}, \ \beta = 99°, \ V = 657.6\text{Å}^3, \ D_{\text{calc}} = 5.86 \text{g/c.c.}\). The data is given in Table III.

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CHAPTER III
DISCUSSION

The preparative technique which had proved valuable in the preparation of PdF$_4^9$ and RhF$_5^6$ produced platinum pentafluoride in greater purity than that previously described. The new material melts sharply at 98.5°, a temperature considerably higher than the previously given melting point of 80°.

The pentafluoride described by Bartlett and Lohmann$^3$ was not obtained in a sufficiently crystalline form for x-ray powder or single crystal photography, but that obtained in this work gave sharp line, low background powder photographs. Unfortunately attempts to grow single crystals failed, but as a consequence of the similarity of the powder pattern to those of RuF$_5^4$, IrF$_5^7$ and RhF$_5^6$ the isomorphism of the compound with the related pentafluorides was established, the close structural similarity is revealed by Plate 1. In particular the close similarity of the photograph of PtF$_5$ with that of RhF$_5$, indicates that the unit cells are almost isodimensional. The crystallographic and physical properties of the known pentafluorides of the second and third transition metals are given in Table 1.

The anticipated isomorphism of platinum pentafluoride with the pentafluorides of ruthenium, osmium, rhodium, and iridium has been confirmed. It is particularly noteworthy that the diagonal relationship observed in the hexafluorides$^{17}$ is again seen here. Platinum pentafluoride is not only almost isodimensional with rhodium pentafluoride but is like it in colour and in thermal stability. This parallels the similarity in unit cell size, colour and stability of the RuF$_5$, IrF$_5$ pair. These relationships may be attributed to the similarity in polarizing power of the metal atoms in the
pairs Pt(V), Rh(V) and Ir(V), Ru(V). Presumably the screening effectiveness of the non-bonding electrons in the second transition series is not as great as in the third.\textsuperscript{17}

Although it is by no means certain that the difference between the monoclinic I structure and the monoclinic II structure, is, that in the former the M-F-M bridges are linear, whereas in the latter they are bent, it is highly probable that this is so. It is certainly established that in all of the monoclinic I cases the bonds are linear.\textsuperscript{2,3} It of course remains to be demonstrated that the M-F-M bonds in OsF\textsubscript{5}, RhF\textsubscript{5}, IrF\textsubscript{5} and PtF\textsubscript{5} are non-linear but it is instructive at this point to enquire if this is a reasonable theoretical expectation.

Although WF\textsubscript{5} is as yet unknown, the pattern of known structures would indicate a monoclinic I type here. Although TcF\textsubscript{5} and ReF\textsubscript{5} are known to be isomorphous,\textsuperscript{18} there are unfortunately no structural details available. The structural change in passing from group VI to group VII and the further but final change in passing from group VII to group VIIA must be significant and is presumably associated with the non-bonding d electron configuration.

It is probable that a linear symmetrical M-F-M bridge can only occur where $\pi$ bonding as well as $\sigma$ bonding is operative between M and F. A linear bridge will result if the bridging F ligand forms $\pi$ bonds with the atom M. A possible scheme is represented in the following Fig. IV.
Figure IV. Bonding in 2nd and 3rd Transition Metal Pentafluorides.
Presumably such a bonding arrangement would be most probable with appropriate vacant d orbitals on the atom M. Each bridging F atom would make a σ bond and a π bond to each bridged metal atom M. Now in the monoclinic I structure each metal atom M is joined cis to two bridging F ligands. Thus each atom M requires two vacant d orbitals for the type of bonding under consideration. Since in the tetrameric arrangements each atom M is six coordinated in fluorine, approximately octahedrally, it is a fair approximation to use the d orbital model usual for O₅⁻ symmetry. The two required vacant orbitals would approximate to t2g orbitals. In NbF₅, TaF₅ (d₂g⁰) and MoF₅ (d₂g¹) two t2g type orbitals are available and linear M-F-M bridges therefore seem appropriate. On the other hand with RuF₅, OsF₅ (d₂g³), RhF₅, IrF₅ (d₂g⁵) and PtF₅ (d₂g⁵) no vacant d orbitals are available to facilitate σ bonding. In these cases σ bonding alone must suffice. The bridge system is no longer linear presumably because of the more effective bonding, consequent on sp² or sp³ hybridization¹⁹ of the fluorine orbitals. This would account for the bent bridge observed in RuF₅⁴. This simple theory certainly groups the pentafluorides appropriately. It allows that TcF₅ and ReF₅ in which the metal atom possess a d₂g² configuration with only one vacant d orbital could not form a wholly linear fluorine bridged tetramer. If a tetramer structure pertains in these fluorides the theory would permit two linear M-F-M bridges and two bent. A structural difference between the group seven pentafluorides and the other pentafluoride types certainly seems appropriate. The structures of TcF₅ and ReF₅ are awaited with great interest.

The moment of [PtF₆]⁻ ion varies from 1.5 to 1.74 B.M. in the temperature range of 77-304°K while that of PtF₅ varies from 1.7 to 1.97 B.M. in the same temperature range. The value of the magnetic moment μ, of PtF₅ is at all temperatures higher than that observed for the [PtF]⁻ ion at the
same temperature. The susceptibility obeys the Curie Weiss law for both species and in neither case is there a significant deviation from this behaviour above 77°K. The data for the \([PtF_6]^−\) is very close to that anticipated by theory.

In an octahedral environment the \(d_{t2g5}\) configuration has been shown by Kotani\(^{20}\) to give moments approaching the spin only value of 1.73 B.M. with high spin orbit coupling, as shown in the accompanying Fig. V, where \(A = s.o.\) coupling constant, and \(k =\) Boltzmann constant.

![Figure V. Plot of \(\mu_{\text{eff}}\) vs. \(kT/A\) for \(d^5\) ion.](image)

Spin orbit coupling for Pt(V) is undoubtedly very high and \(A\) has been estimated to be \(~10,000\ \text{cm}^{-1}\)\(^{21}\) for the Free Ion Single-Electron value. Consequently the magnetic moment of Pt(V) in an octahedral environment is anticipated to be \(~1.73\ \text{B.M.}\) and almost temperature independent. This is the situation which pertains in the \([PtF_6]^−\) ion and here the temperature independent moment is, approximately 1.74 B.M. a value in close agreement with theory. The higher value of the moment of PtF\(_5\) is not easily accounted for. The departure of the environmental symmetry from \(Q^\prime\) may be responsible for the higher moment but it is more likely to be due to a cooperative effect. The bridging of the platinum atoms by fluorine atoms may produce a coupling of spins, in a ferromagnetic sense, in adjacent metal atoms, to yield a somewhat enhanced moment. In the absence of a detailed structure further conjecture is not worthwhile. It is noteworthy however that cases of other third transition series \((d_{t2g5}\) cases), where again the spin orbit coupling
should be high, higher moments than anticipated have been observed. Thus \( \text{IrCl}_4 \) possesses a room temperature moment of 1.98 B.M. whereas \( \text{M}_2(\text{I})\text{IrCl}_6 \) salts invariably show moments slightly less than 1.73 B.M.\(^{22}\)

The new findings on \( \text{PtF}_5 \) have shown that the crystalline material does not occur in any of the \( \text{Xe}(\text{PtF})_x \) adducts (where \( x \) lies between 1 and 2). The susceptibility data should be of value in the interpretation of any magnetic data which becomes available for \( \text{XePtF}_6 \) and \( \text{Xe}(\text{PtF}_6)_2 \). If the moments based on platinum for these products more closely resemble \( [\text{PtF}_6]^− \) than \( \text{PtF}_5 \) then some support will be given to the ionic formulations \( \text{Xe}^+[\text{PtF}_6]^− \) and \( \text{Xe}^{2+}[\text{PtF}_6]_2^− \).
SECTION II

SOME PROPERTIES OF GERMANIUM DIFLUORIDE
CHAPTER I
INTRODUCTION

Winkler was the first to claim the existence of a difluoride of germanium. By heating potassium fluorogermanate in a stream of hydrogen he obtained a dark coloured mass which he claimed to be the difluoride, an aqueous extract of which gave germanous sulphide with hydrogen sulphide. It is probable that Dennis and Laubengayer were the first to obtain the compound however. They described the difluoride as a white sublimable solid formed in the reduction of germanium tetrafluoride by germanium metal: \[ \text{GeF}_4 + \text{Ge} \rightarrow 2\text{GeF}_2 \]. Their germanium tetrafluoride was obtained by pyrolysis of barium hexafluogermanate \[ \text{BaGeF}_6 \rightarrow \text{BaF}_2 + \text{GeV}_4 \] and it was perhaps because of the rather impure nature of this tetrafluoride that they did not report analysis to support their claim. Presumably the impure nature of their \( \text{GeF}_4 \) prevented the preparation of a large enough sample of \( \text{GeF}_2 \) for proper characterization. They were able to show that the material possessed strong reducing properties. Although this first meagre report appeared in 1927 and a more lengthy description was promised, this had not appeared by 1960 and the report of germanium difluoride was generally discounted.

The existence of the difluoride of germanium was established independently in 1961 by Muetterties and Castle and by Bartlett and Yu. The latter workers used the method of Dennis and Laubengayer with however the important modification that the tetrafluoride used was pure material obtained by fluorination of germanium metal. Muetterties and Castle obtained the fluoride by hydrofluorination of germanium metal: \[ 2\text{HF} + \text{Ge} \rightarrow \text{GeF}_2 + \text{H}_2 \]. The nature of the material was clearly independent of the preparative method. Muetterties and Castle gave a melting point of 111-112° which closely agreed
with the value of 110° given by Bartlett and Yu. The other physical and chemical findings separately reported were in agreement. Bartlett and Yu were able to give some structural information on the difluoride. They reported the unit cell to be primitive orthorhombic and to contain four molecules. On the basis of the low density and the similarity with two of the cell dimensions of SeO$_2$ Bartlett and Yu concluded that the compound probably possessed an open (poorly packed) SeO$_2$ type structure. They pointed out that the difluoride structure was quite unlike the two forms of GeO$_2$ (rutile and low quartz). They conjectured that the germanium atoms were probably three coordinated in fluorine, the sterically active nonbonding pair assuming a fourth coordination position.

It has most often been supposed in considering the bonding in compounds like tin dichloride (a chemical relative of GeF$_2$) that the unsymmetrical ligand environment about the central atom was distorted by the steric activity of the nonbonding electron pair on that atom. The solid tin dichloride x-ray structure elucidation has shown that each tin atom has three close (bonded) chlorine ligands, all Cl-Sn-Cl bond angles being close to 90°, the structural unit being a trigonal pyramid with the tin at the apex. Descriptions of the bonding in this case have usually maintained steric activity of the nonbonding electron pair and have "visualized" the pair as being on the side of the tin atom farthest from the ligands (i.e. at the top of the trigonal SnCl$_3$ pyramid). This has implied that the "pair" is housed in an sp$^x$ or sp$^x$d$^y$ hybrid orbital. Rundle however has taken a contrary view and has maintained that an adequate description of the tin chloride structure and many related nonbonding electron pair containing structures, can be given in terms of the involvement of p orbitals of the central atom alone in bonding, the non-
bonding pair being accommodated in an s orbital. In Rundle's description of the structure of SnCl$_2$ the pyramidal SnCl$_3$ unit with its $\sim$90° Cl-Sn-Cl angles is a consequence of the use of only the three orthogonal p orbitals of the tin in bonding, the nonbonding pair being located in the s valence orbital.

It was hoped that a complete crystal structure determination of germanium difluoride would prove of value in discussing which of these theories of bonding was more appropriate in the description of fluorides of the nontransition elements where a nonbonding electron pair is present.

Bartlett and Yu$^{26}$ also investigated some of the reducing properties of germanium difluoride. They studied its reactions with selenium tetrafluoride, sulphur trioxide and with chlorine and iodine. All of the reactions studied showed the difluoride to be a powerful reducing agent, e.g. selenium tetrafluoride being reduced at ordinary temperatures to selenium. They suggested that germanium difluoride might be a useful reducing agent for the preparation of lower fluorides of the transition metals. Indeed the synthetic value of germanium difluoride as an agent in the preparation of lower fluorides remained largely unexplored prior to this work. Germanium difluoride is of course particularly attractive as a reducing agent since the tetrafluoride which is formed in the oxidation-reduction reaction is a gas at ordinary temperatures and pressures, and so is readily removed from the reaction site.

Although Bartlett and Yu reported that germanium difluoride reacted with chlorine to give a mixture of all of the chlorofluorides it was not clear from this preliminary work that this mixture was a consequence of rearrangements of the type:
2\text{GeF}_2\text{Cl}_2 \rightarrow \text{GeF}_3\text{Cl} + \text{GeFCl}_3

2\text{GeF}_3\text{Cl} \rightarrow \text{GeF}_4 + \text{GeF}_2\text{Cl}_2 \text{ etc.}

4\text{GeFCl}_3 \rightarrow \text{GeF}_4 + 3\text{GeCl}_4

as asserted by Booth and Morris,\textsuperscript{31} or whether the various chlorofluorides were primary products of the reaction. Accordingly a \textsuperscript{19}F n.m.r. study of the products of the reaction was undertaken with a view to establishing the exchange reaction claimed by Booth and Morris.\textsuperscript{31}
CHAPTER II
EXPERIMENTAL AND RESULTS

(i) Preparation of Germanium Difluoride

Germanium difluoride was prepared by the methods, described by Bartlett and Yu,\(^\text{26}\) and Meuetherties and Castle,\(^\text{25}\) with only slight modifications of their apparatus. The purity of the samples was checked by x-ray powder photography and by melting point determination.

(a) Reduction of Germanium Tetrafluoride by Germanium.

\[
\text{GeF}_4 + \text{Ge} \rightarrow 2\text{GeF}_2
\]

Germanium tetrafluoride was prepared by the fluorination of germanium metal in a leak tight 100 ml. capacity monel can. Stoichiometric quantities of high purity germanium metal (from Johnson Matthey and Co. London) and fluorine were taken and after the initial reaction at -76° the mixture was heated to \(~ 200°\) for four hours. Excess fluorine was pumped out of the can at -196°. The pressure of germanium tetrafluoride in the can was checked at room temperature. The tetrafluoride was reduced by germanium in the apparatus represented in Fig. VI. The apparatus was dried in the usual way, then, with the GeF\(_4\) pot held at -76° in Drikold-alcohol mixture, the gas was passed slowly over the hot germanium, which was kept at \(~ 200°\) by application of a small flame. The rate of flow of GeF\(_4\) over the hot germanium was controlled by means of a Hoke A431 valve. White solid GeF\(_2\) collected on the cooler parts of the glass, beyond the hot zone. Unreacted GeF\(_4\) collected in the traps at -196°, beyond the reaction zone. When all of the GeF\(_4\) from the monel can had been passed, the valve connecting the apparatus to the vacuum pump was closed and the monel can was immersed in a liquid N\(_2\) bath and the unreacted GeF\(_4\) was sublimed back into it.
Figure VI. Apparatus for GeF₂ Preparation.
This procedure was repeated three to four times, after which the germanium metal became much less active and the reaction became so inefficient that it was terminated. The difluoride was collected by melting and pouring, in the presence of GeF$_4$, into small tubes each provided with a break-seal connection. The samples were kept at room temperature.

(b) Hydrofluorination of Germanium.

\[
\text{Ge} + 2\text{HF} \rightarrow \text{GeF}_2 + \text{H}_2
\]

Muettertties and Castle prepared germanium difluoride by taking stoichiometric quantities of germanium metal and hydrogen fluoride in a Hastelloy-C-lined pressure vessel, the mixture being heated at 225°. They purified their product by vacuum sublimation at 110-130°.

Their procedure was followed, the reactor as described in the preparation of PtF$_5$ being substituted for the Hastelloy vessel. High purity grade germanium metal (5.69g.) (from Johnson Matthey and Co. London) and anhydrous hydrogen fluoride (3.16g.) supplied by Matheson Co. Canada, were used. The bottom of the reactor was heated to ~225° while its top was kept cool by passing a stream of compressed air. After twenty-four hours the volatiles, hydrogen, excess hydrogen fluoride and a small amount of germanium tetrafluoride were pumped off. To ensure complete removal of volatile material, the reactor was pumped out for an hour. When the vessel was opened in the DRI-LAB the product was found as a white crystalline deposit on the cooled top of the reactor. This material (m.p. 65°) gave a complex x-ray powder pattern, which was considerably more complex than that of germanium difluoride.

The material thus obtained was sublimed under vacuum in the same reactor, with the base at 110-140° and the top cooled with a stream of cold air. The sublimate obtained in this way melted at 90° and gave an x-ray powder pattern identical with that characteristic of difluoride obtained by
the tetrafluoride reduction. Since a quantity of yellow solid remained at the bottom of the reactor after the vacuum sublimation it is probable that some disproportionation occurred: \( \text{GeF}_2 \rightarrow \text{GeF}_4 + \text{GeF}_x \).

(ii) The Preparation of Single Crystals of Germanium Difluoride

Germanium difluoride prepared by reduction of the tetrafluoride described above, was poured, after melting, into the small bulb of the crystal growing device shown in Fig. VII. This was a 7 mm. diameter Pyrex glass tube provided with several branches bearing 0.5 mm. diameter quartz capillaries. The capillaries were mounted by graded seals at the tips of B-7 drip cones and the fragile capillaries were protected from damage by Pyrex caps with B-7 sockets. The apparatus was provided at its open end with a Whitey valve. The apparatus was set up vertically and pumped out via the Whitey valve. Meanwhile the \( \text{GeF}_2 \) was heated under good vacuum by immersion of the bulb in an oil bath, the temperature of which was raised slowly. The final temperature of the oil bath was maintained at 110-120° while pumping the glass bulb continuously. At this temperature \( \text{GeF}_2 \) melted and some of it collected on the cooler parts of the apparatus and single crystals of \( \text{GeF}_2 \) appeared in the capillaries. Meanwhile a large proportion of \( \text{GeF}_2 \) decomposed to a yellow solid in the bulb. The single crystal containing capillaries were sealed with a small hot flame.

Crystal Data.

The single crystals of germanium difluoride were examined by the x-ray single crystal techniques by Professor J. Trotter. His findings
Figure VII.

Apparatus for growing Single Crystals of GeP₂.
confirmed that the single crystals were representative samples of germanium difluoride since the unit cell dimensions which he found were the same as those given\textsuperscript{26} by Bartlett and Yu from their powder data. The powder photographs of samples made in the course of this work were always the same as that originally indexed by Bartlett and Yu.

Professor Trotter's single crystal data were:-(\(\lambda\), Cu-K\(_{\alpha}\) = 1.54051 Å; \(\lambda\), Cu-K\(_{\alpha}^2\) = 1.54433 Å). — Germanium difluoride, GeF\(_2\), \(M = 110.6\), Orthorhombic, \(a = 4.682 \pm 0.001\), \(b = 5.178 \pm 0.001\), \(c = 8.312 \pm 0.001\) Å, \(U = 201.51\) Å\(^3\), \(D_\text{m} = 3.7\) (displacement of carbon tetrachloride) = 3.7, \(Z = 4\), \(D^* = 3.644\) g. cm.\(^{-3}\), \(F(000) = 200\). Absorption coefficients for x-rays, \(\mu(\text{Cu-}K_{\alpha}) = 201\) cm.\(^{-1}\), \(\mu(\text{Mo-}K_{\alpha}) = 157\) cm.\(^{-1}\). Absent spectra: \(h00\) when \(h\) is odd, \(0k0\) when \(k\) is odd, \(00l\) when \(l\) is odd; space group is \(P2_12_12_1\) (\(D_2^4\)).

(iii) Reducing Properties of Germanium Difluoride

(a) The GeF\(_2\) + Cl\(_2\) and GeF\(_2\) + Br\(_2\) Reactions.

Gaseous chlorine did not react with germanium difluoride even when the difluoride was melted.

Excess of chlorine (2 ml. of liquid) was condensed on to germanium difluoride (0.8g.) contained in a 3 mm. diameter glass tube which was drawn off from the rest of the apparatus. It was allowed to warm slowly to room temperature. Liquid chlorine under pressure acted as solvent and dissolved the germanium difluoride to form a yellow solution. A \(^{19}\)F n.m.r. spectrum of this sample was recorded.

Bromine, dried by phosphorous pentoxide, was condensed on germanium difluoride in a 3 mm. glass tube, an excess of germanium difluoride being employed. The sealed tube was brought to room temperature, when a clear
Figure VIII. $^{19}$F n.m.r. Spectra of GeF$_2$/Br$_2$ and GeF$_2$/Cl$_2$ Reaction Products.
colourless liquid was produced which remained in contact with a slight excess of the difluoride. A $^{19}\text{F n.m.r.}$ spectrum was recorded. The spectrum is shown in Fig. VIII.

$^{19}\text{F n.m.r.}$ Results.

$\text{GeF}_2/\text{Cl}_2$ and $\text{GeF}_2/\text{Br}_2$ reaction samples each gave rise to a four sharp peak $^{19}\text{F n.m.r.}$ spectrum at 21°. The four peak spectrum had indicated four separate fluorine containing species, assumed to be $\text{GeF}_4$, $\text{GeF}_3\text{X}$, $\text{GeF}_2\text{X}_2$, and $\text{GeFX}_3$. The infrared spectroscopic studies of Bartlett and Yu\textsuperscript{26} and Bartlett and Mak\textsuperscript{33} had previously established the production of $\text{GeF}_4$, $\text{GeF}_3\text{X}$, $\text{GeF}_2\text{X}_2$, $\text{GeFX}_3$ and $\text{GeX}_4$ in the $\text{GeF}_2/\text{X}_2$ reactions. The chemical shifts and assignments given in Table IV were made on the assumption that, as in the case of the carbon analogues\textsuperscript{34}, the tetrafluoride would exhibit $^{19}\text{F}$ resonance to highest field.

\begin{table}[h]
\centering
\begin{tabular}{llll}
\hline
Compound & Chemical Shift* (ppm.) & Compound & Chemical Shift* (ppm.) \\
\hline
$\text{GeF}_4$ & 0 & $\text{GeF}_4$ & 0 \\
$\text{GeF}_3\text{Cl}$ & -27.8 & $\text{GeF}_3\text{Br}$ & -38.6 \\
$\text{GeF}_2\text{Cl}_2$ & -51.5 & $\text{GeF}_2\text{Br}_2$ & -68.8 \\
$\text{GeFCl}_3$ & -70.0 & $\text{GeFBr}_3$ & -89.8 \\
\hline
\end{tabular}
\caption{$^{19}\text{F n.m.r.}$ Chemical Shift Data for $\text{GeF}_{4-x}\text{Cl}_x$ and $\text{GeF}_{4-x}\text{Br}_x$ Compounds.}
\end{table}

*Based on the assumption of similarity to the carbon analogue sequence\textsuperscript{34}.

Since the $\text{GeF}_2\text{X}_2$ and $\text{GeF}_3\text{X}$ $^{19}\text{F n.m.r.}$ peaks are of comparable intensity it is likely that the $\text{GeF}_2\text{X}_2$ concentration is greater than that of $\text{GeF}_3\text{X}$. Furthermore the low intensity of the $\text{GeF}_4$ resonance absorption is indicative of low concentration of this species.
(b) Reduction of Iodine Pentafluoride.

Iodine pentafluoride, supplied by the Matheson Co. N.J., was transferred to a monel can, and purified by treating with a small amount of fluorine, the mixture being allowed to warm to room temperature. Remaining fluorine was pumped from the above mixture at liquid $N_2$ temperature, and the pentafluoride was vacuum distilled before use. An infrared spectrum of the material showed $IF_7$ and $IOF_5$ to be absent.

Germanium difluoride (1g.) was taken in a leak tight Kel-F trap and an excess of pure iodine pentafluoride was condensed on to it at liquid $N_2$ temperature. The pentafluoride was allowed to melt slowly on to the germanium difluoride and the Kel-F trap was kept immersed in an ice cold water bath. On contact, iodine was immediately evolved in an exothermic reaction, the bottom of the Kel-F trap becoming hot. The germanium difluoride was entirely consumed by the reaction and vacuum distillation of the products at room temperature did not yield an involatile residue. The volatile products were examined by infrared spectroscopy, which indicated only iodine pentafluoride and germanium tetrafluoride. Evidently the overall reaction was:

$$5GeF_2 + 2IF_5 \rightarrow 5GeF_4 + I_2.$$  

(c) The $PtF_4 + GeF_2$ Reaction in Anhydrous HF.

Platinum tetrafluoride (0.306g.), obtained as described under $PtF_5$, and germanium difluoride (0.123g.) appropriate for stoichiometric reaction: $GeF_2 + PtF_4 \rightarrow GeF_4 \uparrow + PtF_2$, were weighed out separately, in the DRI-LAB, into a monel reactor. The reactor was similar to that already described under the $PtF_5$ preparation. Anhydrous hydrogen fluoride (4-5 ml.) was condensed under vacuum into the reactor from a Kel-F container (The Kel-F
tube container served as a simple measuring device for the anhydrous HF, since the amount of HF transferred could be gauged visually with fair accuracy, the tube being previously calibrated).

The closed reactor was brought to room temperature and after twenty minutes the volatiles were removed under vacuum. The reactor was opened in the DRI-LAB and the black solid residue it contained was examined by x-ray powder photography. The solid showed no noticeable reaction with water but proved to be hygroscopic. The x-ray powder photographs revealed a sharp line pattern characteristic of the PtF₄ and a broad line pattern (characteristic of very small particle size) of platinum metal.

(d) The Reaction between WF₆ and GeF₂ in Glass:

The Preparation of WO₂F.

A small breakseal tube containing germanium difluoride was joined to a Pyrex apparatus as shown in Fig. IX. The glassware was carefully vacuum dried, in the usual manner, after which the breakseal was opened and tungsten hexafluoride was transferred under vacuum to the germanium difluoride containing tube. The whole apparatus was then closed under vacuum. The glass trap and the collecting tube were immersed in ice cold water baths. The tube containing germanium difluoride and tungsten hexafluoride was allowed to warm to room temperature. The tungsten hexafluoride melted on to the germanium difluoride, but did not dissolve it or react with it. The mixture was heated gradually and it was not until a temperature of 240° was reached (using an oil bath) that an interaction was observed. A deep blue solid appeared on the hot glass adjacent to the germanium difluoride. When the difluoride was entirely consumed, the tube containing the blue solid was drawn off under vacuum. X-ray powder photographs of this solid indicated that the unit cell was simple cubic.
To Vacuum Pump

To WF$_6$ Cylinder

Figure IX.

Apparatus for WF$_6$ + GeF$_2$ Reaction.
with $a = 3.838 \, \text{Å}$. The crystallographic data is given in Table V. Analysis by pyrohydrolysis indicated a composition close to $\text{WO}_2\text{F}$. Found: F, 9.1; W, 75.95%. $\text{WO}_2\text{F}$ requires F, 8.1; W, 78.28%. Unfortunately samples large enough for accurate magnetic susceptibility measurements were not obtained.

Line intensities of the x-ray powder photographs were measured with a Hilger & Watts recording micro photometer L.486 provided with a FA17 power supply.

<table>
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<tr>
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<th>Obs.</th>
<th>Calc</th>
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<td>1.1551</td>
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<td>330,411</td>
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<td>1.2231</td>
<td>47</td>
</tr>
</tbody>
</table>

TABLE V

X-Ray Powder Data for $\text{WO}_2\text{F}$. 

$\alpha = 3.838 \, \text{Å}, \quad \gamma = 56.53 \, \text{Å}^3, \quad \gamma = 1, \quad D_{\text{calc}} = 6.89 \, \text{g/c.c.}$
(e) The Reaction between WF$_6$ and Ge metal in Glass.

Tungsten hexafluoride was passed over hot germanium contained in a glass U tube connected to an apparatus similar to that employed in the preparation of germanium difluoride. A white solid appeared on the cooler glass beyond the hot germanium whereas a deep blue solid appeared in the hot region of the U tube. The blue compound gave the x-ray powder pattern characteristic of WO$_2$F. The white solid (m.p. 65°) gave a complex powder picture which closely resembled that of tungsten oxide tetrafluoride. Analysis of the white solid by Willard-Winter$^{35}$ distillation for fluorine, tungsten being estimated as the trioxide, indicated that the compound was WOF$_4$. Found: F, 24.5; W, 65.0%. Calc. for WOF$_4$: F, 27.55; W, 66.64%.

(f) The WF$_6$-Ge metal Reaction in Monel Apparatus.

An attempt was made to reduce tungsten hexafluoride to tungsten pentafluoride using germanium metal. Powdered germanium metal and tungsten hexafluoride were taken in stoichiometric quantities into a leak tight monel reactor, similar to the one used in PtF$_5$ preparation. The reactants were heated to $>$350° for 48 hours. The lid of the monel reactor was kept cool in the usual way. The volatiles were removed from the cooled reactor,
and the reactor opened in the DRI-LAB, to reveal a white compound on the lid. This compound melted at 96.5°. The white solid quickly became light blue when exposed to moist air. A qualitative test showed it to be paramagnetic. It gave a complex x-ray powder picture.

Analysis of the material, (fluorine by Willard-Winter distillation, tungsten being estimated as trioxide by treating with conc. HCl and HNO₃), showed it to have an empirical formula close to Ge₂WF₈.

Found: W, 38.2; F, 29.42; Ge by difference 32.4%. Ge₂WF₈ requires: W, 38.2; F, 31.6; Ge, 30.18%.
CHAPTER III
DISCUSSION

(i) The Crystal Structure of Germanium Difluoride

The complete three dimensional x-ray structural analysis carried out on single crystals grown by slow sublimation under vacuum has confirmed the orthorhombic unit cell with \( a = 4.682 \); \( b = 5.178 \); \( c = 8.312 \) Å, derived by Bartlett and Yu from x-ray powder data, and has shown the SeO\(_2\) type structure proposed\(^{26}\) by Bartlett and Yu to be approximately correct.

Germanium difluoride is a chain polymer consisting of a three dimensional fluorine bridged array. The structure is represented in Plate II, where a projection along axis \( b \) is shown. It consists of infinite \(-\text{F-Ge-F-Ge-}\) chains parallel to \( b \), having each fluorine atom almost equidistant from the two coordinated germanium atoms. The F-Ge distances are 1.91 and 2.09 Å and the Ge-F-Ge angle 157.4°. All fluorine atoms of such a chain are structurally equivalent. Such chains are cross linked by a second system of weak fluorine bridges parallel to \( a \), in which the fluorine atoms are less symmetrically placed, the Ge-F distances being 1.79 and 2.57 Å. The fluorine atom at 1.79 Å from one germanium atom is at 2.57 Å from the germanium atom in an adjacent chain. These bridges then, form weak linkages between the parallel chains. The two types of fluorine bridges are represented in Fig. X.

The three short bonded fluorine ligands (are F, 1.79, 1.91 and 2.09 Å) form a trigonal pyramid with the apical germanium atom, the apical angles being 85.0, 85.6 and 91.6°. This unit is similar to the molecular shape attributed to antimony trifluoride, in crystalline Sb\(_3\)F\(_5\), where the Sb-F distance is 2.03 Å and F-Sb-F angle is 88°.
The Crystal Structure of Germanium Difluoride

By James Trotter,* M. Akhtar, and Neil Bartlett *†

Projection of the structure along the \( b \) axis

* Projection of the structure along the \( b \) axis

† Projection of the structure along the \( b \) axis
Figure X. Fluorine Bridging in GeF$_2$
Similar structural units have been observed in other Ge(II) and Sn(II) compounds, and for the most part the discussion of bonding in these compounds has merely had reference to a three coordinated Ge or Sn group. It is clear that discussion of the structure and bonding in GeF$_2$ requires that the fluorine ligand 2.57Å distant from each germanium atom must be considered as a bonded ligand also. Thus a [GeF$_4$] group is appropriate for the discussion of the bonding. The [GeF$_4$] group may be described as a distorted trigonal bipyramid arrangement of four fluorine ligands and a sterically active electron pair about the central metal atom. This group is represented in Fig. XI. As is usual for such an arrangement (e.g. SF$_4$) the shorter bonded ligands and the non-bonding electron pair are located in the equatorial plane.

Similar coordination of the metal atom has been observed in the salt NaSn$_2$F$_5$, where Sn$_2$F$_5$ units, resulting from strong fluorine bridging of two trigonal pyramidal groups, exist. The weak fluorine bridges link the Sn$_2$F$_5$ units together. Each tin atom is four coordinated, having three close fluorine atoms, one of these being the bridging fluorine of the Sn$_2$F$_5$ unit, while the fourth fluorine is of an adjacent Sn$_2$F$_5$ unit. In Table VI the interatomic distances and angles in NaSn$_2$F$_5$ are compared with those of GeF$_2$. The notation is the same as that of Fig. XI.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>ab</th>
<th>cd</th>
<th>ac</th>
<th>bc</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeF$_2$</td>
<td>1.79</td>
<td>1.91</td>
<td>2.09</td>
<td>2.57</td>
<td>91.6°</td>
<td>162.8°</td>
<td>85.6°</td>
<td>85.0°</td>
</tr>
<tr>
<td>NaSn$_2$F$_5$</td>
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<td>2.07</td>
<td>2.22</td>
<td>2.53</td>
<td>89.3°</td>
<td>142.4°</td>
<td>81.2°</td>
<td>84.1°</td>
</tr>
<tr>
<td>Compound</td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>d</td>
<td>ab</td>
<td>cd</td>
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<tr>
<td>GeF₂</td>
<td>1.79</td>
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<td>2.09</td>
<td>2.57</td>
<td>91.6</td>
<td>162.8</td>
<td>85.6</td>
<td>85.0</td>
</tr>
</tbody>
</table>

Figure XI. [GeF₄] Group in GeF₂.
Rundle has discussed the nature of bonding in Sn(II) and Ge(II) compounds. He describes the SnCl₂ structure, which consists of -Sn-Cl-Sn-Cl- chains in which each tin atom has two bridging chlorine neighbours and a third closely bound unique chlorine ligand, in terms of the SnCl₃ structural unit. Rundle's description of the bonding in this compound assumes the Sn(II) nonbonding electron pair to be located in the valence set s orbital. The three chlorine ligands are considered to be bonded as a consequence of the use of the three p orbitals of the Sn(II) valence set. Thus a pair of electrons from one of the chlorine ligands and one electron pair from each of the other two chlorine ligands satisfy the octet condition. The ~90° bond angles are accounted for by this hypothesis. If such a description, using p orbitals alone, is chosen for the structure of germanium difluoride, it is necessary that, two fluorine ligands could be bonded to germanium by three centre four electron pair bonding involving only one Ge(II) p orbital and two by conventional electron pair bonds. Thus a unit with two long bonded fluorine atoms with a F-Ge-F angle of 180° and two short bonded fluorine atoms with a F-Ge-F angle of 90° would arise. Ligand-ligand repulsions should lead to bond angles even greater than this. But the [GeF₄] group in germanium difluoride shows four F-Ge-F angles <90°. Indeed although Rundle points out to the repeated occurrence of X-M-X bond angles of 90° as support for his p orbital hypothesis, it is noteworthy that the bond angles are considerably less than 90°. With the non-bonding valence electron pair in a s orbital, one would expect that ligand ligand repulsions increase the bond angles to >90°.

It appears that the best bonding description of the GeF₂ structure should allow for steric activity of the non-bonding valence electron pair. The trigonal bipyramid arrangement of one electron and four ligands with two
long axial bonds of 2.09 and 2.57Å and with two short equatorial bonds of 1.79 and 1.91Å round the germanium atom is in agreement with the predictions of the simple valence electron pair repulsion rules. That all of the bond angles are less than the ideal values may be accounted for in terms of lone pair-bond pair repulsions. Furthermore the long empty tunnels in the structure are consistent with the presence of sterically active nonbonding valence electron pairs on the side of each germanium distant from the fluorine ligands. It would appear then that a bonding scheme which uses p orbitals alone is unsatisfactory, and the involvement of outer orbitals, presumably d, at least in germanium difluoride, appears likely.
(ii) Chemistry of GeF₂

(a) Reactions with Halogens

The findings of Bartlett and Yu²⁶ and Bartlett and Mak³³ in infrared spectroscopic examination of the products of the GeF₂/Cl₂ and GeF₂/Br₂ reactions agreed with the earlier observations of Booth and Morris,³¹ that the chlorofluorides and bromofluorides of germanium (IV) slowly rearrange to unmixed tetrahalides, for example;

\[
\begin{align*}
2\text{GeF}_2\text{Cl}_2 & \rightarrow \text{GeF}_3\text{Cl} + \text{GeCl}_3\text{F} \\
2\text{GeF}_3\text{Cl} & \rightarrow \text{GeF}_4 + \text{GeF}_2\text{Cl}_2 \text{ etc.}
\end{align*}
\]

The \(^{19}\)F n.m.r. findings show, however, that the rearrangements must, in the absence of a catalyst, be very slow, since the resonance spectra at room temperature showed no evidence of fluorine ligand exchange, and showed no change over a period of several days. It is probable that the exchange observed by the previous workers may have been catalysed by HF impurity, an impurity likely to be present in the mixtures of the earlier studies but not in this investigation, where rigorously anhydrous conditions were maintained.

The observed mixtures of chlorofluorides and bromofluorides from the halogen - GeF₂ reactions: with a very low tetrafluoride content, a slight excess of \(\text{GeF}_2\text{X}_2\) and approximately equal concentrations of \(\text{GeFX}_3\) and \(\text{GeF}_3\text{X}\), are consistent with the structural findings on GeF₂. Since each germanium atom is short bonded to three fluorine ligands, a \(\text{GeF}_3\text{X}\) product is expected. Since the fourth fluorine ligand is more distant it is not surprising that this bond is more readily cleaved by halogen. Significantly, though the tetrafluoride is observed, its concentration is small. Of the four fluorine ligands about each germanium
atom in the crystal (GeF: 1.79; 1.91; 2.09; 2.57Å) the unusually long bond is likely to be most easily cleaved in the oxidation. On the other hand the shortest bond is least likely to be broken. Thus the chlorination (or bromination) of the solid is seen to be unlikely to produce large concentration of tetrafluoride or tetrachloride (or tetrabromide). Presumably the 1.91Å GeF bond is slightly more difficult to break than the 2.09Å bond. This being so, the preferred species resulting from the oxidations would be GeF₂X₂, with GeFX₃ and GeF₃X in somewhat lower concentrations.

(b) Fluoride Reduction Reactions.

The inability to produce a lower fluoride of iodine by the reduction of the pentafluoride, with the difluoride, matched the lack of success which Bartlett and Yu had in their efforts to derive a lower selenium fluoride from the tetrafluoride (elemental selenium was formed). The ready separation of iodine and the absence of a solid residue on removal of the excess iodine pentafluoride, indicated that the reaction had proceeded according to the equation;

$$5\text{GeF}_2 + 2\text{IF}_5 \rightarrow 5\text{GeF}_4 + \text{I}_2$$

The alleged instability of the trifluoride towards disproportionation: $$5\text{IF}_3 \rightarrow \text{I}_2 + 3\text{IF}_5$$ in any case gave little prospect of success. Clearly if germanium difluoride is to be a suitable reagent for the preparation of unstable lower fluorides like SeF₂ and IF₃, a solvent convenient for low temperature work will need to be found. Anhydrous hydrogen fluoride does dissolve the difluoride and remains fluid to low temperatures. It may therefore have application in this area.

A solution of the difluoride in anhydrous hydrogen fluoride
proved to be capable of reducing platinum tetrafluoride. Unfortunately the lower fluoride of platinum which had been hoped for was not produced. The tetrafluoride-germanium difluoride ratio was appropriate for the formation of platinum difluoride: $\text{PtF}_4 + \text{GeF}_2 \rightarrow \text{PtF}_2 + \text{GeF}_4$, but only half of the platinum tetrafluoride was reduced and that directly to the metal: $2\text{PtF}_4 + 2\text{GeF}_2 \rightarrow \text{Pt} + 2\text{GeF}_4 + \text{PtF}_4$. The sharpness of the x-ray powder diffraction pattern of the platinum tetrafluoride in the product indicated that it was the unchanged starting material. If the tetrafluoride in the product had arisen by the disproportionation: $2\text{PtF}_2 \rightarrow \text{Pt} + \text{PtF}_4$ the pattern would undoubtedly have been diffuse. The diffuse platinum metal pattern, which was recognised in the powder diffraction photographs of the residue, were consistent with the rapid production of the element at low temperature: $\text{PtF}_4 + 2\text{GeF}_2 \rightarrow \text{Pt} + 2\text{GeF}_4$. Since this reaction occurred below or at room temperature, there is little hope that it could be easily controlled to produce a pure lower fluoride. Clearly, if a lower fluoride is produced initially, its reduction is preferred to that of the original higher fluoride.

Since tungsten hexafluoride is not easily reduced and since, other than a poorly characterized tetrafluoride, no other binary fluorides of tungsten were known, an effort was made to reduce the hexafluoride with germanium difluoride. The initial reaction was carried out in glass apparatus. Since the only identifiable reduced tungsten product was an oxyfluoride of empirical formula $\text{WO}_2\text{F}$, it is possible that this arose by a reaction sequence:

$$2\text{WF}_6 + \text{SiO}_2 \rightarrow \text{SiF}_4 + 2\text{WO}_2\text{F}$$

$$2\text{WO}_2\text{F} + \text{GeF}_2 \rightarrow \text{GeF}_4 + 2\text{WO}_3\text{F}$$

$$2\text{WO}_3\text{F} + \text{SiO}_2 \rightarrow 2\text{WO}_2\text{F} + \text{SiF}_4$$
The involatile tungsten oxyfluoride is of some structural and magnetic interest, but it is unlikely that it has been obtained pure. Insufficient material was secured for magnetic susceptibility measurements over a temperature range by the Guoy technique. Clearly it would be more satisfactory to prepare the material in higher yield and purity by reduction of the appropriate tungsten (VI) oxyfluoride:

$$2\text{WO}_2\text{F}_2 + \text{GeF}_2 \rightarrow 2\text{WO}_2\text{F} + \text{GeF}_4$$

The observed x-ray diffraction data show that the $\text{WO}_2\text{F}$ has an ReO$_3$ structure. The oxygen and fluorine atom arrangement must be disordered. With the tungsten atoms at the origin of the simple cubic unit cell, the light atom arrangement which gives the best fit with the observed intensity data is that with the atoms in the mid point cube edge locations i.e., an ReO$_3$ arrangement. This may be seen by reference to Table VII:

<table>
<thead>
<tr>
<th>Table VII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structural Data for $\text{WO}_2\text{F}$</td>
</tr>
</tbody>
</table>

**Primitive Cubic unit cell alternatives**

1. W at 0,0,0; 3F(0) at $\frac{1}{2},0,0; 0,\frac{1}{2},0; 0,0,\frac{1}{2}$; etc.

2. W at 0,0,0; 3F(0) at $\frac{1}{2},\frac{1}{2},0; 0,\frac{1}{2},\frac{1}{2}; \frac{1}{2},0,\frac{1}{2}$; etc.

**Relative Intensities - I**

<table>
<thead>
<tr>
<th>hk1</th>
<th>I obs</th>
<th>I calc (1)*</th>
<th>I calc (2)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>13.2</td>
<td>17.2</td>
<td>10.9</td>
</tr>
<tr>
<td>110</td>
<td>17.9</td>
<td>18.2</td>
<td>18.2</td>
</tr>
<tr>
<td>111</td>
<td>7.3</td>
<td>6.7</td>
<td>20.2</td>
</tr>
<tr>
<td>200</td>
<td>16.9</td>
<td>12.7</td>
<td>12.7</td>
</tr>
<tr>
<td>210</td>
<td>42.9</td>
<td>32.9</td>
<td>23.8</td>
</tr>
<tr>
<td>211</td>
<td>20.7</td>
<td>21.1</td>
<td>21.1</td>
</tr>
<tr>
<td>220</td>
<td>12.4</td>
<td>15.1</td>
<td>15.1</td>
</tr>
</tbody>
</table>
Table VIII (continued)

* Intensity data calculated for ReO$_3$ by Meisel.$^{40}$

The intensity agreement with the alternative model in which the light atoms are located at the face centre positions of the cube (with W at 0,0,0) is much less satisfactory. It is perhaps not without significance that ReO$_3$ and this new and isostructural oxyfluoride of tungsten are isoelectronic. It remains to be seen if WOF$_2^{39}$ will possess the same structure.

The attempts to prepare a lower binary fluoride of tungsten by reduction of the hexafluoride either by germanium difluoride or by germanium metal, both with and without anhydrous hydrogen fluoride solvent, were unsuccessful. The material which was produced both in the WF$_6$ + GeF$_2$ and WF$_6$ + Ge reactions is as yet poorly characterized, having an empirical formula approximating to Ge$_2$WF$_8$. Surprisingly, this white paramagnetic solid is sublimable (m.p. 96.5°) and yet formally the tungsten is required to be four valent (if the germanium, as seems reasonable, is counted as divalent). It is conceivable, although unexpected, that the germanium difluoride is here acting as an electron pair donor and that the tungsten is four coordinated by fluorine ligands and two coordinated by GeF$_2$ groups as shown:

Unfortunately neither single crystals nor interpretable x-ray powder photographs were obtained and there is as yet no structural information for this interesting compound.
REFERENCES


30. R. E. Rundle, "Coordination Number and Valence in Modern Structural Chemistry", in "Record of Chemical Progress", Vol. 23, No. 4, December 1962.


33. N. Bartlett and S. Y. C. Mak, unpublished results.


$IBFTC$ APPROX

C FORTRAN FOUR CONVERSION OF STRAIGHT LINE APPROXIMATION

C ESTIMATION OF PARAMETERS FOR A STRAIGHT-LINE APPROXIMATION

C LET $N$ = NUMBER OF OBSERVATIONS

C LET $X$ = INDEPENDENT VARIABLE

C LET $Y$ = DEPENDENT VARIABLE

C THIS PROGRAM FITS LINE TO $1/$MAGS VS TEMP

C LET $Y(J)$ BE MAGS NOT $1/$MAGS

C LET $X(J)$ BE TEMP

14 $SX = 0.$

$SY = 0.$

$SXX = 0.$

$SXY = 0.$

$SYY = 0.$

$J = 0$

READ(5,1)$N,AX,AY$

1 FORMAT(16,2X,A4,2X,A4)

DIMENSIONX(100),Y(100)

DO 2 $I = 1,N$

$J = J + 1$

READ(5,3)$X(J),Y(J)$

3 FORMAT(F7.0,F7.0)

$Y(J) = 1./Y(J)$

$SX = SX + X(J)$

$SY = SY + Y(J)$
SXX = SXX + X(J) * X(J)
SXY = SXY + X(J) * Y(J)
2
SYY = SYY + Y(J) * Y(J)
READ(5,20) TEST
20 FORMAT(A3)
    CALL SETHOL(CHECK,3HEND)
IF (TEST - CHECK) 11, 12, 11
11 WRITE(6,13)
13 FORMAT(51H WRONG NUMBER OF DATA CARDS OR LAST DATA CARD NOT ,
1 32H FOLLOWED BY AN END-OF-DATA CARD )
STOP
12 FN = N
    DN = 1./FN
    AVX = SX*DN
    AVY = SY*DN
    CALL SKIP TO (1)
    WRITE(6,4) AX, AVX, AY, AVY
4 FORMAT(16H MEAN VALUE OF A4, 3H = E13.6/15X, A4, 3H = E13.6)
    DNN = 1./(FN - 1.)
    S = SXX - SX*AVX
    COVX = S*DNN
    COVX = (SYY - SY*AVY)*DNN
    COVXY = (SXY - SX*AVY)*DNN
    STDX=SQRT(COVX)
    STDY=SQRT(COVY)
    WRITE(6,5) AX, STDX, AY, STDY
5 FORMAT(/23H STANDARD DEVIATION OF A4, 3H = E13.6/22X, A4, 3H = E13.6
1 )
CORR = COVXY/(STDX*STDY)
WRITE(6,6)AX,AY,CORR

A = COVXY/COVX
WRITE(6,7)A

B = AVY - A*AVX
WRITE(6,8)B

R = SQRT( (FN-1.)*(COVY-A*A*COVX)/(FN-2.))
WRITE(6,9)R

SI = R*SQRT(DN+AVX*AVX/S)
SS = R*SQRT(1./S)
WRITE(6,10)SS,SI

WRITE(6,22)

N=FN
J=0
DO421=1,N
J=J+1
YCALC=A*X(J)+B
SCALC=1000000./YCALC
SOBSV=1000000./Y(J)
SDEVI=SOBSV-SCALC
TINV = 1./X(J)
WRITE (6, 33) X(J), SOBSV, SCALC, SDEVI, TINV, Y(J)
33 FORMAT (F10.2, 8H , F10.2, 9H , F10.2, 9H , F10.2,
116H , F10.5, 2H , F10.2)
42 CONTINUE
WRITE (6, 44)
44 FORMAT (///28H TEMP SUSC(CALC)//)
TEMP = 60.
D0521 = 1, 12
TEMP = TEMP + 20,
YCALC = A*TEMP + B
SCALC = 1000000./YCALC
WRITE (6, 55) TEMP, SCALC
55 FORMAT (F10.2, 8H , F10.2)
52 CONTINUE
GO TO 14
END
APPENDIX II

$IBFTC INDEXX

44  BN=0.
    CN=0.
    SCP=0.
    SBP=0.

C  CALC OF BEAM STOP CENTRE BPA=AV(X1+X2/2)
C  DATA CARD WITH X1=X2=0 SIGNALS END OF DATA
1  READ(5,30)XI,X2
30  FORMAT(2F10.3)
    BP=(XI+X2)/2.
    SBP=SBP+BP
    IF(BP.EQ.0.)GO TO 3
    BN=BN+1.
    GO TO 1
3  BPA=SBP/BN

C  CALC OF COLLIMATOR CENTRE CPA=AV(X1+X2)/2
C  DATA CARD WITH X1=X2=0. SIGNALS END OF DATA
4  READ(5,30)XI,X2
    CP=(XI+X2)/2.
    SCP=SCP+CP
    IF(CP.EQ.0.)GO TO 5
    CN=CN+1.
    GO TO 4
5  CPA=SCP/CN

WRITE(6,75)
C FACTOR TO CONVERT ARC TO ANGLE
ANGLE=3.1415/(CPA-BPA)
IF(ANGLE.LT.0.)GO TO 7
GO TO 13
7 ANGLE=-ANGLE:
C CALC OF 2THETA,DCORR,1/D*D
C IF X FOR ALPHAL ADD 100 TO X VALUE
C IF X FOR ALPHAL, ADD 200 TO X VALUE
C X1=0 SIGNALS END OF DATA + NO OTHER SET
C X1=999 SIGNALS END OF DATA + ANOTHER SET FOLLOWING
13 READ(5,2)X1
2 FORMAT(F10.3)
IF(X1.EQ.0.)GO TO 17
IF(X1.EQ.999.)GO TO 70
IF(X1.GT.200.)GO TO 14
IF(X1.GT.100.)GO TO 15
AMBDA=0.7709
GO TO 16
14 X1=X1-200.
AMBDA=0.77217
GO TO 16
15 X1=X1-100.
AMBDA=0.77025
GO TO 16
16 X2=X1-BPA
THETA2=X2*ANGLE
IF(THETA2.LT.0.)GO TO 20
GO TO 21
20 THETA2=-THETA2
21 THETA=THETA2/2.
CTHETA=COS(THETA)
STHETA=SIN(THETA)
XTHETA=1./STHETA
DHKL=AMBD*A*XTHETA
DINSQ=1./(DHKL*DHKL)
XNRFN=0.5*((CTHETA*CTHETA/STHETA)+(CTHETA*CTHETA/THETA))
THETA2=360./6.2828*THETA2
WRITE(6,18)X1,THETA2,DHKL,DINSQ,XNRFN
18 FORMAT(1X,F10.3,10H,F10.3,10H,F10.5,10H,F10.6,20H,F10.3/)
GO TO 13
70 CALL SKIP TO (1)
GO TO 44
17 STOP
END