

# A new variety of PdF<sub>2</sub> synthesised by low-temperature reaction in anhydrous HF

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This work is dedicated to the memory of Dr. Karel LUTAR, deceased on 2 September 2000

## Abstract

A new variety of palladium difluoride has been prepared via a low temperature (LT) process in anhydrous hydrogen fluoride (aHF). Reaction between solutions of Pd(AsF<sub>6</sub>)<sub>2</sub> and CsF in aHF results in the precipitation of the light-brown LT form of PdF<sub>2</sub>. This phase crystallises in the *Pa*3 cubic space group with *a* = 532.4(1) pm and can be derived from the fluorite structure. The co-ordination of Pd is: 6F at 217.6(3) pm + 2F at 316.8(3) pm. The structural network can be described either as PdF<sub>8</sub> rhombohedra sharing edges — as MX<sub>8</sub> cubes in the fluorite — or as flattened PdF<sub>6</sub> octahedra sharing corners. Each F atom is common to 3 octahedra. The relationships with the fluorite and pyrite structures have been raised. LT-PdF<sub>2</sub> is antiferromagnetic, with a Néel temperature evaluated at around 180 K. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** PdF<sub>2</sub>; Divalent palladium; Transition element difluoride; Anhydrous HF; Fluorite; Pyrite; Antiferromagnetism

## 1. Introduction

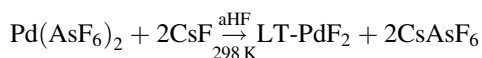
All MF<sub>2</sub> difluorides of transition elements crystallise in the rutile structure when prepared under normal pressure conditions [1,2]. This is the case for VF<sub>2</sub>, CrF<sub>2</sub>, MnF<sub>2</sub>, FeF<sub>2</sub>, CoF<sub>2</sub> and NiF<sub>2</sub> in the 3d transition element row and for PdF<sub>2</sub> which is the only stable difluoride among the 4d transition elements. It is also well known that CuF<sub>2</sub> and AgF<sub>2</sub> exhibit a distorted structure because of Jahn–Teller configuration of these elements in their d<sup>9</sup> state. In both fluorides the (MF<sub>6</sub>)<sup>4-</sup> octahedra are axially elongated with a 4 + 2 co-ordination number. On the other hand, the structural arrangement of many other difluorides with larger M<sup>2+</sup> cations is derived from the fluorite type, e.g. for M = Ca, Sr, Ba, Cd, Hg, Pb.

In the following, we describe the synthesis and magnetic properties of a new form of palladium difluoride which has been obtained via a low-temperature (LT) reaction at ambient pressure and whose structure is intermediate between the pyrite and the fluorite structural types.

## 2. Results and discussion

### 2.1. Synthesis of LT-PdF<sub>2</sub>

The slow mixing of solutions of Pd(AsF<sub>6</sub>)<sub>2</sub> and CsF in anhydrous hydrogen fluoride (aHF) gives light brown LT-PdF<sub>2</sub>, insoluble in aHF, following the reaction



Because of the higher solubility of CsAsF<sub>6</sub> in aHF thorough washing of the LT-PdF<sub>2</sub> precipitate with aHF allows to eliminate CsAsF<sub>6</sub>. X-ray powder diffraction pattern showed no detectable lines of CsAsF<sub>6</sub>. However, the presence of very small amounts of Pd and rutile-type form of PdF<sub>2</sub> were noticed in some cases. The presence of traces of Pd metal in the final product can be explained by an incomplete oxidation of Pd in the presence of fluorine and AsF<sub>5</sub> in aHF medium. Great care has to be taken while adding fluorine to the reaction mixture Pd/AsF<sub>5</sub>/aHF: a slight excess of fluorine only is required to oxidise Pd into Pd<sup>2+</sup>, otherwise the oxidation proceeds to Pd<sup>4+</sup> with the formation of in an aHF insoluble by-product Pd<sub>2</sub>F<sub>6</sub> (Pd<sup>II</sup>Pd<sup>IV</sup>F<sub>6</sub>), which can be formed instead of the desired solution of Pd(AsF<sub>6</sub>)<sub>2</sub> in aHF [3].

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It has been previously reported that clear-blue solutions of the Pd in  $\text{SbF}_5/\text{aHF}$  give a precipitate of lilac  $\text{PdF}_2$  when treated with solutions of alkali fluoride in aHF [4]. In these conditions, the obtained  $\text{PdF}_2$  was identified by its type X-ray powder diffraction pattern as the conventional rutile form. In our experiment the result of the mixing of solutions of  $\text{Pd}(\text{AsF}_6)_2$  and CsF in aHF gives mainly the fluorite-derived form and only traces of the rutile form are observed. A clear explanation of the difference between the reaction of  $\text{Pd}(\text{SbF}_6)_2$  with alkali fluoride in aHF one hand, and that of  $\text{Pd}(\text{AsF}_6)_2$  with alkali fluoride on the other hand has not been elucidated so far.

## 2.2. Structural determination of LT- $\text{PdF}_2$

The X-ray diffraction (XRD) pattern of the LT form of  $\text{PdF}_2$  is given in Fig. 1. All peaks can be indexed in the cubic symmetry, with an unit-cell constant of 532.4(1) pm, except four weak peaks which can be attributed to Pd metal ( $2\theta = 40.22$  and  $46.24^\circ$ ) and rutile  $\text{PdF}_2$  ( $2\theta = 25.41$  and  $32.00^\circ$ ) (Fig. 1). The XRD pattern of LT- $\text{PdF}_2$  has many similarities with those of fluorite-type patterns. The systematic extinctions correspond to  $Pa\bar{3}$  space group (no. 205). It is the first time that such characteristics are observed for a transition element difluoride prepared at ambient pressure. It can be noted that similar features had been previously obtained when  $\text{PdF}_2$  (or  $\text{AgF}_2$  [5]) was prepared under very

high pressures [6]. Transformation from the rutile-type structure started at about 15 kbar solid state pressure and more drastic conditions were required, e.g. reactions at 673 K and 50 kbar, to get fairly crystallised high pressure (HP) form of  $\text{PdF}_2$  [7].

The structural refinement of LT- $\text{PdF}_2$  has been carried out by analogy with the fluorite-type structure. Pd atoms occupy the 4a positions (0, 0, 0) and the F atoms are located in the 8c positions ( $x, x, x$ , with  $x = 0.3436(4)$ ). The final  $R$  values are  $R_1 = 3.34\%$ ,  $R_p = 7.71\%$ , and  $R_{wp} = 12.00\%$ . The isotropic displacement factors are  $B = 0.75(2) \text{ \AA}^2$  for Pd, and  $B = 1.41(9) \text{ \AA}^2$  for F atoms. The observed, calculated, and difference X-ray profiles are shown in Fig. 1. A representation of the structure is given in Fig. 2. The palladium atoms form a fcc network and are surrounded by six fluorine atoms as nearest neighbours at  $\text{Pd-F} = 217.6(3)$  (Fig. 2). In this octahedral configuration, the Pd-F distances are identical but the F-Pd-F angles differ from  $90^\circ$  ( $87.5^\circ$ ) leading to a flattened octahedra with two opposite faces much larger than the three other pairs. Two further fluorine atoms at  $\text{Pd-F} = 316.8(3)$  pm are located on each side of these larger triangular faces. The total co-ordination number of Pd is  $6 + 2$  and can be represented either as a regular rhombohedron or as a bicapped flattened octahedron (Fig. 3).

The structural network can be therefore described either as formed of edge-shared  $\text{PdF}_8$  rhombohedra, as  $\text{MX}_8$  cubes in the fluorite (see Fig. 3), or of distorted corner-shared

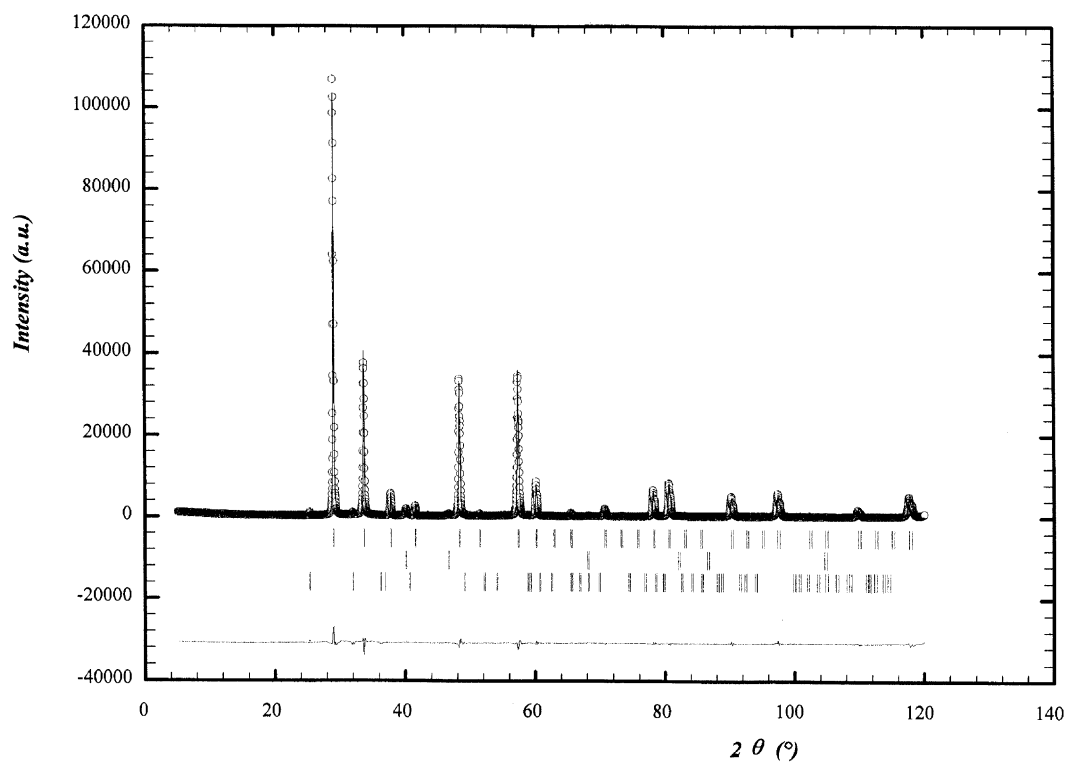
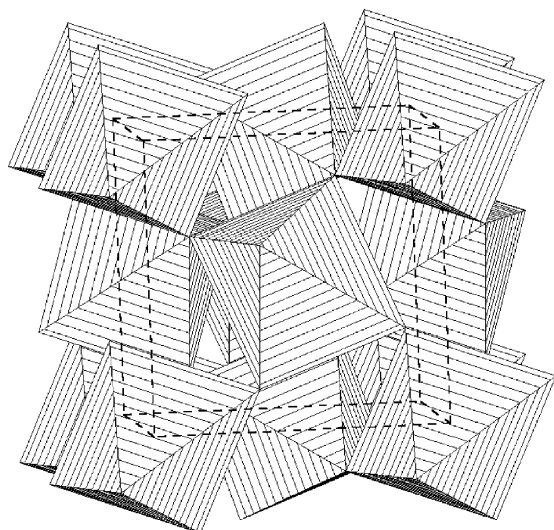
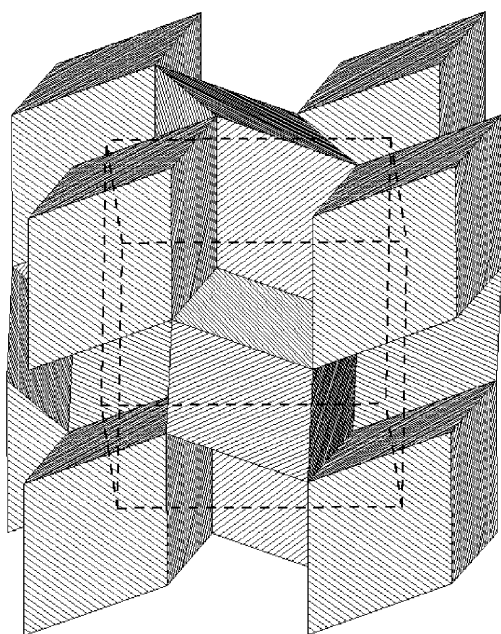
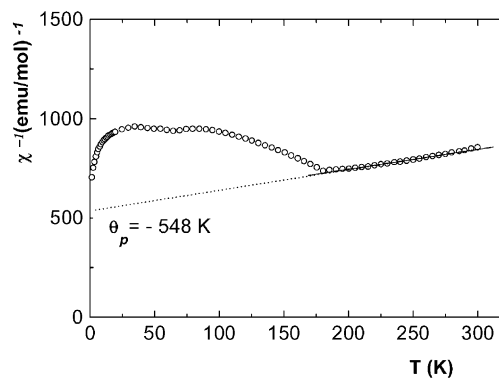


Fig. 1. X-ray profile of LT- $\text{PdF}_2$ : (o) experimental points; (full lines) calculated and difference profiles; vertical ticks: LT- $\text{PdF}_2$ , Pd metal, rutile- $\text{PdF}_2$ , successively.

Fig. 2. Network of PdF<sub>6</sub> distorted octahedra in the structure of LT-PdF<sub>2</sub>.Fig. 3. Network of PdF<sub>8</sub> rhombohedra in LT-PdF<sub>2</sub>.

octahedra. In this latter presentation, each fluorine atom would be shared by three octahedra, as shown in Fig. 2. The structure is thus intermediate between the fluorite type and the pyrite type. The anionic positions (8c sites) are indeed

Fig. 4. Temperature dependence of the reciprocal magnetic susceptibility of LT-PdF<sub>2</sub>.

intermediate with  $x = 0.25$  in the fluorite,  $x = 0.3436$  in LT-PdF<sub>2</sub>,  $x = 0.39$  in pyrite-type FeS<sub>2</sub>.

Both LT-PdF<sub>2</sub> and pyrite compounds crystallise in the same  $Pa\bar{3}$  space group with similar unit-cell constants. It is clear however that in the case of LT-PdF<sub>2</sub> no F–F pairs are found as for S–S pairs in the pyrite, and F–F distances between two octahedra exhibit usual bond lengths, i.e.  $\approx 280$  pm. Environments of M cations in various MX<sub>2</sub> structures are compared in Table 1.

### 2.3. Magnetic properties

The temperature dependence of the reciprocal susceptibility is shown in Fig. 4 for a LT-PdF<sub>2</sub> sample which could be obtained free of rutile-type impurity in very small amount. The general shape is consistent with an antiferromagnetic behaviour. A linear magnetic field dependence of the magnetisation is observed down to 4.2 K. No parasitic ferromagnetic component occurs, in contrast to that observed in the case of rutile PdF<sub>2</sub> [8]. The temperature corresponding to the minimum of reciprocal susceptibility is around 180 K, a value which is similar to the Néel temperature of HP-PdF<sub>2</sub> ( $T_N = 190$  K) determined from neutron diffraction data [7]. The Curie constant  $C_{\text{mol}} = 1$  can be deduced from the value of the paramagnetic Curie temperature:  $\theta_p = -548$  K, and that of room temperature reciprocal susceptibility:  $\chi_M^{-1} = 848$  emu at 300 K. This value is consistent with the  $S = 2/2$  electronic configuration (spin-only) of high-spin Pd(+II).

Table 1  
Environment of M<sup>2+</sup> cations in various MX<sub>2</sub> structures

Compound	Coordination number of M <sup>2+</sup> cation	Closest X–X distance (pm)
$\beta$ -HgO <sub>2</sub>	2 + 4: compressed octahedra	150 (O–O pairs)
PdS <sub>2</sub>	4 + 2: elongated octahedra	213 (S–S pairs)
FeS <sub>2</sub> (pyrite)	6: regular octahedra	217 (S–S pairs)
AgF <sub>2</sub>	4 + 2: elongated octahedra	286 [12]
PdF <sub>2</sub> (rutile)	6: regular octahedra	272 [13]
LT-PdF <sub>2</sub>	6 + 2: bicapped flattened octahedra	284 <sup>a</sup>

<sup>a</sup> This work.

### 3. Concluding remarks

In the transition-metal difluorides, the sequence of compactness is the following for a same cation: fluorite > LT-PdF<sub>2</sub> > rutile, and may explain why the obtained form is stabilised with respect to the rutile form via a LT process. It has been proposed that under high pressure conditions rutile-type fluorides reversibly transform into this structure in a first step and then into fluorite or  $\alpha$ -PbCl<sub>2</sub> structures [9]. It can be considered that this peculiar structural type appears only for divalent cations with anion radii intermediate between those of d transition elements and of bigger alkaline earth elements: Cd<sub>0.5</sub>Pd<sub>0.5</sub>F<sub>2</sub>, Mg<sub>0.5</sub>Pd<sub>0.5</sub>F<sub>2</sub>, high pressure forms of PdF<sub>2</sub> and AgF<sub>2</sub> [2].

### 4. Experimental

#### 4.1. Materials

Volatile materials (AsF<sub>5</sub>, aHF) were manipulated in an all-Teflon vacuum line equipped with Teflon valves. The manipulation of the non-volatile materials was done in a dry-box (M. Braun). The residual water in the atmosphere of the dry-box never exceeded 1 ppm. The synthesis of LT-PdF<sub>2</sub> was carried out in a T-shape FEP reaction vessel (i.d. 15.5 mm, o.d. 18.75 mm) equipped with two Teflon valves and Teflon coated stirring bars. An additional Teflon valve separated both arms of the T-shape reaction vessel. Prior to use, the reaction vessel was passivated with elemental fluorine.

CsF (Ventron, 99.9%) and Pd (Alfa Products, 99.9%) were used as supplied. Purity of CsF was checked by chemical analysis (obtained %F, 12.4; calculated %F, 12.51). AsF<sub>5</sub> was synthesised by pressure fluorination of arsenic trioxide with elemental fluorine in a nickel reactor at 573 K as previously described for the synthesis of PF<sub>5</sub> [10]. Fluorine was used as supplied (Solvay, 99.98%). Anhydrous HF (Praxair, 99.9%) was treated with K<sub>2</sub>NiF<sub>6</sub> for several hours prior to use.

#### 4.2. Reaction process

Synthesis of LT-PdF<sub>2</sub> was done several times in the same manner. Only one typical procedure is described. An amount of 0.261 g (2.45 mmol) of Pd was loaded in the dry-box into one arm and 1.100 g (7.24 mmol) of CsF into the other arm of a T-shape FEP reaction vessel equipped with two Teflon valves. aHF (10 ml) was then condensed onto CsF from a FEP reservoir containing K<sub>2</sub>NiF<sub>6</sub>. The Teflon valve separating both arms of reaction vessel was closed and 10 ml of aHF with 1.190 g (7.00 mmol) of AsF<sub>5</sub> were added onto Pd, both at 77 K. The reaction vessel was warmed up to 298 K and a approx. 2.60 mmol of fluorine was slowly added into the arm containing Pd, AsF<sub>5</sub> and aHF. Pd metal otherwise insoluble in aHF, slowly dissolved due to the presence of AsF<sub>5</sub>. The reaction was carried out at room temperature until a clear green-blue solution of Pd(AsF<sub>6</sub>)<sub>2</sub> [3] in aHF was obtained. The reaction vessel was cooled down on 77 K and volatile

components were pumped away. After warming the reaction vessel up to 298 K, the Teflon valve separating both tubes of the T-shape reaction vessel was opened and the solution of Pd(AsF<sub>6</sub>)<sub>2</sub> in aHF was slowly added in small batches to the solution of CsF in aHF. A dark solid immediately precipitated, which slowly changed to a light brown product. After 1 h of intensive stirring, the solution of CsAsF<sub>6</sub> in aHF was decanted away from the precipitate and aHF was condensed back onto the light brown solid at 77 K. After warming the reaction vessel to room temperature and 10 min of intensive stirring, the liquid phase was decanted again. This operation was repeated 25 times to eliminate CsAsF<sub>6</sub> from the light brown solid. Finally, volatile materials were pumped away at room temperature and the light brown material was recovered in one arm of the T-shape reaction vessel. The X-ray diffraction pattern of the light brown product showed that most lines corresponded to an original pattern having a cubic cell deriving from the fluorite type. Very weak lines of Pd metal and rutile-type form of PdF<sub>2</sub> were also identified in some cases.

The X-ray diffraction powder pattern of the brownish material isolated from the decanted solution gave only the pattern of CsAsF<sub>6</sub>; the colour indicated however the presence of a small amount of PdF<sub>2</sub>.

#### 4.3. X-ray diffraction (XRD) analysis

The XRD analysis was performed on powder samples using the Bragg–Brentano technique. Cu K $\alpha$  radiation was diffracted through a beam graphite monochromator with scan up to 120° with steps of 0.02° (2 $\theta$ ). Because of its high reactivity to moisture, the sample was set in an air-tight cell with Teflon O-rings and a mylar window. The powder was deposited onto the holder of the cell inside the glove box. Rietveld refinement of the XRD pattern was carried out using the FULLPROF program [11], and the pseudo-Voigt function  $PV = \eta L + (1 - \eta)G$  for diffraction line profile.

#### 4.4. Magnetic measurements

Cylindrical screw-capped sample containers ( $V \approx 0.5$  ml,  $m \approx 0.250$  mg) for magnetic measurements of PdF<sub>2</sub> were made of Kel-F (polytrifluorochloroethylene) and were additionally tightened with Teflon gaskets. Prior to their use, both the container and Kel-F packing tool were passivated with elemental fluorine. The field dependence of the magnetisation was measured between 0 and 5 T for various temperatures in the 4.2–300 K range using a SQUID magnetometer (MPMS-5S, Quantum Design).

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