

SOME PHYSICAL PROPERTIES OF d-TRANSITION METAL FLUORIDES IN UNUSUAL OXIDATION STATES

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SUMMARY

Unusual oxidation states can be obtained in d-transition metal fluorides by way of various experimental procedures: high-pressure elementary fluorine, high pressure in the solid state, high temperature, etc ... Relationships between structures and physical properties are described in some selected examples.

INTRODUCTION

During recent years fluorine chemistry has met with important development due to new prospects in various fields : optical properties, electrochemistry, etc. A number of fluorides may also be used for fluorinating organic molecules.

Because of the fundamental and applied interest of materials with new oxidation states, we have carried out the synthesis of fluorides of transition elements characterized by unusual oxidation states. Many phases of this type have been isolated by various research teams. We have selected here some characteristic examples obtained in this laboratory. We shall point out the preparation techniques, the stabilization conditions and some relationships between structure and physical properties.

EXPERIMENTAL PROCEDURE

Several preparative methods have been used :

- solid state reactions at normal pressure in gold or palladium sealed tubes (e.g. $\text{Rb}_2\text{NaPdF}_6$) ;
- reactions in platinum sealed tubes under 70 kbar pressure up to 600°C in a 'belt'-type device (e.g. NaPdF_4) ;
- syntheses in a nickel boat under a flow of fluorine up to 550°C (e.g. $\text{Na}_2\text{LiNiF}_6$) ;
- reactions in thick-walled bombs under 12 bar fluorine pressure for volatile compounds (e.g. RhF_5 type) or under 300 bar up to 500°C for high oxidation states (e.g. Rb_2CuF_6).

ELECTRONIC PROPERTIES OF $\text{M}^{\text{II}}\text{M}'^{\text{IV}}\text{F}_6$ FLUORIDESFerromagnetic behaviour

Most of $\text{M}^{\text{II}}\text{M}'^{\text{IV}}\text{F}_6$ fluorides (with M^{II} , M'^{IV} = transition elements) crystallize in the LiSbF_6 type. This structure can be derived from ReO_3 by a rhombohedral distortion and a cationic ordering. However neutron diffraction experiments are often required to determine the exact space group [1,2] .

Ferromagnetic properties may be associated with ordering between the M^{II} and M'^{IV} cations. In $\text{Ni}^{\text{II}}\text{Mn}^{\text{IV}}\text{F}_6$ for instance - which is the ferromagnetic fluoride with the highest Curie point - Ni^{II} has a high spin $t_{2g}^6 e_g^2$ configuration, whereas Mn^{IV} has a $t_{2g}^3 e_g^0$ configuration. The e_g orbitals are ferromagnetically coupled thanks to superexchange involving the 2p fluorine orbitals. This type of coupling, which is enhanced here by additional ferromagnetic t_{2g} -p- t_{2g} interactions, is responsible for the ferromagnetic behaviour of most $\text{M}^{\text{II}}\text{M}'^{\text{IV}}\text{F}_6$ compounds (Table I). It probably explains the existence of $\text{Pt}^{\text{II}}\text{Pt}^{\text{IV}}\text{F}_6$ in which Pt^{II} has been stabilized for the first time with a high spin configuration [4] .

TABLE I

Magnetic data of some $M^{II}M^{IV}F_6$ compounds

Compound	NiMnF ₆	ZnMnF ₆	CdMnF ₆	NiPdF ₆	CuPdF ₆	PdPdF ₆	NiPtF ₆	PdPtF ₆	PtPtF ₆
T _C (K)	39	9.5	8	6	10	10	8	25	16
Magnetization at 4.2K (μ _B)	4.5	2.9	2.3	1.4	1.0	1.8	1.1	1.7	1.5
Ref.	2	2	2	3	3	1	3	3	4

Piezoresistive behaviour

For $M^{II}M^{IV}F_6$ fluorides in which the appropriate transition element has extended d orbitals (4d and 5d series) a reversible electronic transition is observed under high pressure.

The pressure dependence of the resistivity is illustrated in Fig. 1 for Pd₂F₆. Between 1 bar and 25 kbar a strong decrease of the resistivity is observed with $\frac{d \log \rho}{dp} = -0.18$ kbar⁻¹. Simultaneously, the activation energy varies from $\Delta E \approx 1.34$ eV at normal pressure down to 0.07 eV at 60 kbar [5]. Such properties can be interpreted on the basis of an electron hopping mechanism largely attributable to the equilibrium: $Pd^{II} + Pd^{IV} \xrightarrow{H.P.} 2Pd^{III}$.

Similar electronic transitions have been observed in $M^{II}Pd^{IV}F_6$ (M = Ni, Cu) or $M^{II}Pt^{IV}F_6$ (M = Ni, Cu, Pd) compounds [6].

This type of material could be used for measuring or calibrating gauges for high pressure systems.

STABILIZATION OF OXIDATION STATE+III IN SOME CRYOLITES AND A_2BMF_6 COMPOUNDS (A, B = alkali element ; M = Ni, Cu, Pd)

Although oxidation state +III can be easily obtained for other d elements, it appeared more difficult to stabilize for nickel, copper or palladium. We succeeded in preparing phases

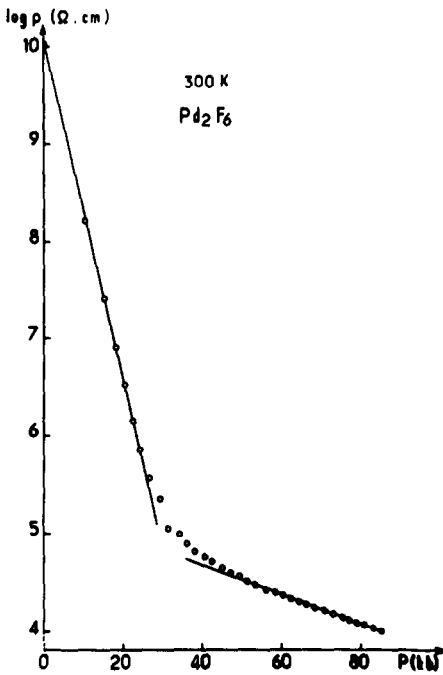


Fig. 1 : Piezoresistive behaviour of Pd_2F_6 at 300 K.

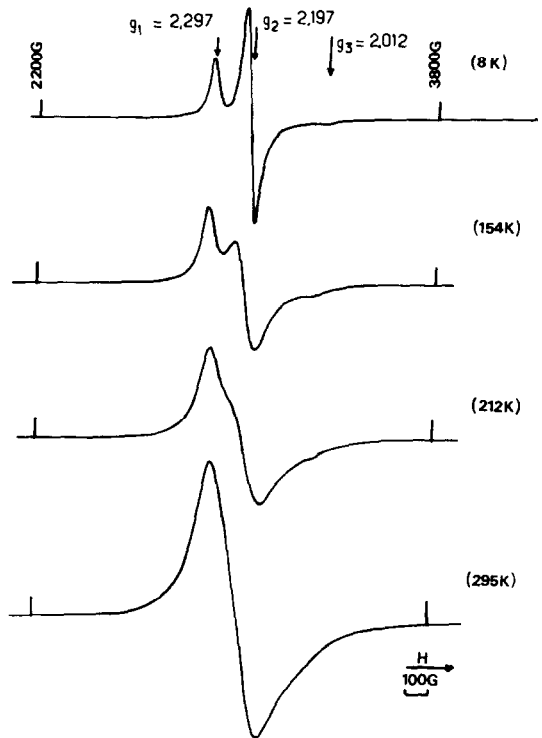


Fig. 2 : Variation of the Cs_2KPdF_6 ESR spectra with temperature.

which crystallize in the cryolite or elpasolite-type. Such structures are indeed very suitable, as the MF_6 octahedra are separated from each other by AF_6 octahedra.

Table II reports some of the fluorides involving two different alkali cations which crystallize in one structural type or the other.

For palladium there was no unequivocal evidence for Pd+III until recently due to a dismutation mechanism yielding preferentially the stable +II ($t_{2g}^6 e_g^2$) and +IV (t_{2g}^6) oxidation states - at least under normal pressure - as previously mentioned. Pd+III has been unambiguously obtained in elpasolites (Table II). The ESR spectra characterize a doublet ground state ; evidence is given of a $t_{2g}^6 e_g^1$ configuration. Fig. 2 illustrates for Cs_2KPdF_6 a transition

TABLE II

Ternary fluorides of cryolite and elpasolite types containing Ni+III, Cu+III or Pd+III.

Element	Ni	Cu	Pd
Cryolite-type	Na ₂ LiNiF ₆ [7] Na ₃ NiF ₆ [8]	Na ₂ LiCuF ₆ [7] Na ₃ CuF ₆ [9]	Na ₃ PdF ₆ [10]
Elpasolite-type	K ₂ NaNiF ₆ [12] Rb ₂ NaNiF ₆ [12] Rb ₂ KNiF ₆ [12] Cs ₂ KNiF ₆ [12]	K ₂ LiCuF ₆ [11] K ₂ NaCuF ₆ [13] Rb ₂ NaCuF ₆ [13] Rb ₂ KCuF ₆ [13] Cs ₂ KCuF ₆ [15] Cs ₂ RbCuF ₆ [15]	K ₂ LiPdF ₆ [10] K ₂ NaPdF ₆ (distorted) [14] Rb ₂ NaPdF ₆ (") [10] Rb ₂ KPdF ₆ (") [10] Cs ₂ KPdF ₆ (") [10] Cs ₂ RbPdF ₆ (") [10]

from a static Jahn-Teller effect (with an orthorhombic symmetry) to a dynamic one. Moreover Pd+III has been obtained in NaPdF₄, whose structure derives from KBrF₄ [16].

A similar $t_{2g}^6 e_g^1$ low spin configuration has been detected for Ni+III at low temperature by magnetic measurements. The variation of the Curie constant with increasing temperature might be due to a low spin \uparrow high spin transition; investigations on such behaviour are in progress [17]. On the contrary, Cu+III (d^8) presents in similar elpasolite phases a $t_{2g}^6 e_g^2$ high spin configuration in the whole measurement range.

STABILIZATION OF COBALT+IV OR COPPER+IV UNDER F₂ HIGH PRESSURE

Oxidation state +IV is very difficult to stabilize for the last elements of the 3d series. However it can be obtained with the K₂PtCl₆-type structure. The octahedra containing the transition element are here completely isolated from each other, which allows us to minimize the electrostatic repulsions. Bonding between fluorine and the alkali metal competes with that between fluorine and the transition element: therefore the synthesis of the Cs₂MF₆ phases is greatly facilitated thanks to the strong ionic character of the Cs-F bond.

Use of fluorine under high pressure is absolutely necessary to synthesize the M_2CoF_6 and M_2CuF_6 phases ($M =$ alkali metal). Co^{+IV} may already be obtained under 60 bar in the case of Cs or Rb [18, 19], but F_2 pressures of 250 bar are necessary for K [20]. Cs_2CuF_6 [21] and Rb_2CuF_6 [22] can only be isolated under 300 bar fluorine pressure.

MAGNETIC CLUSTERS IN PLATINUM-METAL PENTAFLUORIDES

Platinum metal pentafluorides of RhF_5 -type consist of closely packed M_4F_{20} tetrameric units [23]. In a tetramer, octahedral MF_6 groups share two corners in *cis*-position. Neutron diffraction and magnetic susceptibility data have clearly shown that the magnetic properties of RuF_5 and OsF_5 can be interpreted in terms of a tetranuclear cluster model over a large temperature range [24-26]. Comparison between experimental and calculated data is shown in Fig.3 for RuF_5 . The best fitting is obtained for an intracuster antiferromagnetic constant $J/k = -8.3$ K [24].

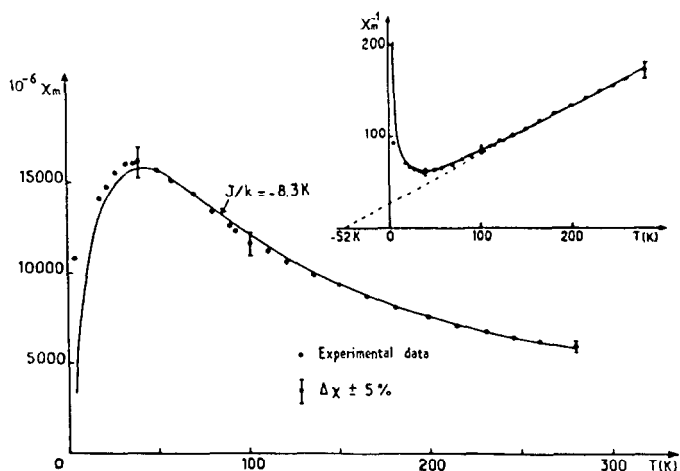


Fig. 3 : Thermal variation of the magnetic susceptibility of RuF_5 .

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