New Ideas for Understanding the Structure and Magnetism in AgF₂: Prediction of Ferroelasticity

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Abstract: In the search for new high-temperature superconductors, it has been proposed that there are strong similarities between the fluoroargentate AgF₂ and the cuprate La₂CuO₄. We explored the origin of the possible layered structure of AgF₂ by studying its parent high-symmetry phase and comparing these results with those of a seemingly analogous cuprate, CuF₂. Our findings first stress the large differences between CuF₂ and AgF₂. Indeed, the parent structure of AgF₂ is found to be cubic, naturally devoid of any layering, even though Ag⁺⁺ ions occupy trigonal sites that, nevertheless, allow the existence of a Jahn-Teller effect. The observed Pbca orthorhombic phase is found when the system is cooperatively distorted by a local Ese trigonal Jahn-Teller effect around the silver sites that creates both geometrical and magnetic layering. While the distortion implies that two Ag⁺⁺–F⁻ bonds increase their distance by 15% and become softer, our simulations indicate that covalent bonding and interlayer electron hopping is strong, unlike the situation in cuprate superconductors, and that, in fact, exfoliation of individual planes might be a harder task than previously suggested. As a salient feature, these results prove that the actual magnetic structure in AgF₂ is a direct consequence of vibronic contributions involved in the Jahn-Teller effect. Finally, our findings show that, due to the multiple minima intrinsic to the Jahn-Teller energy surface, the system is ferroelastic, a property that is strongly coupled to magnetism in this argentate.

Introduction

The existence of high-temperature (high-Tc) superconductivity in some layered oxocuprates has stimulated research on transition metal compounds containing different d⁰ ions.[1–5] In these cases, the search for superconductivity is guided by the presence of three key ingredients found in the high-Tc cuprates, namely 1) a crystal lattice with layered structure, 2) the existence of elongated sixfold coordinated metal complexes often associated to the Jahn-Teller (JT) effect, and 3) a strongly antiferromagnetic (AFM) ground state in each of the metal planes.

In this hunt for new d⁰-superconductors during the last two decades intense efforts[1–9] have been focused on the exploration of materials involving 4d⁰ Ag⁺⁺ cations. As this cation exhibits a higher electronegativity than Cu⁺⁺,[6] all known Ag⁺⁺ compounds are fluorides. Up to now one hundred stable Ag⁺⁺ compounds, such as AgF₂, Cs₄AgF₆, or KAgF₆[1,2] have been synthesized. Moreover, in oxides,[3,4] chlorides[8–11] and bromides[10,12,13] the Ag⁺⁺ cation has been stabilized but only in the form of impurity. This handful of bulk materials have to be further dredged to find those that present an adequate layered AFM ground state.[1–9] Among these fluorides particular attention has been paid to the simple AgF₂ lattice, characterized by an unusually large oxidizing power.[14]

The structure of this compound is customarily[2,4,5,15] represented in the form shown in Figure 1, displaying stacked...
AgF$_2$ layers along the c-axis that host a strong, quasi-2D AFM order. It has been argued that the key to unlock stronger AFM and, possibly, high-temperature superconductivity in this system is related to the internal geometry of these AgF$_2$ sheets. As can be seen in Figure 1 the layers are significantly buckled with vertex-sharing AgF$_2$ complexes assembled in alternating directions. Systematic analyses of the magnetic structure indicate that flattening the geometry of these slabs would reinforce the AFM coupling allowing that found in the parent material of high-Tc, La$_2$CuO$_4$. More recently, based on first-principles simulations, it has been proposed that these layers are surprisingly bound by weak van der Waals interactions with a cleavage energy that is comparable to that of graphite and, as a consequence, they should be easily exfoliable. In the same study, Xu et al. find that in their free-standing configuration each individual AgF$_2$ sheet is still buckled but, due to the JT effect, they undergo a cooperative deformation into one of three equivalent minima separated by small energy barriers that provides the system with ferroelastic properties. Combined with the inherent anti-ferromagnetism of the system, they showed that bidimensional AgF$_2$ is a multi-ferroic material. While previous works on AgF$_2$ focus on the layered nature of the system and the similarities with other quasi-bidimensional systems, like La$_2$CuO$_4$, there are still many open questions on the nature of the tridimensional crystal and the way the individual sheets and magnetism emerge in its bulk. For example, in layered perovskites like La$_2$CuO$_4$, magnetism is contained within CuO$_2$ atomic planes that are separated from each other physically by two LaO planes with certain likeness with the rock-salt structure (Figure 1). The difference in composition between CuO$_2$ and LaO planes also helps localizing electrons in their respective sheets, preventing inter-layer hopping. This clearly contrasts with the situation in AgF$_2$, where the composition is homogeneous and the origin of the layered structure is not a local change in the chemistry of the system. On the other hand, the claims of van der Waals bonding between AgF$_2$ sheets seem at odds with the strong bonding expected for the crystal. In fact, it is important to note that the single AgF$_2$ layer studied by Xu et al. is more closely related to the hexagonal structure of bulk CuCl$_2$ basis of some graphite intercalation compounds (see, e.g., ref. [21]), than the orthorhombic lattice of AgF$_2$ shown in Figure 1. Thus, the production of AgF$_2$ layers, like the one studied in ref. [16], seems to be a much more involved process than the peeling-off graphene from graphite. In this work we use density functional theory (DFT) calculations in order to discuss the origin of the apparently layered structure of AgF$_2$ and its connection with the magnetism of this system. In a first step, we prove the existence of a trigonal JT effect in AgF$_2$. In a second step, we show that crystalline and magnetic structures are strongly interconnected through the cooperative JT effect and that, due to the presence of this phenomenon, the system displays multiple equivalent minima leading to the emergence of ferroelasticity in the system. This shows that bulk AgF$_2$ is multi-ferroic, combining strongly intertwined magnetic and elastic properties.

Finally, in order to establish links and differences between argentates and cuprates we will analyze AgF$_2$ in parallel with CuF$_2$ (see also ref. [3]). We feel that this is a much closer analog to AgF$_2$ than La$_2$CuO$_4$ since this system avoids the presence of chemically foreign LaO sheets. In both (CuF$_2$, AgF$_2$) systems, and due to the localization of active d$^9$ electrons, it is crucial to know the origin of the local distortion and the nature of ground state of MX$_6$ complexes (M = d$^9$ ion, X = ligand), to understand their associated optical and magnetic properties.

The local distortion in compounds with d$^9$ cations, like CuF$_2$, has widely been ascribed to an octahedral Ee JT effect despite the low symmetry displayed by such crystalline lattices. As the crystal structure of AgF$_2$ bears similarities with that of CuF$_2$, it has been assumed that the geometry of both compounds is the result of a JT distortion of the MX$_6$ octahedra of D$_{6h}$ symmetry with a hole in a d$_{xy}$ type orbital. Nevertheless, it has recently been shown, by means of first principles calculations, that CuF$_2$ octahedra have a compressed geometry followed by an additional orthorhombic distortion that preserves a dominant d$_{xy}$ character for the hole a situation that is not due to the JT effect. Similarly, the equilibrium geometry of the parent phase can display a higher symmetry than the observed one and be a good starting point for understanding the AgF$_2$ structure.

Bearing these facts in mind, the present work aims to gain a better insight into the structure of AgF$_2$ and the ground state of AgF$_2$ units using DFT calculations. In order to achieve this goal, the present study is based on five fundamental steps: 1) To explore the structure of the so-called parent phase of Pbca AgF$_{2n}$ formed when all open shell 4d$^9$ Ag$^{+}$ cations are substituted by closed shell 4d$^{10}$ Cd$^{2+}$ ions, with similar ionic radii but a more spherical electronic density. Accordingly, the equilibrium geometry of the parent phase can display a higher symmetry than the observed one and be a good starting point for understanding the AgF$_2$ structure. 2) To analyze the behavior of a single Ag$^{+}$ impurity into the parent phase of the AgF$_2$ compound. 3) To study the cooperative effects analyzing the influence of the silver content on the lattice structure. 4) To carry out a parallel analysis of CuF$_2$ comparing the results obtained for copper and silver fluorides. 5) Once this matter is clarified, we will discuss the cooperative JT effect to highlight the relationship between local distortion and magnetism to show the presence of ferroelasticity and multi-ferroic properties in AgF$_2$.

This work is organized as follows. Computational details of DFT calculations are shortly described in the next section, while main results of this work are displayed in the Results and Discussion. For the sake of clarity, we first apply the methodology to CuF$_2$ and subsequently to AgF$_2$. Some final remarks are provided in the last section.

Computational Methods

DFT periodic simulations on pure AgF$_2$ and its parent CdF$_2$ phase (either pure or doped with Ag$^{+}$) were carried out using the Crystal17 code, where Bloch wavefunctions are expanded as linear combinations of local functions which are, in turn, linear combinations of Gaussian type functions centered at atomic sites.
It is worth noting that this code exploits at all steps of the calculations both translational invariance and point-symmetry of the crystals. 

In order to accurately perform both geometry optimizations and energy calculations, all ions were described by high-quality basis sets, specifically triple-$\zeta$ valence with polarization consistent basis optimized by Pfitzinger and coworkers, which are provided by Crystal software. The combination of these basis sets together with the hybrid exchange-correlation functional PW1PW, which includes 20% of Hartree-Fock exchange, has provided accurate crystal structures and properties for a wide range of different systems.

As mentioned in the previous section, we have carried out geometry optimizations both on AgF$_6$ which belongs to the orthorhombic space group Pbca, and in a lattice where all Ag$^{+}$ ions have been replaced by closed shell Cd$^{2+}$ ions (the parent phase), causing the system to undergo a phase transition to the parent cubic structure Pm-3m (see Results). These calculations were performed under the framework of spin unrestricted Kohn-Sham DFT, imposing tight convergence criteria for energy changes per ion (10$^{-9}$ a.u.) and RMS of gradient and atomic displacements (0.0001 a.u.). The integration in reciprocal space was carried out by sampling the Brillouin zone with 8x8x8 Monkhorst-Pack grid (that is the the distance between consecutive values of k according to the 3 reciprocal directions is 0.155, 0.142 and 0.135 Å$^{-1}$), which is enough to provide a full energy convergence. These results show great accordance between experimental and calculated distances in AgF$_6^{+}$ complex and lattice parameters. Both ferromagnetic (FM) and AFM states have been considered in the calculations, where we have noticed an increase in the energy per formula unit of 40 meV in the FM with respect to the AFM state at equilibrium.

Calculations on Ag$^{+}$-doped CdF$_6$, where Ag$^{+}$ impurity initially occupies a Cd$^{2+}$ lattice site on the parent phase Pa-3, were also performed. In these optimizations, atomic positions were relaxed within Pbcn space group, keeping the lattice parameter of the parent phase fixed, which leads to a distorted AgF$_6^{+}$ complex. Primitive cell and 2x2x2 conventional supercell containing 12 and 96 ions, respectively, have been used, obtaining Ag$^{+}$-$\mathrm{F}^{-}$ distances that are quite similar in both cases, with slight variations of less than 2%.

Additional energy calculations have been carried out for AgF$_2$, starting from the cubic Pa-3 structure and distorting the four AgF$_6^{+}$ complexes of the unit cell following a trigonal distortion, denoted as $\gamma$. Then, lattice parameters have been relaxed in order to show how the previous distortion affects the global lattice structure, specifically cell vectors.

Results and Discussion

Seeking to explain the methodology employed in the analysis of crystal structures we first deal with the simpler case of CuF$_2$ which was previously investigated. With these results in mind, we subsequently tackle the problem of AgF$_2$.

Structure and ground state of CuF$_6^{4-}$ units in CuF$_2$

At normal conditions, CuF$_2$ exhibits a monoclinic structure with standard P2$_1$/c space group that can be represented, alternatively, using the nonstandard P2$_1$/n group, which allows a distorted rutile structure to be identified (Figure 2).

As shown in Figure 2, the experimental geometry of CuF$_6^{4-}$ units in CuF$_2$ involves an orthorhombically distorted octahedron where the three Cu$^{+}$-$\mathrm{F}^{-}$ distances, $R_1=1.917$ Å, $R_2=1.932$ Å, and $R_3=2.298$ Å and lattice parameters, measured at 4.2 K, have previously been well reproduced by first principles calculations (Table 1). The values of $R_1$ and $R_2$ at room temperature are coincident with those determined at 4.2 K while the length of the softest bond increases only by 0.5%. Due to the closeness of $R_1$ and $R_2$ values that equilibrium geometry has been described in most scientific literature as the result of an octahedral JT effect leading to an elongated complex with $y$ as main axis and a hole located in a $x^2-y^2$ type orbital.

In order to have a closer look at this relevant issue, it is useful to calculate the parent (high-symmetry) structure of CuF$_2$. To achieve this goal, we replace all Cu$^{+}$ ions in CuF$_2$ by the closed shell Zn$^{2+}$ ions, involving a more spherical electronic density, and then a geometry optimization is performed starting from the monoclinic P2$_1$/c space group of CuF$_2$. The result of this process allows a reference, high-symmetry parent structure that can have a higher symmetry than P2$_1$/c to be easily found.

The results obtained in this work for the parent phase of CuF$_2$ are also shown in Table 1. Upon the Cu$^{+}$-$\mathrm{Zn}^{2+}$ substitution, the monoclinic P2$_1$/c structure evolves until reaching the final tetragonal P4$_2$/mmm space group characteristic of the stable phase of ZnF$_2$ at normal conditions (Figure 1).

Interestingly, the octahedron surrounding a Zn$^{2+}$ cation involves two Zn$^{2+}$-$\mathrm{F}^{-}$ distances which are equal, $R_1=R_2=2.041$ Å, and is slightly compressed along the $z$-axis as $R_3=$

![Figure 2](image-url)

### Table 1

| System          | Spacgroup | $R_1$ [Å] | $R_2$ [Å] | $R_3$ [Å] | $\psi$ (°) |
|-----------------|-----------|-----------|-----------|-----------|------------|
| CuF$_2$         | P2$_1$/c  | 1.918     | 1.936     | 2.265     | 77.6       |
| parent phase    | P4$_2$/mmm| 2.007     | 2.041     | 2.041     | 78.6       |
| ZnF$_2$/Cu$^{+}$| P4$_2$/mmm| 1.932     | 2.074     | 2.074     | 77.8       |

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Comparative study of AgF₂

In a similar way to what happens for CuF₂ in AgF₂, the cation is also sixfold coordinated (Figure 3). Nonetheless, AgF₂ exhibits a higher symmetry than CuF₂ as it is orthorhombic (space group Pbca) rather than monoclinic.[35] Calculated values of lattice parameters and Ag²⁺–F⁻ distances (Table 2) coincide with experimental values within 2%. It can be noticed that the Ag²⁺–F⁻ distances along the x- (2.074 Å) and y- (2.067 Å) axes of Figure 3 are close but not equal while those for ligands along the z-axis are higher (2.584 Å). Moreover, the F–Ag–F angles in AgF₂ are not equal to 90°.

Using a similar process to that employed for CuF₂, we can try to elucidate the parent, high-symmetry structure that leads to the final, layered structure of AgF₂. In particular, we optimized the full geometry of the Pbca phase of AgF₂ when all the Ag²⁺ were replaced by closed-shell Cd²⁺ ions in order to eliminate distortions due to the anisotropic electronic shell of the Ag²⁺ ions. The results of the geometry optimization, displayed in Figure 4 and Table 3, show that the parent phase of AgF₂ is actually cubic and thus the substitution of Ag²⁺ by Cd²⁺ makes the lattice evolve from the orthorhombic Pbca to

Table 2. Experimental[35] and calculated lattice parameters and metal-ligand distances for AgF₂. All values are in Å. Experimental values have been obtained at room temperature.

| Parameter | Experimental | Calculated |
|-----------|--------------|------------|
| a (Å)     | 5.073        | 5.178      |
| b (Å)     | 5.229        | 5.622      |
| c (Å)     | 5.813        | 5.766      |
| R_x (Å)   | 2.584        | 2.618      |
| R_y (Å)   | 2.067        | 2.094      |
| R_z (Å)   | 2.074        | 2.096      |

Figure 3. Unit cell of AgF₂ at ambient pressure, with an orthorhombic Pbca space group. One AgF₂⁺ complex is also shown, where the Rₓ and Rᵧ distances are slightly different, and the F–Ag–F angles are rather different from 90°. Dashed blue lines mark the two fluorine triangles distorted from equilateral ones in the parent cubic phase (Figure 4).

Table 3. Optimized values of the lattice parameter, a, and Cd²⁺–F⁻ distance, R(Cd²⁺–F⁻), for CdF₂ in two different phases. First row data corresponds to the Pm-3m phase of AgF₂, while second row data corresponds to the stable Fm-3m phase of CdF₂ at normal conditions displaying the fluorite structure. The different Cd²⁺ coordination number (CN) for both lattices is also shown.

| System       | Space group | Cd CN | a [Å] | R(Cd²⁺–F⁻) [Å] |
|--------------|-------------|-------|-------|----------------|
| parent phase of AgF₂ | Pm-3      | 6     | 5.497 | 2.246          |
| stable CdF₂   | Fm-3m      | 8     | 5.393 | 2.335          |
the cubic Pa-3 space group. Nevertheless, even though the parent phase is cubic the fluorine coordination shell surrounding a Cd\(^{2+}\) is not a perfect octahedron as the F—Cd\(^{2+}\)–F angles are rather different from 90° resulting in a flattened, trigonal CdF\(_6\) complex (Figure 4). Even though the local symmetry is low, the trigonal axis of the complex surrounding each of the four Cd\(^{2+}\) ions in the motif is oriented along one of the four major diagonals of the cube leading to a global cubic symmetry of the system.

The structure of CdF\(_6\) in the cubic Pa-3 phase looks rather similar to that of CdF\(_2\) in the fluorite structure (cubic space group Fm-3 m) observed experimentally at normal conditions (Figure 5). Nevertheless, the coordination number for Cd\(^{2+}\) in the fluorite structure is eight while in the Pa-3 parent phase of AgF\(_2\) it is only six. Thus, according to Pauling’s rules,\(^{[41]}\) the Cd\(^{2+}\)–F\(^-\) distance (Table 3) is a somewhat higher for the Fm-3 m phase (2.335 Å) than for the Pa-3 one (2.246 Å). At the same time, the change from eightfold to sixfold coordination implies that in the parent phase there are two Cd\(^{2+}\)–F\(^-\) distances at 3.096 Å reflecting the breaking of the corresponding bonds (Figure 4). This fact increases the lattice parameter of the Pa-3 phase with respect to that of the Fm-3 m structure as shown in Table 3.

It is worth noting that the calculated structure for the Pa-3 parent phase of AgF\(_2\) is just the equilibrium structure at ambient pressure observed for Cd\(_{2+}\)Pd\(_{3+}\)F\(_6\) where Cd\(^{2+}\) and Pd\(^{3+}\) ions occupy the same sites at 50%\(^{[42]}\). It was also claimed that one of the high-pressure phases of AgF\(_2\) exhibits the same Pa-3 structure\(^{[43]}\) although this matter is still debated\(^{[44]}\).

A crucial point in the present analysis concerns the behavior of a single Ag\(^{2+}\) impurity in the Pa-3 parent phase. We have verified that under the Cd\(^{2+}\)→Ag\(^{2+}\) substitution, and maintaining fixed the position of the rest of lattice ions, the ground state of AgF\(_2\) units is orbitally doubly degenerate. This result may in principle be surprising as the local symmetry of a Cd\(^{2+}\) ion in the parent Pa-3 phase is not octahedral. However, it was also claimed\(^{[44]}\) that under a perfect octahedral symmetry the ground state of a AgF\(_2\) unit is E\(_g\) and that the nature of the ground state remains twofold-degenerate after a descent in symmetry from O\(_h\) to D\(_{3d}\).\(^{[45,46]}\) Such an electronic doublet can also be preserved in lower trigonal symmetries like C\(_{2v}\) or C\(_{3v}\), while an E\(_g\) state in O\(_h\) already splits into A\(_{1g}\) and B\(_{1g}\) under a tetragonal perturbation.\(^{[39]}\) Accordingly, the ground state under a D\(_{3d}\) symmetry is no longer degenerate thus excluding the existence of a JT effect, a matter well verified in cases like K\(_2\)ZnF\(_6\):Cu\(^{2+}\) or Ba\(_2\)ZnF\(_6\):Cu\(^{2+}\).\(^{[43,46]}\) By contrast, under the O\(_h\)→D\(_{3d}\) symmetry descent the ground state of an AgF\(_2\) unit in the parent phase is still degenerate and thus can experience a JT effect. The existence of a static JT effect under trigonal symmetry has been verified in cases like ZnSiF\(_6\), 6H\(_2\)O:Cu\(^{2+}\)\(_{47,48}\) or CdCl\(_6\):M\(^{2+}\) (M=Cu, Ag)\(_{49,50}\) or CdF\(_2\):\(_{51}\).

Despite the ground state of a d\(^0\) ion in trigonal symmetry can still be degenerate there are differences with the behavior under a higher octahedral symmetry. So, considering the trigonal (X, Y, Z) coordinates depicted in Figure 6 there is no one but two pairs of d-waves functions belonging to the E\(_g\) irrep in D\(_{3d}\).\(^{[46]}\) Such pairs are simply described by (X, Y, Z) and (X\(_2\), YZ) in the trigonal basis (Figure 6). Accordingly, the highest, partially occupied d-level of Ag\(^{2+}\) in AgF\(_2\) involves a linear combination of four different d-waves functions. In the same vein, although in D\(_{3d}\) symmetry the JT effect gives rise to three adiabatic minima they do not exhibit a tetragonal symmetry.
such as it happens when the initial, high-symmetry configuration is octahedral.

The equilibrium geometry corresponding to one of the adiabatic minima obtained for a single Ag$^{2+}$ impurity is displayed in Table 4 and shown in Figure 7. Results are compared to experimental ones for AgF$_2$[35] and also to those calculated in this work for NaF:Ag$^{2+}$ where the initial geometry is octahedral.

The results on NaF:Ag$^{2+}$ are consistent with the EPR measurements by Monier et al.[32] proving the existence of an elongated geometry due to a static JT effect. This geometry is usually observed for d$^0$ impurities in cubic lattices and sixfold coordination[28,53] with the exception of CaO:Ni$^{2+}$.[54] a matter discussed in ref. [55]. A geometry close to the elongated one in octahedral symmetry has also been observed when the host lattice is trigonal such as for ZnSiF$_4·$6H$_2$O·Cu$^{2+}$[47–49] or CdCl$_2·$M$^{2+}$ (M = Cu, Ag).[10,16]

These calculations for the Ag$^{2+}$ impurity in Pa-3 CdF$_2$ lead to bond distances in the AgF$_{6}^{4-}$ unit that are rather close to those derived for NaF:Ag$^{2+}$. However, it is important to note that while the F-Cd$^{2+}$-F angles in the Pa-3 phase differ from 90° only by ≈10° the global shape of the flattened trigonal complex is significantly different from the octahedral case (Figures 4 and 7) and have important differences in the JT distortion of the complex.

As shown on Table 4, on passing from Ag$^{2+}$-doped CdF$_2$ to pure AgF$_2$, the value of the average metal-ligand distance, $<R>$, is the same but the distortion increases. We have verified that this fact is related to the silver content of the lattice. For instance, if in the unit cell of the Pa-3 phase we replace three of four Cd$^{2+}$ ions by Ag$^{2+}$ we find elongated AgF$_{6}^{4-}$ complexes whose metal-ligand distances ($R_x$ = 2.532 Å, $R_y$ = 2.077 Å and $R_z$ = 2.146 Å) are closer to that found for pure AgF$_2$ (Figure 2 and Table 4). It is important to note that, at difference with the usual octahedral JT effect, in this case the distortion is not directly produced along the Ag–F bond axes but it is rather a distortion that changes the shape of the equilateral triangular faces of the complex, elongating them into acute triangular faces that remain parallel throughout the distortion (Figure 5). Nevertheless, the change from an equilateral to an acute triangle implies a reduction of the distance between two ligands and consequently that between them and the central cation (see blue arrows on the diagram on the right side of Figure 7).

Due to the perfect degeneracy at the initial geometry, a fingerprint of a JT effect in an octahedral unit is the existence of two different distortions whose energies are very close as they differ by an energy barrier, $B$, lying typically in the range 10–100 meV.[56] To explore this key issue, we have built a linear transformation that allows us to smoothly interpolate between the high-symmetry Pa-3 geometry of CdF$_2$ to the distorted Pbc$a$ minimum of AgF$_2$. We can further use this transformation to extrapolate the geometry to negative values of the distortion that in a usual JT system would correspond with the transition state between minima. In this process the distortion of a single complex can be characterized through a parameter $\eta$ as follows

$$R_y = (R) + 2\eta; R_x = R_z = (R) - \eta$$

We have calculated the energy associated with the Jahn-Teller deformation associated to $\eta$ both in the fractional coordinates and the lattice parameters by using the information contained in Table 5. Using the two extrema presented in Table 5 and the geometry of the parent structure we can interpolate the geometries that allow the energy surfaces characteristic of a JT effect in Figure 8 to be plotted. There, we have verified that for both $\eta > 0$ and $\eta < 0$ branches a lower energy is always reached including the lattice relaxation.

If we designate by $\eta_i$ the local distortion corresponding to the lowest energy value of a given branch, the equilibrium situation is obtained for the $\eta > 0$ branch with $\eta_i = 0.16$ Å and a JT stabilization energy $E_J = 193$ meV, comparable to $E_J = 201$ meV previously determined for NaCl:Ag$^{2+}$.[11]

### Table 4. Equilibrium geometry corresponding to one of the adiabatic minima obtained for a single Ag$^{2+}$ impurity in the sixfold coordinated Pa-3 CdF$_2$ lattice showing the relaxation effects. Results are compared to the experimental equilibrium values of AgF$_{6}^{4-}$ units in pure AgF$_2$, derived at room temperature,[19] and also to those calculated in the cubic NaF lattice where the initial geometry around the impurity is $O_h$ ($R$) just means the average value of three metal-ligand distances. All distances are in Å.

| System          | $R_x$ | $R_y$ | $R_z$ | $<R>$ |
|-----------------|-------|-------|-------|-------|
| NaF:Ag$^{2+}$   | 2.399 | 2.114 | 2.114 | 2.209 |
| CdF$_2$:Ag$^{2+}$ | 2.445 | 2.128 | 2.134 | 2.235 |
| AgF$_2$ (experimental) | 2.584 | 2.067 | 2.074 | 2.241 |

### Table 5. Description of local and lattice distortions associated with the lowest energy value of a given branch.

| Branch | $\eta_i$ [Å] | Relative energy [meV] | $a$ [Å] | $b$ [Å] | $c$ [Å] |
|--------|---------------|-----------------------|--------|--------|--------|
| $\eta > 0$ | 0.16          | 0                     | 5.138  | 5.544  | 5.847  |
| $\eta < 0$ | $-0.10$      | 88                    | 5.715  | 5.320  | 5.372  |

Figure 7. Distortion of one of the trigonal AgF$_{6}^{4-}$ complexes of the parent high-symmetry Pa-3 phase of AgF$_2$. The faces of AgF$_{6}^{4-}$ complexes go from being equilateral triangles in Pa-3 to acute triangles in the experimental Pbc$a$ structure. Notice that, unlike with the usual JT effect in octahedral systems, the elongation of the complex (red arrows) is not along the bond axis as it keeps the top and bottom faces of the complex parallel to each other. This can be clearly seen in the lateral view complex, on the right-bottom side of the figure, where the Ag–F bonds point in a different direction from the distortion (red arrows).
As shown on Figure 8, the lowest energy value in the $\eta < 0$ branch appears at $\eta_1 = -0.10 \text{ Å}$ involving an energy barrier per single complex equal to $B = 88 \text{ meV}$ above the absolute minimum at $\eta_1 = 0.16 \text{ Å}$. This situation is thus akin to that found for $d^0$ impurities in cubic crystals under a static JT effect. In these cases, with the known exception of CaO: Ni$^{2+}$, the equilibrium geometry corresponds to an elongated octahedron while the compressed geometry ($\eta < 0$) is located at an energy above the minimum equal to $B = 28 \text{ meV}$ for NaF:Ag$^{2+}$ or $B = 62 \text{ meV}$ for NaCl:Ag$^{2+}$.111

Layered structure, magnetism and ferroelasticity in AgF$_2$

After discussing the local distortions around the Ag$^{2+}$ ion in AgF$_2$, we are in position to analyze the origin of the layered structure and subsequently the magnetism of this material.53,54 Both AgF$_2$ phases, the parent cubic $Pm-3$ one (Figure 4) and the experimental orthorhombic $Pbca$ (Figure 7), contain four vertex-sharing trigonal AgF$_6^{2-}$ complexes positioned in a face-centered configuration. In the cubic $Pm-3$ phase, each of these complexes has its trigonal axis oriented along one of the four main diagonals of the cube. In the orthorhombic $Pbca$ structure, the local distortion is equivalent on all complexes and extends one bond in the upper and lower faces of the flattened trigonal complexes (Figure 7) whose shape changes from equilateral triangle to acute one. Note that this transformation is quite different from the usual elongation of the octahedral complex in the cubic JT problem.

Considering the combined action of the local elongation of each of the trigonal complexes in the cubic lattice and their different orientation, we find that the resulting cooperative distortion produces an extension of bonds along one of the cubic lattice's cell vectors while keeping the length of another one roughly fixed and contracting the third one. We can observe this in detail by looking at the linear transformation from the cubic $Pa-3$ structure to the orthorhombic $Pbca$ one represented in Figure 8. Here, we can see how the cell vectors relax with the distortion leading to the splitting of the cubic lattice parameter $a = 5.497 \text{ Å}$ into the contracted, roughly constant and extended lattice parameters ($a = 5.073 \text{ Å}$, $b = 5.529 \text{ Å}$ and $c = 5.813 \text{ Å}$, respectively) of the orthorhombic structure. This extension along one of the main cubic axes is the reason why AgF$_2$ is usually considered as a layered compound as the bonds along the orthorhombic c-axis are clearly weakened due to the cooperative JT effect. From a symmetry standpoint it is clear that the complexes can elongate equivalently along the three cubic axes and so the system may end up in one of three well-separated minima characteristic of the JT effect. This property shows that bulk AgF$_2$ is ferroelastic, a very usual property of many cooperative JT crystals (see, e.g., ref. [58]). The barrier between each of the configurations is, as reflected in Figure 8, 88 meV/unit formula, a value that could be tuned by the application of pressure or growing the lattice on a substrate.

From this point of view, when one considers AgF$_2$ as a layered system it is clear that the atomic sheets in this material are clearly different from those of a layered perovskite like La$_2$CuO$_4$ (Figure 1). In particular, AgF$_2$ complexes have short in-layer ($R \approx 2.13 \text{ Å}$) and long inter-layer ($R \approx 2.58 \text{ Å}$) bonds while in the perovskite the complexes are located exclusively on one layer. These differences are further reflected on the electronic structure. While in the layered perovskites the dispersion of the bands in the direction perpendicular to the layers is negligible, in AgF$_2$ the equivalent band dispersion (see the Supporting Information) is significant, clearly indicating that bond-length extension is not enough to destroy interlayer bonding. As mentioned in the introduction, Xu et al.113 calculated a cleavage energy similar to that of graphite for AgF$_2$ leading to the conclusion that interlayer bonding is van der Waals. This conclusion does not stand with the analysis carried out here where we show that significant mixed ionic covalent bonding, typical of transition metal complexes, exists between layers and thus the role played by the longest Ag–F bonds at 2.58 Å cannot be neglected.

In order to look in more detail at this issue we have performed simulations on AgF$_2$ where the long cell parameter is extended to a very long distance (15 Å) and resulting structure...
is relaxed. Interestingly, we have found that this process involves an increase of energy of 0.42 eV per unit formula which is thus similar to what is obtained in a similar transformation in NaCl (0.54 eV/unit formula). Thus, in both cases the energy turns out to be one order of magnitude larger to that of graphite (0.05 eV/unit formula). Furthermore, the final AgF$_2$ layer structure obtained by extending the lattice in one direction, where the silver complexes are nearly square planar, is quite different from the one considered by Xu et al.$^{[13]}$ where the complexes are flattened trigonal, as in bulk and systems like CuCl$_2$.$^{[13]}$ Thus, it seems that reaching the proposed nearly trigonal geometry by peeling-off one layer of AgF$_2$ would be difficult as the necessary rearrangement of atoms involves overcoming significant energy barriers.

Coming, finally, to the determination of the magnetic structure and its correlation with the JT distortion discussed above, it can be noticed that in the cubic Po-3 phase no AFM state has pure cubic symmetry. This state, that in a cubic perovskite is realized as the AFM–G state where an ion with its magnetic moment pointing up (or down) is completely surrounded along the three main axes of the crystal by magnetic ions where the spin points down (respectively up). By contrast in AgF$_2$, the antiferromagnetic coupling cannot be produced along the three main axes of the crystal, implying frustration, that is, in the first coordination sphere of an ion there are always magnetic moments that are parallel and antiparallel to the central one. In fact, for $\eta = 0$ (cubic Po-3 phase), the FM state is lower in energy than any AFM state, as shown in Figure 8. This magnetic frustration is broken when the JT effect comes into play and produces an elongation of one of the axes of the lattice and a contraction along the other one. Observing Figure 8 we can see that the existence of the JT distortion plays a key role for stabilizing an AFM coupling between two Ag$^{+}$ ions separated by a short bond (Ag–F distance of 2.07 Å) and involving an Ag–F–Ag angle of 130°. This conclusion is underpinned by experimental findings.$^{[15]}$ Moreover, the present results lead to a weak FM coupling for two Ag$^{+}$ ions separated by a long bond (Ag–F distance of 2.58 Å) and involving an Ag–F–Ag angle of 118°, which is also in agreement with experiments.$^{[15]}$ These results are consistent with the usual behavior of superexchange interactions favoring AFM coupling on FM one 1) the stronger the bond is, and 2) the more linear the metal–ligand–metal bond is.$^{[15,60]}$

Moreover, we can study the change in the direction of the AFM planes with the JT distortion. Indeed, as can be observed in Figure 8, as the AgF$_2$ complexes go from an elongated (acute triangular faces, $\eta > 0$) to a compressed (obtuse triangular faces, $\eta < 0$) configuration, the direction of the elongation/compression of the lattice axes switches from $a$ to $c$ axes. This process is accompanied with a change of the order of the AFM states of the system. When $\eta > 0$ (c > b > a) the ground state shows AFM coupling in the $ba$ plane, that is, the green line is the ground state, while this coupling occurs in the $bc$ plane when $\eta < 0$ (c < b < a; the red line is the ground state). These results thus stress that the actual magnetic structure in AgF$_2$ is a direct consequence of vibronic contributions involved in the JT effect. Indeed, as shown in Figure 8, vibronic effects lead to energy shifts of ~0.2 eV per complex while the energy change induced by varying the magnetic structure is one order of magnitude lower.

Conclusions

In this work, we have shown that the geometry and magnetic structures of AgF$_2$, usually referred in the literature$^{[1–5,14–18]}$ as a layered silver analog to high-temperature cuprate superconductors, are a direct consequence of the cooperative Jahn–Teller effect in this lattice. This is an important difference from the layered structures of cuprates like La$_2$CuO$_4$, where the origin of the layers is chemical, as CuO$_2$ planes are separated from each other by rock-salt LaO planes. In fact, it was proven that the parent phase of this argentate is cubic (Po-3 group), where symmetry prevents the appearance of any layers. The Jahn–Teller distortions taking place in the lattice, while significant, are far from strong enough to destroy interlayer band dispersion. In cuprates, the interlayer band dispersion is almost completely quenched due to the strong barriers created to electron hoping due to a region with a different composition from that of the CuO$_2$ atomic sheets. Moreover, we have shown that interlayer bonding has a strong mixed ionic/covalent character that contrasts with previous suggestions of van der Waals bonding.$^{[14]}$ Another consequence of the Jahn–Teller origin of the geometry of the system is that AgF$_2$ is a ferroelastic system in which the distortion-induced strain is directly connected with and controls the direction of antiferromagnetic coupling, a signal of consistent multiferroic behavior.

Finally, we would like to stress the importance of symmetry when analyzing the properties of a system. Although CuF$_2$ and AgF$_2$ would, at first sight, seem relatively similar,$^{[2,3,57]}$ the different symmetry of the parent phase, tetragonal and cubic, respectively, leads to quite different behavior. In CuF$_2$, the tetragonal symmetry of the parent phase already excludes the existence of a Jahn–Teller effect, while a true degeneracy exists in the parent phase of AgF$_2$ giving rise to many interesting features characteristic of the Jahn–Teller effect in solids, like ferroelasticity and multiferroicity. Moreover, the nature of the three-minimum Jahn–Teller energy surface found in the flattened trigonal AgF$_2$$^{++}$ complexes of AgF$_2$, is quite different from that in systems where the symmetry of AgF$_2$$^{++}$ complexes is initially octahedral. In fact, the distortion in the trigonal $D_{4d}$ complex always occurs in the same plane, breaking the third-order axis of the system, while in the octahedral ($Q_4$) one, the distortions take place in orthogonal directions along metal–ligand bonds. Understanding these delicate differences are key to correctly predicting the properties of these systems.

Supporting Information

The Supporting Information contains the DFT-calculated band structure of AgF$_2$ and La$_2$CuO$_4$.
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Conflict of Interest

The authors declare no conflict of interest.

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