

Pressure-induced transformations of $\text{Ag}^{\text{II}}\text{F}_2$ —towards an ‘infinite layer’ d^9 material

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Abstract

The enthalpy of seven polymorphs of AgF_2 has been scrutinized up to 50 GPa using density functional theory (DFT) calculations. We show that $\alpha\text{-Ag}^{\text{II}}\text{F}_2$ (*Pbca*, with its puckered-sheet structure and an elongated octahedral $4 + 2$ coordination of Ag) transforms above 15 GPa into a layered polymorph δ (*Abma*). The Jahn–Teller effect persists and the coordination of $\text{Ag}(\text{II})$ is of the $4 + 4$ type; the Ag–F–Ag bridges are bent. Cubic γ structure of the CaF_2 type (*Fm $\bar{3}m$*), and its *Pa3* variant (η), rutile (ζ), and tetragonal ‘infinite chain’ *P4mm* structure related to AgFBF_4 (ε) are not preferred in the entire pressure window that was investigated. Electronic structure of high-pressure $\delta\text{-Ag}^{\text{II}}\text{F}_2$ form shows features that are characteristic for two-dimensional (2D) materials, a prerequisite for high- T_{C} superconductivity.

Our calculations also suggest that experimentally observed high-temperature $\beta\text{-AgF}_2$ (*Imcm*, disproportionated, i.e. a charge-density-wave form, $\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{F}_4$) is indeed metastable; it is slightly endothermic compared to $\alpha\text{-Ag}^{\text{II}}\text{F}_2$.

This contribution is dedicated to Professor Andrzej Sadlej, eminent Polish quantum chemist, on the occasion of his 65th birthday

1. Introduction

About one hundred fluorides of divalent silver (Ag^{2+}) are known [1]. The majority of these unique materials have been synthesized over many years in three laboratories *only* (Hoppe and Müller in Giessen, Germany; Žemva in Ljubljana, Slovenia; Bartlett in Berkeley, USA).

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They are poorly known even to inorganic chemists, and unsatisfactorily described in chemistry textbooks. Due to the enormously large electron affinity of⁴ Ag^{2+} , these compounds are capable of oxidizing ‘noble’ gas Xe, and incandescently react with elemental metals; they corrode the surfaces of gold or platinum as well. Fluorides of trivalent silver (Ag^{3+}) are even rarer, due to their unprecedented oxidizing properties. They can be obtained only by the action of large pressures of gaseous F_2 [2] or of photochemically generated F radicals in anhydrous HF [3]. All of them decompose easily upon heating, liberating elemental fluorine:



In the reaction equations above, we have underlined the species which bear *one hole* in their valence subshell (Ag^{2+} , d^9 ; F^0 , s^2p^5).

This spectacular, thermally induced depopulation of 2p valence states of F^- (recollect, it is *the* least oxidizable anion available in chemistry) has unleashed a series of investigations. Grochala and Hoffmann [1] have argued that the Ag–F bonding in higher fluorides of silver must be substantially covalent, a result which was later confirmed by x-ray photoelectron spectroscopy (XPS) measurements [4] and by independent *molecular* [5] and periodic crystal calculations [6]. They have also postulated—based on a multitude of qualitative and semi-quantitative arguments—that properly doped fluorides of Ag^{2+} might exhibit metallic conductivity and/or high-temperature superconductivity [1]. Indeed, Meissner–Ochsenfeld anomalies have been postulated for an unknown impurity in the $\text{AgF}_2/\text{BeF}_2$ system [7].

The recent experimental study of Cs_2AgF_4 [8] has revitalized interest in layered fluorides of Ag^{2+} . The structure of this 2D fluoride is related to that of the first oxocuprate superconductor, $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ [9]. Cs_2AgF_4 is built of flat $[\text{AgF}_2]$ sheets intercalated by two $[\text{CsF}]$ layers, but the Ag–F bond pattern within the sheet is different from the analogous pattern seen in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. Cs_2AgF_4 is a strongly correlated material; it exhibits ferromagnetism below 15 K with a negative—and appreciable—superexchange constant of ~ 50 K [8]. It has been suggested that this compound might be transformed to the $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ structure type by the use of external pressure [9], with the concomitant appearance of antiferromagnetic ordering.

Triggered by the results of [8, 3, 9], we recently compared the band structure of a hypothetical difluoride of Ag(II) with flat $[\text{AgF}_2]$ sheets, with the known band structure of CaCuO_2 , an infinite layer compound [10]. A difluoride of Ag(II) with flat $[\text{AgF}_2]$ layers might possibly be obtained from genuine binary $\alpha\text{-AgF}_2$ (with its puckered sheet structure; figure 1(a)) via (i) the intercalation of various oxidation-resistant Lewis bases between the sheets, with the concomitant flattening of $[\text{AgF}_2]$ layers, or (ii) by applying external pressure [9]. Our calculations have shown that the electronic structure of $[\text{AgF}_2]$ is strikingly similar to that of CaCuO_2 [4]; the latter is the parent compound for a series of hole- or electron-doped oxocuprate superconductors.

In this contribution we deliver theoretical evidence that another layered polymorph of AgF_2 (δ) might be obtained by applying modest external pressure (> 15 GPa, or 150 000 atm) to the orthorhombic $\alpha\text{-AgF}_2$. The subsequent pressure-induced metallization of $\delta\text{-Ag}^{\text{II}}\text{F}_2$ is of interest for a possible generation of superconductivity in this genuinely 2D structure [11]⁵.

⁴ The second ionization potential of Ag (21.5 eV) is the largest among all metallic elements in the periodic table, except for the alkalis. It is only 7% smaller than that of Cs (23.2 eV).

⁵ The theoretical search for superconductivity in 2D structures is now progressing rapidly in many laboratories worldwide. For two examples, see [11].

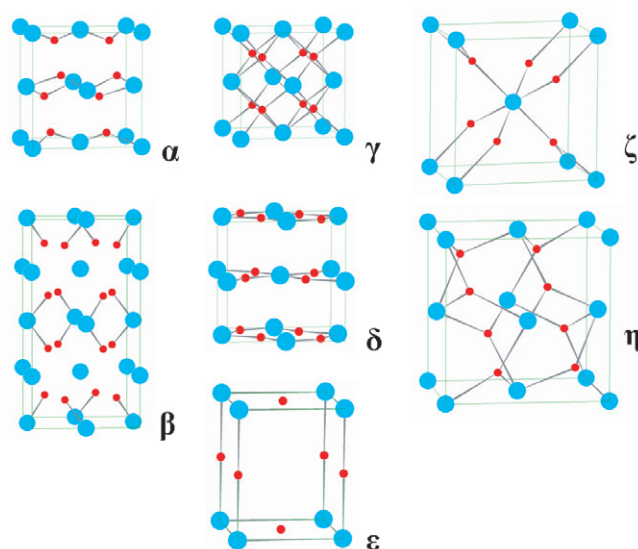


Figure 1. View of the unit cells (at a pressure of 0 GPa) of seven polymorphs of AgF_2 : α —low-temperature and low-pressure orthorhombic form ($Pbca$, No. 61), which is a spin-canted ferromagnet; β —a charge density wave (disproportionated) high-temperature form ($Imcm$, No. 140), which is diamagnetic; γ —a hypothetical CaF_2 -type cubic form ($Fm\bar{3}m$, No. 225); δ —a hypothetical orthorhombic polymorph with flat $[\text{AgF}_2]$ sheets ($Abma$, No. 64); ϵ —a hypothetical $[\text{AgF}^+](\text{F}^-)$ ‘infinite chain’ polymorph ($P4mm$, No. 123); ζ —a hypothetical TiO_2 -type tetragonal form ($P4_2mm$, No. 136); η —a hypothetical CdPdF_4 -type cubic form ($Pa3$, No. 205). Silver atoms are in blue; fluorine atoms in red.

2. Computational details

Our calculations were performed by means of the CASTEP code [12], employing DFT theory with the Perdew–Burke–Ernzerhof correlation-exchange potential, ultrasoft Vanderbilt pseudopotentials for the atomic cores, and the plane-wave basis for the valence electrons with a typical energy cutoff of 600 eV. A typical k -point grid of about 0.05 \AA^{-1} (volume-independent setting) was used; subsequent single-point calculations for such pre-optimized cells, but utilizing a denser k -point grid, gave a similar ordering of polymorphs in the energy scale. Spin polarization was neglected, since the calculations of [6] indicated only a marginal energy decrease (0.003 eV/Ag atom) in the spin-polarized description of Cs_2AgF_4 , a ternary fluoride of silver(II).

Our enthalpy optimizations (at 0 K and a pressure in the range 0–50 GPa) were performed for the conventional unit cells (i.e. those indicated in the respective space-group symbols); the only exception was the beta form of AgF_2 at elevated pressures, where a primitive cell was employed to speed up the calculations (this approach was validated in a comparative calculations for 0 GPa).

3. Results and discussion

3.1. Polymorphs of AgF_2

We begin our discussion by introducing the reader to the known and hypothetical forms of AgF_2 .

The binary fluoride of divalent silver is known experimentally in its ferromagnetic insulator α form (figure 1(a)), α -AgF₂. It crystallizes in an orthorhombic form, adopting the structure type related to that of its lighter congener, monoclinic CuF₂. [AgF₂] sheets are puckered in this compound, and each Ag is coordinated horizontally by four nearly equidistant F atoms (at 2.068–2.074 Å; experimental data [13]). There are two additional apical contacts at 2.584 Å; the distortion of the elongated AgF₆ octahedron is substantial, i.e. the Jahn–Teller effect is very strong⁶. The unit cell volume ($Z = 4$) is 165.61 Å³, which translates to 41.40 Å³ per formula unit. However, the computed volume of one formula unit is as much as 10% larger (45.76 Å³). Slight overestimation of the Ag–F bond lengths is, of course, typical for general gradient approximation (GGA) calculations, but the discrepancy must originate from the deficiency of classical the DFT treatment of weak (inter-sheet) interactions of layered AgF₂.

Below 165 K, paramagnetic brown α -AgF₂ becomes a spin-canted ferromagnet (which is seen in the magnetic susceptibility, but also in microwave cavity resonance measurements [14]), but this transition does not have any immediate structural consequences.

The reaction in anhydrous HF between salts of Ag¹⁺ and AgF₄^{1−} has allowed for the formation of the metastable red-brown diamagnetic β phase, which is believed to be simply Ag^IAg^{III}F₄ [15] (figure 1(b)). Its crystal structure could not have been determined, but β polymorph most likely adopts the KBrF₄ structure type, which is typical for all MAg^{III}F₄ salts (M = Li . . . Cs). Notably, β -AgF₂ transforms exothermically to α -AgF₂ on cooling, which is direct evidence of its stoichiometry. In this structure, Ag¹⁺ is surrounded by eight equidistant Fs, while Ag³⁺ adopts its much preferred square tetragonal coordination within the AgF₄^{1−} moiety.

In the present study we take into account several other structures, which might possibly be adopted by AgF₂ at elevated pressures.

One of them is of cubic CaF₂-type, which we will further denote γ (figure 1(c)). This structure type has been chosen for computation because of the resemblance of orthorhombic α -AgF₂ to cubic CaF₂ structure type. The unit cell vectors of α -AgF₂ are quite similar to each other (5.10, 5.57, 5.83 Å), while the heavy atoms are in special positions (0.0, 0.0, 0.0 and 0.5, 0.5, 0.0) for both structures. In addition, Ag is 8-coordinated in the γ polymorph, and γ is more densely packed than α ; these features might suggest that, at high pressures, the γ form might take over α in terms of enthalpy. Indeed, the calculated unit cell volume of γ -AgF₂ is 161.18 Å³ (at 0 GPa), which yields 40.30 Å³ per formula unit; this is much less (by 12%) than that computed for α -AgF₂.

We also consider the orthorhombic δ form (figure 1(d)) in our analysis. This form is strictly related to α -AgF₂, but it contains flat (and not puckered) [AgF₂] sheets. As will become clear from section 3, the importance of this polymorph has become apparent while studying the behaviour of α -AgF₂ under compression. The calculated unit cell volume of δ -AgF₂ is as large as 190.33 Å³, i.e. 47.58 Å³ per ‘AgF₂’ formula unit (at 0 GPa). This is more than the analogous values for α - and γ -AgF₂, but a caveat is necessary here: δ -AgF₂ has large van der Waals spacings, so its volume will be severely overestimated by DFT.

Another polymorph that is taken into account is the tetragonal ε form (figure 1(e)). In proposing the structure of this polymorph we have been inspired by the frequent appearance of Ag²⁺ in the ligand environment of a compressed octahedral type, especially if infinite AgF⁺ chains are present. Indeed, the optimized structure of ε -AgF₂ (at 0 GPa) reveals two short bonds (2.043 Å) and four long bonds (2.360 Å). The inverse Jahn–Teller effect is very strong in this structure⁷. The ε polymorph is analogous to [AgF⁺](BF₄[−]) [16], and it might formally

⁶ The Jahn–Teller distortion ratio, D , reaches 1.25 (see [19]).

⁷ The Jahn–Teller distortion ratio, D , reaches 0.87 (see [19]).

be written as $[\text{AgF}^+](\text{F}^-)$.⁸ The calculated volume of $\varepsilon\text{-AgF}_2$ is 45.50 \AA^3 per formula unit (at 0 GPa), which is slightly less than for $\delta\text{-AgF}_2$.

We have also considered the rutile (TiO_2) type, denoted here as $\zeta\text{-AgF}_2$. The optimized structure contains two short (2.099 \AA) and four longer (2.317 \AA , bridging) Ag–F contacts, at a volume of 45.67 \AA^3 per formula unit (at 0 GPa). As we will see, the rutile structure will prove noncompetitive in terms of enthalpy over the entire pressure range.

The last structure considered in this work, $\eta\text{-AgF}_2$ (CdPdF_4 structure type), has been suggested by experimental studies of AgF_2 under compression, performed over quarter of century ago [17]. This is the only experimental study of AgF_2 at high pressure in the literature. $\alpha\text{-AgF}_2$ has been subjected to modest pressures of up to 6 GPa, and the formation of a metastable $Pa3$ polymorph has been claimed, similar to the high-pressure form of PdF_2 [17]. The unit cell vector of 4.88 \AA has been derived for a cubic $\eta\text{-AgF}_2$ structure relaxed back to 1 atm.

The formation of a metastable $Pa3$ polymorph is very surprising for several reasons:

- (i) in this structure, Ag^{2+} would attain the ligand environment of a nearly undistorted octahedron; this is very suspicious, provided that a $4d^9$ system is subject to a very strong Jahn–Teller effect [19];
- (ii) the claimed unit cell volume per formula unit is as small as 29.05 \AA^3 for this polymorph, i.e. this is 30% less than for related $\alpha\text{-AgF}_2$; phase transitions characterized by such a huge volume drop are a rarity among transition metal compounds;
- (iii) the suggested unit cell vector of cubic $\eta\text{-AgF}_2$ is *much* smaller than for the cubic high pressure form of PdF_2 (5.32 \AA), despite the fact that the electron-rich $\text{Ag}^{2+} d^9$ cation has slightly larger volume than a high- or a low-spin $d^8 \text{Pd}^{2+}$;
- (iv) we are also surprised by the relative lack of sensitivity of the value of Curie temperature on the structure type adopted by AgF_2 (orthorhombic, 163 K; cubic, 160 K) [17]⁹.

Despite these doubts, we have decided to take the $\eta\text{-AgF}_2$ ($Pa3$) polymorph into calculations. The optimized unit cell vector of cubic $\eta\text{-AgF}_2$ is 5.494 \AA , which is much larger than the claimed value of 4.88 \AA . Nevertheless, the structure of $\eta\text{-AgF}_2$ is still pretty compact, the volume of one formula unit being as small as 41.47 \AA^3 (which is only 3% more than that of the γ (CaF_2) form). The shortest F \cdots F contacts are at 2.62 \AA , which is less than the sum of the van der Waals radii of two F atoms (2.94 \AA), indicating a modest bonding (pairing) interaction.

The choice of polymorphs considered in this study does not, of course, saturate the spectrum of all possible structures, which an AB_2 -type compound might adopt under high pressure¹⁰. However, it takes into account all bonding environments which predominate in the chemistry of Ag^{2+} (tetragonal, elongated octahedral, compressed octahedral [19]) or are as yet unknown (quasi-cubic), and a broad selection of possible arrangements of these units, which leads to a variety of more or less compact structures. Therefore, provisionally adopting the conclusions from the present work, more bonding patterns might be generated and tested in the future (in particular, those that are achievable via angular distortions of the structures studied here). Indeed, we plan to extend this study soon, while using efficient structure–prediction algorithms [20].

⁸ An alternative view would emphasize its intercalate-like composition with the alternating $[\text{AgF}^+]$ and $[\text{F}^-]$ layers, but such a choice of building blocks does not reflect its one-dimensional nature.

⁹ The reduction in magnetic moment, from $1.07 \mu_B$ to $0.94 \mu_B$ (at 250 K), might be an artifact, and related to the appearance of a diamagnetic AgF impurity. In our own recent attempts to compress AgF_2 , we have detected lots of AgF (which is a product of chemical or photochemical reaction inside the diamond anvil) [18].

¹⁰ Valuable suggestions might arise from studies of the high-pressure behaviour of related CuF_2 ; unfortunately, to the best of our knowledge, this has not yet been studied.

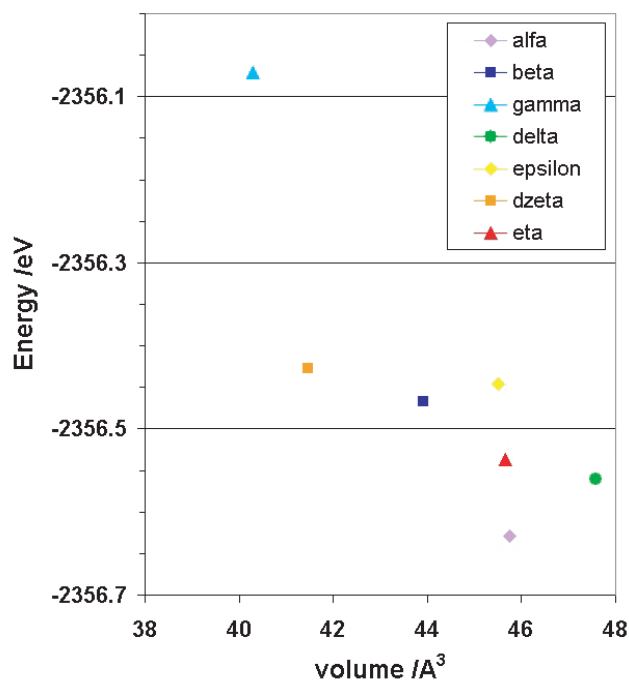


Figure 2. Plot of the calculated energies (E) versus unit cell volumes (V) at 0 GPa, for seven polymorphs of AgF_2 , i.e. the experimental α structure, and six hypothetical structures: β (CsAgF_4 -type), γ (CaF_2 -type), δ (infinite-layer-type), ε (infinite-chain-type), ζ (rutile) and η (fluorite variant). E and V are per AgF_2 unit.

Table 1. The calculated energies, E , and volumes, V , per formula unit, for the seven polymorphs of AgF_2 considered in this work. Entries are for 0 GPa, 0 K.

Polymorph	E (eV)	V (\AA^3)
α	-2356.63	45.76
β	-2356.47	43.92
γ	-2356.07	40.30
δ	-2356.56	47.58
ε	-2356.45	45.51
ζ	-2356.54	45.67
η	-2356.43	41.47

The calculated energies and volumes (per formula unit) of all polymorphs considered here are shown in figure 2, and collected in table 1. The structural data is contained in the *ESD*.

A preliminary analysis, based only on the energies and unit cell volumes of all polymorphs, indicates that:

- (i) α is indeed the lowest-energy polymorph at 0 GPa;
- (ii) γ and η types have unit cell volumes that are significantly smaller than that for α , therefore γ and/or η are likely to outperform α in enthalpy when at sufficiently high pressure;
- (iii) β , δ , ε and ζ , which are not equally compact, should stay relatively high in enthalpy;

(iv) conclusions (ii) and (iii) should hold only if the compressibilities of all polymorphs are comparable to each other.

Hypotheses (ii) and (iii) obviously require confirmation by quantum mechanical calculations as a function of external pressure. As we will see in section 3, and to some surprise, they will prove wrong. But before we pass to the analysis of computational results, we would like to stop for a while at an interesting, high-temperature charge density wave β phase.

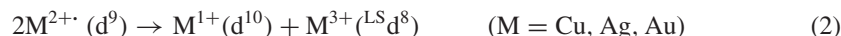
3.2. Metastable, high-temperature, charge density wave β phase

We have optimized the crystal structure of the diamagnetic β -AgF₂, assuming that it adopts the CsAgF₄ (i.e. KBrF₄) structure type. The reasons for this assumption are pretty straightforward: (i) this structure type is preferred for all alkali metal tetrafluoroargentates and even for $\square_{1/2}\text{Ba}_{1/2}\text{AgF}_4$, where \square stands for a vacancy; and (ii) the ionic radius of Ag¹⁺ is pretty similar to that for Na¹⁺, so the compounds of monovalent silver and sodium are most often isostructural (e.g. NaCl–AgCl).

The calculated Ag¹⁺...F[−] contacts are 2.478 Å, while the Ag³⁺–F[−] bond lengths are 2.014 Å. The Ag³⁺–F[−] bond lengths are much *longer* than the ones found for the majority of Ag^{III} compounds (1.89 Å). On the other hand, the Ag¹⁺...F[−] contacts (recollect, Ag is 8-coordinated) are nearly identical to those found for binary Ag¹⁺F (with its 6-coordinated Ag, 2.476 Å). This means that the predicted Ag¹⁺...F[−] distance is now *too short*, since: (i) the cubic ionic radii are always larger than the octahedral ionic radii, and (ii) Ag³⁺ is an extremely strong Lewis acid, so it tries not to share its four F[−] anions (this implies that Ag¹⁺...F[−] contacts *should* be longer than in the binary Ag¹⁺F Lewis base).

These results clearly point to the deficiency of DFT in treating the mixed valence phases; DFT optimization leads to the oxidation states being more uniform than they should really be. Indeed, the Mulliken charges on Ag¹⁺ and Ag³⁺ are +0.78 *e* and +1.08 *e*, respectively (see also ESD for more details).

The disproportionation of d⁹ ions:



poses a highly interesting problem: in the gas phase, the energy of this transformation, calculated by using the respective ionization potentials [21], amounts to +3.98 eV, −0.56, and −1.76 eV (for Cu, Ag, and Au, respectively). The observed trend is related to a decreasing stability of the second oxidation level when going from Cu to Au (genuine Au²⁺ compounds are very difficult to obtain). The above disproportionation is found in some Ag compounds: AgO is in fact Ag¹⁺Ag³⁺O₂ [1], while AgF₂ is only slightly more stable than Ag¹⁺Ag³⁺F₄; see below. However, for two isolated ²Σ_g AgF₂ molecules, disproportionation (2) is forbidden (the corresponding energy is calculated to be +4.02 eV [5]).

It is tempting to relate the energy of reaction (2) to the on-site electronic repulsion parameter *U* of the Hubbard model [22]. For Ag²⁺ and Au²⁺ one would get *U* < 0, which fits the ‘negative-*U* scenario of superconductivity’ proposed by some theorists [23]. However, one should remember that Hubbard’s *U* corresponds to the repulsion energy of two electrons with antiparallel spins occupying the same orbital, while the energy of reaction (2) may be related to the repulsion of two electrons with parallel spins occupying two different d orbitals.

In our calculations, the Ag¹⁺Ag³⁺F₄ (β) form is predicted to have an enthalpy 0.03–0.17 eV per Ag higher than that for the Ag²⁺F₂ (α) form¹¹. This means that β -AgF₂ is a

¹¹ A value of 0.03 eV is calculated from the enthalpies of both phases achieved during the last step of cell optimization; a value of 0.17 eV is based on subsequent more precise calculations of energy and pressure with the use of a denser *k*-point grid. Optimizations using the primitive cell of β -AgF₂ also result in values in the 0.03–0.17 eV range.

metastable high-temperature polymorph, which exothermically transforms to the α phase, in full agreement with experiment [15]. However, taking into account our previous conclusions on the subtle failures of DFT, one should expect that the precise value of the enthalpy difference between the two phases may in fact differ from the one calculated here.

Concluding this section, we note that DFT calculations provide reasonable insight into the energetics of transformation (2), but they are incapable of correctly predicting the minor structural details of the mixed-valence phase β .

3.3. Pressure-induced phase transitions and the decomposition curve of AgF_2

It is of utmost interest whether any hypothetical structures of AgF_2 (β , γ , δ , ε , ζ , η) might outperform the α form in terms of enthalpy, if silver difluoride is compressed, for example in the diamond or ruby anvil cell. Among these phases, the disproportionated one (β) is unlikely to gain importance at high pressure (as is typical for disproportionated systems at moderate pressures [24]), yet for completeness we will not discard it from the forthcoming considerations.

The calculated enthalpy of all polymorphs of AgF_2 (with respect to α) as a function of pressure (up to 50 GPa), and the decomposition curve for the reaction [25]¹²:



are jointly shown in figure 3.

As may be seen from figure 3, β -, γ -, ε -, ζ -, and η - AgF_2 are *not* competitive in terms of enthalpy up to 50 GPa. However, the δ phase takes over the α phase at pressures as low as 15 GPa. At larger pressures, enthalpies of δ - and α - AgF_2 merge into each other, for these phases are, in fact, indistinguishable above 30 GPa.

The lack of preference for the compact γ type and the good performance of δ - AgF_2 are surprising in the context of molar volumes of these phases at 0 GPa (recollect, γ is the most densely packed polymorph at 0 GPa; see section 1). Apparently, the 2D δ polymorph, equipped with the weak inter-sheet van der Waals interactions, exhibits significant compressibility, and at 15 GPa it actually achieves smaller unit cell volume than the γ form. A too large unit cell volume of δ - AgF_2 at 0 GPa is to some extent an artifact, i.e. due to improper treatment of the weak inter-sheet interactions by DFT calculations.

Concluding this section, we note that α - AgF_2 might undergo a smooth transition to the ‘infinite-layer’ δ structure in the vicinity of 15 GPa.¹³ The volume change associated with this transition is null, within the computational error. Most importantly, for any prospective experiments in a diamond anvil cell, AgF_2 should *not* decompose to AgF and elemental F_2 when a high pressure is on [25]. Partial decomposition (with the formation of phases like $\text{Ag}^1+\text{Ag}^2+\text{F}_3$ or $\text{Ag}_2^1+\text{Ag}^2+\text{F}_4$), also seems very unlikely.

3.4. Crystal structure and interesting elastic properties of $\delta - \text{AgF}_2$

It is desirable to analyse the crystal structure of δ - AgF_2 , and its response to external pressure.

At 0 GPa the calculated unit cell vectors are 5.71, 5.83 and 5.71 Å. The coordination of Ag^{2+} is not far from tetragonal, with four nearly equal short Ag–F contacts (2×2.08 Å and 2×2.09 Å) and four inter-sheet distances of 3.28 Å (figure 4). The $[\text{AgF}_4]$ square is, however, substantially angularly distorted; the Ag–F–Ag angle is 150.7° , mid-way between the linear

¹² We have taken into account the ambient-temperature C-centred monoclinic α - F_2 phase, and we have assumed no phase transitions for the products of reaction (3) (see footnote 13).

¹³ A careful search for other candidates for high-pressure structures is now being conducted in our laboratory.

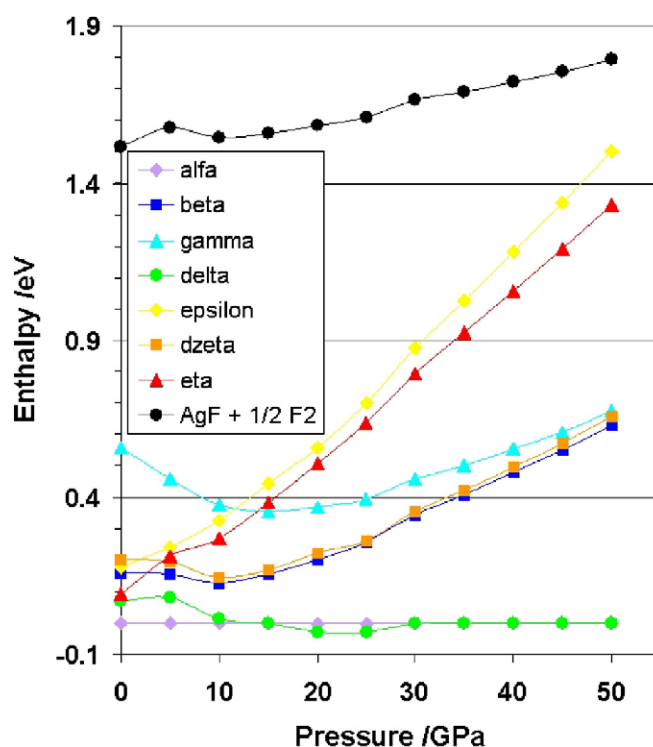


Figure 3. Plot of the calculated enthalpy (H) versus pressure (p) (in the pressure range 0–50 GPa) for seven polymorphs of AgF_2 , i.e. experimental α structure and six hypothetical structures: β , γ , δ , ϵ , ζ and η . The decomposition curve of AgF_2 (onto AgF and $\frac{1}{2}\text{F}_2$) is also shown. The enthalpy of α - AgF_2 has been set to zero for every pressure value. Note that the δ - AgF_2 becomes preferred above 15 GPa, but then merges smoothly with α - AgF_2 . H is per AgF_2 unit.

(sp) and sp^2 fluorine bridge. Partly due to this angular distortion, δ - AgF_2 is not identical to a genuine ‘infinite layer’ model structure studied previously [10], but—as we will see in section 5—it is still similar to it via a strong 2D character. The shortest (intra-sheet) $\text{F} \cdots \text{F}$ contact is 2.95 Å, which is slightly larger than the sum of the van der Waal’s radii of F atoms (2.94 Å).

Compression up to 50 GPa significantly changes all interatomic separations. Now the unit cell vectors are 4.49, 4.20 and 6.04 Å. There are still four F atoms in the first coordination sphere of Ag^{2+} (2×2.02 Å, 2×2.06 Å) but another four secondary separations become shorter, down to 2.4 Å, and the coordination of a transition metal might be considered ‘distorted cubic’ by some. Note that the intra-sheet distances are reduced by ~ 1.5 – 3.3% *only* at a 500 000 atm, which is testimony to a very small compressibility of the Ag–F bonds (see *ESD*). The plasticity of the coordination sphere of a Jahn–Teller d^9 Ag^{2+} , albeit seen in various chemical compounds of this cation [19], can hardly be violated by the use of high pressure; Ag^{2+} is a very *hard* species, in the Pearson’s sense. Also, the Jahn–Teller effect stubbornly persists at high pressures.

The angular distortion of the $[\text{AgF}_4]$ square is even more severe at 50 GPa than at 0 GPa; the Ag–F–Ag angle is now 134.3°. Clearly, the δ structure responds to increased pressure by bending the fluoride bridge, and better exposing the sp^2 -like lone pair on the F centre. The covalent Ag–F bond must lose its ionic component upon squeezing. The shortest $\text{F} \cdots \text{F}$ intra-sheet contacts are now 2.31 and 2.42 Å; the bonding $\text{F} \cdots \text{F}$ interaction is still weak.

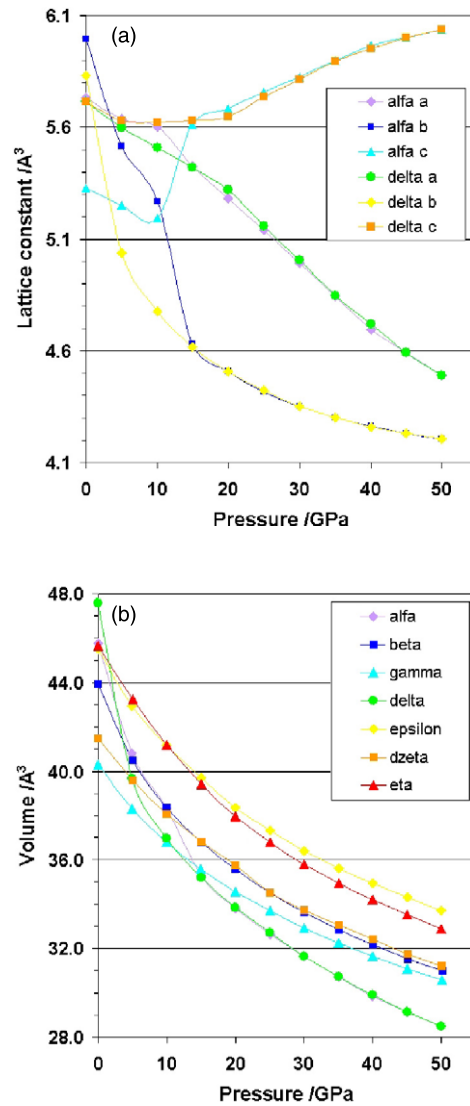


Figure 4. (a) Dependence of the unit cell vectors ((a), (b), (c)) versus pressure (p) for two polymorphs of AgF₂: α and δ . Note the progressive diminution of the unit cell vectors parallel to the [AgF₂] sheets (a and c for α ; a and b for δ), and the initial diminution, followed by expansion, of the unit cell vector perpendicular to the [AgF₂] sheets (b for α ; c for δ). Above 30 GPa, both polymorphs are virtually identical to each other. (b) Dependence of the unit cell volume (V) versus pressure (p) for seven polymorphs of AgF₂ (α , β , γ , δ , ϵ , ζ and η). Note the large compressibility of the 2D δ polymorph, with weak inter-sheet van der Waals interactions; at 15 GPa, δ achieves a smaller unit cell volume than the γ form (which, in turn, is the most densely packed polymorph at 0 GPa).

Remarkably, one out of three unit cell vectors (c) is larger at 50 GPa than at 0 GPa. Compression in the direction perpendicular to the [AgF₂] sheets (b) generates some in-plane relaxation, possibly due to the electron-rich nature of AgF₂, and the associated lone pair–lone pair repulsion. This interesting feature of δ -AgF₂ has been confirmed in explicit calculations of its elastic constants and Poisson ratios (see *ESD*).

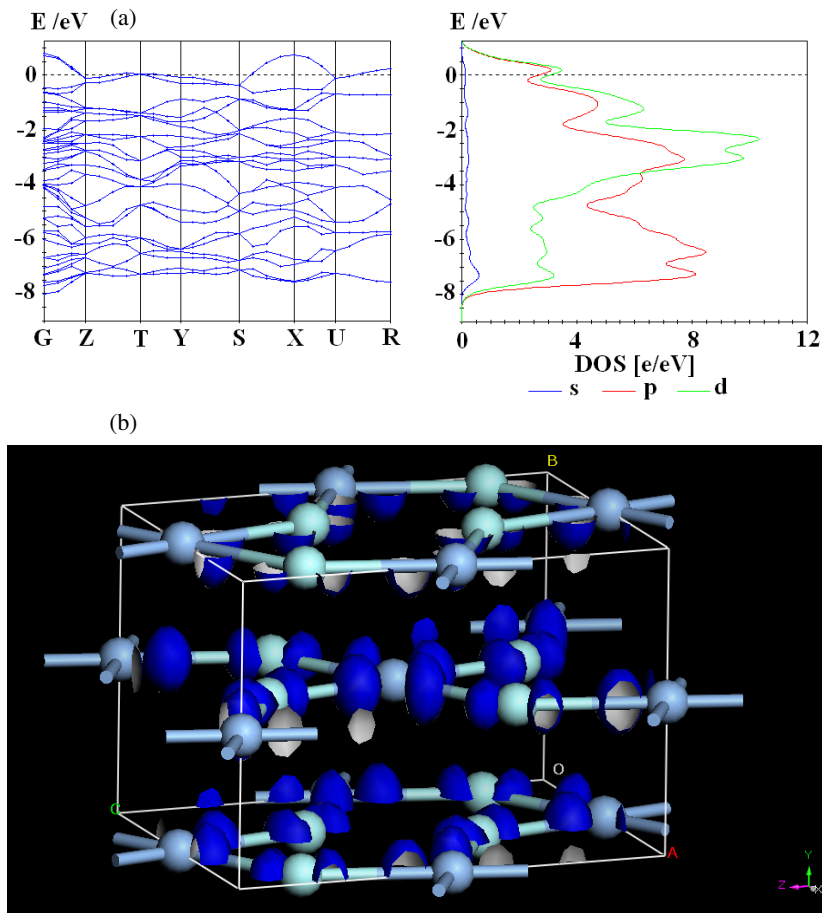


Figure 5. (a) Electronic band structure and density of states for δ -AgF₂ at 50 GPa. The division of DOS into atomic contributions (Ag, 2F) is also shown. (b) Electron density integrated over the last band, which crosses the Fermi level. Note the predominant contribution from the $d(x^2 - y^2)_{\text{Ag}}$ and $p(x, y)_{\text{F}}$ states; this material is electronically still 2D, despite significant compression.

3.5. Electronic structure of δ -AgF₂, metallization and possible superconductivity

It is very instructive to analyse the electronic structure of δ -AgF₂. The band structure, density of states (DOS) and the division of the DOS to atomic contributions for δ -AgF₂ at 50 GPa are collectively shown in figure 5(a). The electron density integrated over the last band, which crosses the Fermi level, is presented in figure 5(b).

The band structure of compressed δ -AgF₂ features many crossing bands, as is typical for matter at a significant compression. The uppermost two bands are distinguished by their appreciable width; this is not only due to compression, but rather due to their origin. Analysis of the electron density sitting in these bands shows that the associated crystal orbitals are composed of the $d(x^2 - y^2)_{\text{Ag}}$ and $p(x, y)_{\text{F}}$ states admixed in the antibonding manner. Since neither $d(z^2)_{\text{Ag}}$ nor the $p(z)_{\text{F}}$ orbitals contribute to the bands crossing the Fermi level, we may anticipate that δ -AgF₂ is—structurally and electronically—a 2D material. This feature sets δ -AgF₂ apart from other compounds with the [AgF₂] sheets, but with the compressed O_h coordination of Ag²⁺ [26], and makes it similar to infinite layer oxocuprate

superconductors [27]. Notably, δ -AgF₂, if experimentally preparable, would be *the* first example of a layered (polymeric) fluoride of Ag²⁺ with flat [AgF₂] sheets and short intra-sheet Ag–F distances [28]¹⁴.

The bottom half (in the energy scale) of DOS is dominated by F(2p) states, while the upper half achieves the greatest contribution from the Ag(3d) states. Indeed, the centre of gravity of the p states is at -4.15 eV, while that of the d states is at -3.09 . Although AgF₂ is probably the most covalent difluoride of any metallic element [1, 4], the ionic component is still significant; the calculated Mulliken charges on atoms are $-0.44e$ (F), $+0.88e$ (Ag) at 50 GPa.^{15,16}

Also, what about metallization and possible superconductivity in layered δ -AgF₂?

Our calculations predict that δ -AgF₂ should be metallic even at 0 GPa. Unfortunately, this result, which originates from deficiencies of either the DFT treatment of the narrow-bandgap systems or the plane-wave representation of the basis set may be misleading. It turns out that even an insulating ferromagnet, α -AgF₂, is metallic in our spin-polarized calculations, while the bandgap of about 1.5 eV (reasonable, in terms of its brownish colour, and large electric resistivity [14]) has been predicted by B3LYP computations with the *atomic* basis set [29]. At this moment we must therefore retreat and make space for more accurate predictions of the bandgap of AgF₂, and of its pressure-induced closure, in the future (see footnote 16). It remains to be seen if superconductivity, this ‘magic electronic state’ [30], could be achieved in binary AgF₂ via compression, electronic self-doping or chemical doping of this fascinating compound.

4. Summary and prospect

We have investigated a set of seven various polymorphs of AgF₂ computationally, subjecting them to external pressures up to 50 GPa (500 000 atm). Silver difluoride is predicted to transform at a pressure of ~ 15 GPa into a layered polymorph, with a substantial 2D electronic character. This new polymorph, if metallic at 15 GPa—or metallized by the subsequent application of more elevated pressures—bears significant potential for 2D superconductivity, by analogy to the known layered copper oxides [31] and MgB₂ [32].

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References

- [1] Grochala W and Hoffmann R 2001 *Angew. Chem. Int. Edn Engl.* **40** 2743
- [2] Hoppe R 1957 *Z. Anorg. Allg. Chem.* **292** 28
- Fischer R and Müller B G 2002 *Z. Anorg. Allg. Chem.* **628** 2592 These two papers probably constitute, respectively, the first paper of Prof. Hoppe on a fluoride of Ag, and the most recent paper on the same subject coming from the laboratory of its successor, Prof. Müller (Giessen, Germany)

¹⁴ We note one attempt of compressing AgF₂, but at pretty small pressures.

¹⁵ In the spin-polarized calculation for this phase, and provisionally assuming its ferromagnetic behaviour, the computed spins on atoms (0.20 \hbar on Ag, 0.08 \hbar on each F) point to a strong magnetic interaction between Ag centres *via* p orbitals of fluoride anions.

¹⁶ Our preliminary simulations for Li, Li⁺, F, F[−], LiF molecule and LiF crystal show, that CASTEP fails to correctly account for long-range electrostatic interactions. Therefore, care is advised when comparing enthalpies of polymorphs with vastly different ionicities.

- [3] Žemva B, Hagiwara R, Casteel W J, Lutar K, Jesih A and Bartlett N 1990 *J. Am. Chem. Soc.* **112** 4846
Goresnik E and Mazej Z 2005 *Solid State Sci.* **7** 1225 In turn, these papers probably constitute the first paper on silver fluorides from the Bartlett/ Žemva team, and the most recent paper by Mazej, one of Žemva's successors (Ljubljana, Slovenia)
- [4] Grochala W, Egde R G, Edwards P P, Mazej Z and Žemva B 2003 *ChemPhysChem* **4** 997
- [5] Muller-Rosing H C, Schulz A and Hargittai M 2005 *J. Am. Chem. Soc.* **127** 8133
- [6] Kasinathan D, Kyker A B and Singh D J 2006 *Phys. Rev. B* **73** 214420
- [7] Grochala W, Porch A and Edwards P P 2004 *Solid State Commun.* **130** 137
- [8] McLain S E, Dolgos M R, Tennant D A, Turner J F C, Barnes T, Proffen T, Sales B C and Bewley R I 2006 *Nat. Mater.* **5** 561
- [9] Grochala W 2006 *Nat. Mater.* **5** 513
- [10] Grochala W 2006 *Scr. Mater.* **55** 811
- [11] Feng J, Grochala W, Jaroń T, Hoffmann R, Bergara A and Ashcroft N W 2006 *Phys. Rev. Lett.* **96** 017006
Martinez-Canales M, Bergara A, Feng J and Grochala W 2006 *J. Phys. Chem. Solids* **67** 2095
- [12] Segall M D, Lindan P J D, Probert M J, Pickard C J, Hasnip P J, Clark S J and Payne M C 2002 *J. Phys.: Condens. Matter* **14** 2717
- [13] Jesih A, Lutar K, Žemva B, Bachmann B, Becker S, Müller B G and Hoppe R 1990 *Z. Anorg. Allg. Chem.* **588** 77
- [14] Grochala W and Edwards P P 2003 *Phys. Status Solidi b* **240** R11
- [15] Shen C P, Žemva B, Lucier G M, Graudejus O, Allman J A and Bartlett N 1999 *Inorg. Chem.* **38** 4570
- [16] Casteel W J, Lucier G, Hagiwara R, Borrmann H and Bartlett N 1992 *J. Solid State Chem.* **96** 84
- [17] Müller B G 1979 *Naturwissenschaften* **66** 519
- [18] Struzhkin V V, Grochala W and Mazej Z 2006 unpublished results
- [19] Grochala W 2006 *Phys. Status Solidi b* **243** R81
- [20] Pickard C J and Needs R J 2006 *Preprint cond-mat/0604454*
- [21] <http://www.chemsoc.org/viselements/pages/pertable fla.htm>
- [22] Hubbard J 1963 *Proc. R. Soc. A* **276** 238
- [23] See e.g. Wilson J A 2001 *J. Phys.: Condens. Matter* **13** R945 and references therein
- [24] Grochala W, Hoffmann R, Feng J and Ashcroft N W 2007 *Angew. Chem. Int. Edn Engl.* at press
- [25] Pauling L, Keaveny I and Robinson A B 1970 *J. Solid State Chem.* **2** 225
Compare also Meyer L, Barrett C S and Greer S C 1968 *J. Chem. Phys.* **49** 1902
- [26] Jaroń T, Grochala W and Hoffmann R 2005 *Phys. Status Solidi b* **242** R1
- [27] Burdett J K 1995 *Chemical Bonding in Solids* (New York: Oxford University Press)
- [28] Müller B G 1979 *Naturwissenschaften* **66** 519
- [29] Harrison N M, private communication
- [30] Burdett J K 1993 *Inorg. Chem.* **32** 3915
- [31] Bednorz J G and Müller A K 1986 *Z. Phys. B* **64** 189
- [32] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 *Nature* **410** 63