Silver route to cuprate analogs

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The parent compound of high-$T_c$ superconducting cuprates is a unique Mott insulator consisting of layers of spin-$1/2$ ions forming a square lattice and with a record high in-plane antiferromagnetic coupling. Compounds with similar characteristics have long been searched for without success. Here, we use a combination of experimental and theoretical tools to show that commercial AgF$_2$ is an excellent cuprate analog with remarkably similar electronic parameters to La$_2$CuO$_4$ but larger buckling of planes. Two-magnon Raman scattering and inelastic neutron scattering reveal a superexchange constant reaching 70% of that of a typical cuprate. We argue that structures that reduce or eliminate the buckling of the AgF$_2$ planes could have an antiferromagnetic coupling that matches or surpasses the cuprates.

silver fluorides | superconductivity | cuprates | strong correlation | quantum magnetism

Cuprates are said to be unique materials in that they combine low-dimensional arrangements of spin-$1/2$ magnetic moments coupled by a record high antiferromagnetic interaction, strong covalence between transition metal (TM) and ligands, and no orbital degeneracy. The strong quantum nature of spin-$1/2$ ions manifests itself in several properties. Materials with a quasi-1D electronic structure and layered materials show heat transport by magnetic excitations in insulators that rivals that of metals (1, 2). In quasi-1D compounds, magnon excitations are not stable, leading to exotic phenomena, such as spin charge separation (3, 4). Insulating two-leg ladder compounds show a spin-gapped ground state and can become superconducting with pressure and doping (5). Even for insulating layered materials, the magnetic excitation spectrum is remarkably different from the predictions of spin wave theory (6–8). This extreme quantum nature of the magnetism is believed to be at the heart of the high-$T_c$ superconductivity of the doped layered materials (9).

There have been several attempts to replicate the quantum magnetism of cuprates with different TM ions (10). One proposal has been to use nickel(I) in place of copper(II) (11, 12). While LaNiO$_2$ is isostructural and isostructural with the infinite-layer parent cuprates, it lacks the strong covalent character between the TM and ligand (13), and antiferromagnetic order has not been found (14, 15). Sr$_2$IrO$_4$ has many similarities with cuprates, including a robust antiferromagnetic order of spin-$1/2$ pseudospins. However, the correlated insulator character is much weaker, and spin–orbit coupling effects dominate (16, 17).

Another obvious possibility is to move down the periodic table from copper to silver (Fig. 1). The electronic structure of silver oxides was explored in the early times of high-$T_c$ superconductivity of cuprates (21–23). Large superexchange constants have been predicted in many fluorargentates (24), and static susceptibility measurements in a quasi-1D system suggest a superexchange constant of the order of that found in the cuprates (25). However, direct access to excitation energies from spectroscopy has not been available to date.

A bonus property of F~ in place of O^2− is that, unlike CuO planes, neutral AgF$_2$ planes are possible, and therefore, the

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Significance

Antiferromagnets can host strong quantum fluctuations in their ground state if they combine both low-dimensional and low spin. Materials based on copper oxides (spin-$1/2$ ions in layered or 1D structures) are unique in optimizing the tendency to strong quantum fluctuations. As a bonus, they show extremely large magnetic effects, which lead to interesting quantum effects at relatively high temperatures as anomalous transport properties and high-$T_c$ superconductivity in doped systems. Obtaining similar features with other ions has been a long-standing goal. We show that silver and fluorine (which are next to copper and oxygen in the periodic table) in the commercial compound AgF$_2$ reach the goal, paving the way for a different generation of quantum materials.

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Fig. 1. Schematic energy levels of cuprates and argentates in an ionic picture. All levels are assumed to be referenced to a common zero energy vacuum so that the $3d^9 \rightarrow 3d^8$ (64eV $\rightarrow$ 63eV) level is located at minus the second ionization energy of Cu (Ag). (A) Levels for CuO and $La_2CuO_4$. Cu is in the $d^9$ configuration. Electron addition ($3d^9 \rightarrow 3d^{10}$) and removal ($3d^{10} \rightarrow 3d^9$) energies from Cu correspond to the centroid of the upper and lower Hubbard bands, while removal from filled oxygen corresponds to the valence band. The charge transfer energy $\Delta CuO$ and the Hubbard $U_{3d}$ parameter are indicated. (B) In the case of AgO, silver is formally $d^8$. However, since the $4d^8 \rightarrow 4d^{10}$ levels are deeper than the $3d$ counterpart, the charge transfer energy is practically zero or even negative, and the pictured filling is unstable toward more complex mixed valence behavior (yellow arrow) (18). (C) Fluorine is more electronegative than O, which translates into deeper 2p$^6$ removal states and restores a positive charge transfer energy in AgF$_2$.

simplest compound is not of the 214 kind but is simply 012. Unexpectedly, as we show here, the binary and commercially available AgF$_2$ compound turns out to be an excellent cuprate analog. Fig. 2 A and B and SI Appendix, Fig. S1 show the structure (26) and stacking of planes in AgF$_2$. The topology is the same as in $La_2CuO_4$, which in the low-temperature orthorhombic (LTO) phase, also has the same pattern of displacements of the ligands out of the plane (+ or −) but with a much smaller magnitude. Also, as in parent cuprates, the ground state of AgF$_2$ is antiferromagnetic (26) with a staggered moment of 0.7 $\mu_B$ (0.6 $\mu_B$), a weak ferromagnetic component of $1 \times 10^{-2}$ $\mu_B$ ($2 \times 10^{-3}$ $\mu_B$) per TM ion, and a Néel temperature of 163 K (325 K), where parentheses enclose reference values (27) in $La_2CuO_4$.

Results

Density functional theory (DFT) computations show that the electronic structure of AgF$_2$ is very similar to that in cuprates. Fig. 2C shows hybrid DFT calculations comparing the characters of the density of states (28). Both compounds have well-separated Hubbard bands of dominant $d_{x^2−y^2}$ character (indicated by red arrows in Fig. 2C), while the first ionization states are of dominant $p$ character; therefore, both compounds are predicted to be charge transfer insulators according to the classification scheme of Zaanen et al. (29). The small charge transfer gap is considered a key characteristic of cuprates. Our unbiased computations in Fig. 2C predict that AgF$_2$ should have an even smaller charge transfer energy than the cuprates, which can provide a test platform for theories based on the smallness of this parameter (30).

As a minimal model of the electronic structure, we consider one $d_{x^2−y^2}$ orbital centered on the TM [as in cuprates (31)] and two $p$ orbitals on the F sites (one more than the cuprates). $p_||$ indicates the $p$ orbital parallel to the TM–TM bond, while $p_\perp$ is perpendicular to the bond but also mixes with the $d_{x^2−y^2}$ orbitals because of the substantial buckling (SI Appendix, SI Text and Fig. S2). From unpolaredized DFT computations, we find that the hopping integral of a hypothetically straight Ag–F–Ag bond with the same interatomic distances is $t_{4d} = 1.38$ eV, practically the same value as the cuprates (32) (SI Appendix, SI Text and Figs. S3 and S4). However, due to the increased corrugation of the planes and the destructive interference of the $p_\perp$ and $p_\parallel$ orbitals, the effective hybridization is smaller, which explains the narrower upper Hubbard band of AgF$_2$ in Fig. 2C (SI Appendix, Table S1).

The similar splitting between Hubbard bands shown in Fig. 2C for AgF$_2$ and $La_2CuO_4$ (9.4 and 10.7 eV, respectively) suggests that the Hubbard $U_4$ parametrizing the Coulomb repulsion on the $d_{x^2−y^2}$ orbitals is similar in the two compounds. However, this estimate does not properly take into account the polarizability of the environment. An empirical estimate of $U_4$ can be obtained from Auger experiments in compounds with similar ions but a filled $d$ shell. Thus, for Cu$_2O$ (Cu $d^{10}$), Sawatzky and coworkers (33) obtained $U_{4d} = 9.2$ eV, which is close to the accepted value for Cu $d^9$ in CuO planes. For Ag$_2$O (Ag $d^{10}$), they obtained $U_{4d} = 5.8$ eV, which is smaller than for $3d$, which is expected for the more diffuse $4d$ orbitals but still quite large. This value, however, cannot be directly transposed to AgF$_2$, because the difference in screening has to be taken into account. Screening of the free ion Hubbard $U_0$ to the value $U$ in the solid is determined by the relaxation energy $R$ of the environment according to $U = U_0 - R$. For TM compounds, $R$ is expected to scale with the polarization of the ligands and to be inversely proportional to the ligand–TM distance to the fourth power (34). For copper oxides, typical values of the oxygen polarizability are in the range $\alpha_O = 1.9 \sim 3.2$ Å$^3$. Instead, in
AgF₂, the ligand–TM distance is larger, and the polarizability of the ligand is much smaller at \( \alpha_F = 0.64 \, \text{Å}^2 \), leading to less efficient screening. This allows for values of \( U_F \) in AgF₂ similar to the cuprates (SI Appendix, SI Text). Interestingly, from a different perspective, the computations of Fig. 2C suggest the same conclusion.

The similarity of the DFT electronic structures confirms the conclusions of the simplistic picture of Fig. 1A and C. From the point of view of the strength of the correlation, the narrower upper Hubbard band of AgF₂ suggests a more correlated system but a smaller \( U_F \) and smaller charge transfer gap point in the opposite direction. Our results imply that AgF₂ is very cova
tent, probably more so than the cuprates, which is consistent with core- and valence-level spectroscopy results (35) but in contrast with the prevailing view that fluorides are ionic compounds.

The more interesting parameter for a cuprate analogue is the magnetic exchange interaction, which determines the scale of magnetic fluctuations in magnetically mediated mechanisms of superconductivity in doped compounds. Not surpris
ingly, AgF₂ is antiferromagnetic (26) as predicted by Anderson superexchange.

A perturbation theory analysis shows that the dominant interaction is antiferromagnetic due to processes in which two holes from neighboring Ag sites occupy simultaneously the bridging F (SI Appendix, SI Text). As in cuprates (36), one needs to also consider processes in which two holes occupy the same Ag site (also antiferromagnetic) and direct ferromagnetic exchange. Buckling tends to reduce the antiferromagnetic contribution as \( \cos^2(\eta) \), where \( \eta = 132.4^\circ \) is the Ag–F–Ag angle (SI Appendix, Eq. S8).

While model computations have been very useful to discuss the dependence of the magnetic interaction in fluroargentates on the structure (37), the present lack of precise parameters does not allow one to obtain an accurate absolute value. An alternative estimate can be obtained from hybrid DFT computations, which yield \( J = 56 \, \text{meV} \) for the nearest neighbor interaction (Table 1). Computations (37) done with a new generation functional (38) yield \( J = 71 \, \text{meV} \).

As in La₂CuO₄, the TM in one plane coincides with the center of the four-TM plaquette in the next plane, which tends to frustrate interplanar magnetic interactions in an antiferromag
tically ordered state. In both compounds, the frustration is partially relieved by the orthorhombicity, but the effect is much larger in AgF₂. For the ratio of interlayer to intralayer couplings, our DFT computations predict values of the order of \( 10^{-2} \) (SI Appendix, Table S2), a larger ratio than the experimental (27) in cuprates (10⁻³) but still well in the regime of a quasi-2D quantum antiferromagnet.

| Polymorph | Cell vectors (Å) | \( R \) (Å) | \( \eta \) (°) | \( J \) (meV) |
|-----------|-----------------|-------------|-------------|-------------|
| \( \alpha \) – AgF₂ | \( 5.191 \) | \( 5.662 \) | \( 6.042 \) | \( 4.198 \) | 132.4 | 56 |
| \( \delta \) – AgF₂ | \( 5.671 \) | \( 5.670 \) | \( 5.607 \) | \( 4.166 \) | 148.5 | 137 |
| \( \omega \) – AgF₂ | \( 5.836 \) | \( 5.836 \) | \( 6.213 \) | \( 4.127 \) | 180 | 195 |

We report key structural parameters and values of the nearest-neighbor magnetic coupling constant calculated with the DFT total energy method. \( R \) is the sum of the two Ag–F distances of the bond. \( \alpha \) – AgF₂ is the known stable phase in which experiments have been done (experimental values are given in parentheses). \( \omega \) – AgF₂ is tetragonal, but cell parameters are reported in the \( \sqrt{2} \times \sqrt{2} \times 1 \) unit cell for comparison. The text has a detailed description of the polymorphs. A hybrid functional was used (Materials and Methods). Notice that this functional yields a value of \( J \) below experiment. After this work was finished, a more accurate value was obtained in ref. 37.

We used a full set of exchange constants with longer-range interactions (SI Appendix, Table S2) from DFT computations to estimate the Néel temperature with classical Monte Carlo computations (SI Appendix, SI Text). Correcting approximately for quantum effects, we found a value higher than the experimental one (by 27%) but of the same order. Given the approxima
tions involved, this fair agreement validates the hybrid DFT computations of exchange constants. As shown below, Raman experiments reveal an even larger value of the effective nearest neighbor exchange. We believe that uncertainties in the interplanar coupling and extra terms in the Hamiltonian, like four-site cyclic exchange, can explain the mild difference between the DFT + Monte Carlo estimate of the Néel temperature and the experiment.

To further test the analogy, we experimentally studied high-quality powder samples of freshly prepared AgF₂. Crystallinity was verified with powder X-ray diffraction, which resulted in a spectrum with similar characteristics but fewer impurity signatures than a commercial sample (SI Appendix, SI Text and Fig. S5).

Specific heat measurements reveal that only about 5% of the maximum possible entropy change \( R \ln(2) \) occurs around the Néel temperature (SI Appendix, SI Text and Fig. S6). This is consistent with a quasi-2D antiferromagnet, where short-range in-plane correlations set in at much higher temperatures than the 3D Néel temperature. A bulk EPR signal was searched over a wide range of temperatures. However, despite several efforts, it was not found. This is also analogous to the situation in the cuprates and points to strong antiferromagnetic interactions (SI Appendix, SI Text). Vibrational spectroscopy (Raman and IR) shows phonon modes in good agreement with the prediction of hybrid DFT, validating the latter computations (SI Appendix, Fig. S7). In addition, the detailed phonon assignment (SI Appendix, SI Text and Table S3) allowed us to check the integrity of the sample under the laser spot and to exclude impurity phases or photochemistry by-products.

For high Raman shifts, we detected a broad band centered at 1,750 cm⁻¹ at room temperature, which hardens and becomes narrower on cooling (Fig. 3A). The temperature dependence is very similar to the one for two-magnon Raman scattering in cuprates (39). This allows us to identify unambiguously this line as due to two-magnon Raman scattering in AgF₂. Comparing with cuprates, we deduce that the antiferromagnetic exchange in this compound is \( J_{AF} = 70 \, \text{meV} \), confirming the expected large antiferromagnetic interaction and in excellent agreement with the computation of ref. 37. The robustness of two-magnon Raman scattering well above the Néel temperature also confirms strong short-range antiferromagnetic correlations, also like in cuprates.

Fig. 3B shows the two-magnon Raman line recorded with three different apparatuses (Materials and Methods). The line shape is clearly visible with excitation energies of 1.17 and 1.58 eV. The feature at 970 cm⁻¹ is assigned to a two-phonon process. For 2.41 eV, the two-magnon feature is weak at high temperature (compared with the two-phonon feature) but becomes stronger on cooling, similar to the behavior for 1.17 eV (Fig. 3A) and for cuprates. Unfortunately, a detailed line shape analysis is not possible in this case due to a strong energy-dependent background (dashed lines in Fig. 3B). The dependence on the excitation energy suggests that the resonance profile of the two-magnon line is shifted to lower laser excitation energies with respect to what is found in cuprates (40), which is consistent with the smaller charge transfer gap found in DFT.

To confirm the large value of \( J \), we performed inelastic neutron scattering experiments in a 150-g AgF₂ powder sample. The experimental excitation spectrum (Fig. 4A and SI Appendix, Fig. S8A) shows a plume (indicated by the arrow in Fig. 4A) at a value of \( |Q| \) corresponding to the propagation vector of the
The above results clearly indicate that AgF$_2$ is an excellent cuprate analog with a very similar electronic structure and large magnetic interaction. Putting AgF$_2$ under high pressure does not flatten but tends to form lower-dimensional structures (46).

Remarkably, it has been predicted that the observed structures as a function of pressure should lead to quasi-1D magnetism and ladders with extremely high antiferromagnetic constants, allowing one to visit practically all of the physics of low-dimensional quantum magnets in the same compound (37).

Historically, the superconducting temperature in cuprates has been optimized starting from simple ternary compounds and increasing the number of chemical elements. In argentates, starting from a binary compound that is already stable leaves substantial freedom for such optimizations.

Clearly, a high priority is to produce doped AgF$_2$ planes. One concern (47) is that ionic distortions may self-trap carriers and hinder metallic conduction and superconductivity. Similar to ref. 48, we computed lattice spin polaron using DFT + U (Materials and Methods). For electron-doped AgF$_2$, we find that polaronic tendencies are very strong and that electrons self-trap. For the hole-doped case, polaronic tendencies are stronger than cuprates due to the large buckling but remain moderate. Indeed, the energy gain due to lattice relaxation is smaller than the estimated bandwidth and of the order of the breathing phonon frequency (~60 meV), indicating that metallic conduction may still be possible if high-enough doping is achieved. Polaronic tendencies should be further reduced in the case of the flat-layer polymorphs discussed below.

The cuprate family of parent high-$T_c$ superconductors is made of materials very similar to each other. Indeed, changes in key parameters, like $J$, are smaller than 15% (49). This severely hampers the identification of clear trends in physical properties. A close cuprate analog but with important differences (less marked 2D character, smaller $J$, narrower bands, smaller charge transfer gap, rich polymorphism) opens the way to the clarification of the mysterious cuprate-phase diagram by revealing clear trends. Another desirable development is to make the planes flat, which according to SI Appendix, Eq. S8, should increase $J$. Such hypothetical polymorphs were studied in the past with DFT (40–53). One such structure (20, 51) dubbed $\delta$--AgF$_2$ is obtained by constraining the AgF$_2$ plane to be a mirror plane but allowing the Ag–F–Ag bond to have an angle inside the plane. This polymorph shows a modest increase in energy at ambient pressure with a large value of $J$ according to DFT computations (20). Since this kind of functional may overestimate the magnetic order, $Q_{AF}$. The plume originates on the powder average of the acoustic wave excitations emanating from $Q_{AF}$ (i.e., the Goldstone mode) and is typical of soft dispersions (41) consistent with a large value of $J$. Fig. 4B is a simulation using spin wave theory (42). Although the plume is well explained by the theory using an in-plane magnetic exchange constant similar to the one in Raman, uncertainty in the data allows for considerable freedom on the admissible values of $J$.

The situation is different for the flat band at 148±3 meV. Simulations show that this flat band originates in the maximum of the magnetic dispersion relation, which produces a Van Hove-like singularity when averaged over all possible grain orientations in our powder sample, and its energy is roughly $2J$ (plus small corrections due to interplanar coupling). The sensitivity to the in-plane exchange allows to confirm $J=70$ meV as found in Raman.

The intensity of the flat band has an interesting dependence on wave vector, which is determined by the magnetic form factor. Unfortunately, the atomic form factor of Ag in the $d^7$ configuration is not available in the standard sources (43). Using instead a Pd $d^9$ form factor (as the closest available $4d$ anion with a known atomic form factor), we find a flat band intensity, which is peaked at much smaller wave vectors respect to experiment (SI Appendix, Fig. S6B). In the simulation in Fig. 4B, we used a DFT form factor computed as in ref. 44, which substantially improves the agreement with respect to the atomic form factor but still yields a maximum of intensity at around 5 Å$^{-1}$ instead of the maximum near 8 Å$^{-1}$ observed in the experiment. Strong covalency of the Ag–F bond is essential for the improvement in the DFT simulation with respect to the atomic form factor. We attribute the differences still observed to the known deficiencies of DFT to accurately describe the bond charges in a correlated material (45).

**Discussion**

The above results clearly indicate that AgF$_2$ is an excellent cuprate analog with a very similar electronic structure and large magnetic interaction. Putting AgF$_2$ under high pressure does not flatten but tends to form lower-dimensional structures (46), which according to DFT computations (SI Appendix, Table S2), we obtain that $J_{AB}=0.1J_{EBCO}$, which yields $J_{AB}=70$ meV for AgF$_2$. A linear background was subtracted to the spectra at 80–15 K but not to the room temperature spectrum, which was measured using a different machine (Materials and Methods). Spectra at different temperatures/apparatus were normalized with the phonon lines as shown in Insert. (B) We show data for AgF$_2$ at various excitation energies. For the 2.41-eV laser line, two temperatures are reported. Dashed lines are estimated non-magnetic backgrounds, which are well defined at high energy but cannot be uniquely defined at low energy.

Fig. 4. Powder inelastic neutron scattering. (A) Measured neutron scattering cross-section taken with incident neutron energy ($E_i$) of 300 meV. The vertical plume of scattering indicated by the arrow corresponds to $|Q|\gtrsim 1$ Å$^{-1}$, where $Q$ is the propagation vector of the magnetic order [(1,0,0) in reciprocal lattice units]. The strong signal at high $|Q|$ extending up to 60 meV corresponds to scattering from phonons, and the strong $|Q|$-independent signal at very low energy corresponds to incoherent elastic scattering. (B) Calculation of a powder-averaged neutron scattering cross-section using spin wave theory, performing a powder average, and convoluting with the instrumental resolution. We used an inplanar value of $J=70$ meV and interplanar $J_{\parallel}=4$ meV as suggested by the DFT computations (SI Appendix, Table S2).

Fig. 3. Two-magnon Raman spectra of AgF$_2$. (A) Temperature dependence for excitation energy 1.17 eV. We also show the low-temperature two-magnon line shape of EuBa$_2$Cu$_3$O$_y$ (EBCO) after ref. 39. The upper scale corresponds to EBCO, while the lower scale corresponds to AgF$_2$ (this work).

Curves are labeled by the temperature in Kelvin. Comparing the energy scales in A, we obtain that $J_{AF}=0.7J_{EBCO}$, which yields $J_{AF}=70$ meV for AgF$_2$. A linear background was subtracted to the spectra at 80–15 K but not to the room temperature spectrum, which was measured using a different machine (Materials and Methods). Spectra at different temperatures/apparatus were normalized with the phonon lines as shown in Insert. (B) We show data for AgF$_2$ at various excitation energies. For the 2.41-eV laser line, two temperatures are reported. Dashed lines are estimated non-magnetic backgrounds, which are well defined at high energy but cannot be uniquely defined at low energy.
interaction, we have repeated the computation with hybrid DFT, which yields a value of 137 meV as shown in Table 1. If one further restricts the bond angles to be straight, a tetragonal polymorph is obtained (52) dubbed $\omega - \text{AgF}_2$. In this case, a nearest-neighbor exchange approaching 200 meV is obtained. Obviously, such polymorphs are not stable at ambient pressure. However, it is possible that they can be stabilized by intercalation or that they may be grown as one or few layers on an appropriate substrate. Generally, we find that flat $\text{AgF}_2$ planes should have an antiferromagnetic J, which is more than twice the one of commercial $\text{AgF}_2$ and assuming a magnetically driven mechanism (54), could potentially lead to superconducting critical temperatures higher than those exhibited by cuprates.

Materials and Methods

Structure. Visualization of the structure was performed with the use of the VESTA software (55). The crystal structure of $\text{AgF}_2$ has been described in detail before based on powder neutron data (56–58). At ambient conditions, $\text{AgF}_2$ crystallizes in a distorted rutile-type structure of orthorhombic symmetry. This structure contains puckered $\text{AgF}_4$ sheets containing corner-sharing $\text{AgF}_4$ plquettes. The octahedral coordination of $\text{Ag}^{2+}$ is completed by two fluorine atoms from neighboring sheets. This structure can thus be described as built of puckered 2D sheets. SI Appendix, Fig. S1 compares the structure of $\text{AgF}_2$ with a typical cuprate.

DFT Computations. Unpolarized DFT calculations have been performed using the projector-augmented waves method as implemented in VASP (59) within the generalized gradient approximation of Perdew et al. (60) (PBE) and the crystal structure of ref. 26. The band structure was obtained for the experimental lattice (26) using a Monkhorst-Pack mesh of $26 \times 26 \times 26$ k points and a 500-eV plane wave cutoff. A smaller mesh of $8 \times 8 \times 8$ k points has been used for the projection onto maximally localized Wannier functions. Polarized calculations were done with the HSE06 functional (61), which is a hybrid functional mixing PBE with 25% of Hartree–Fock exchange energy. For the phonon assignments, dynamical matrix interatomic force constants and polarizabilities (macroscopic dielectric tensors) for computing IR and Raman intensities were obtained from the density functional perturbation theory scheme with $6 \times 6 \times 7$ k-point mesh (including 64 irreducible points) and cutoff = 520 eV using PBEsol functional in combination with Hubbard U for $\text{Ag}^{2+}$ ions with one unpaired electron (electronic configuration $3d^3$) within the DFT + U scheme as implemented in the VASP package (59). The Hubbard $U_{\text{Ag}}$ (23) was set to 5 eV, and $J_{\text{F}}$ was set to 1 eV. The $1\pi$-vibrational frequencies were calculated by diagonalizing the dynamical matrix for the fully converged structural $\text{AgF}_2$ model. IR intensity of $\text{AgF}_2$ has been expressed within dipole approximation in terms of atom-born effective charges and corresponding phonon eigenvectors using the formula for modal oscillator strengths (62, 63) as implemented in ref. 64. Intensity of each Raman mode was calculated in ref. 65. The electronic and ionic convergence was restricted to $10^{-8}$ and $10^{-7}$ eV, respectively. The atomic forces were converged to a maximal value of 0.02 meV/A. For the polaron configurations, we added or removed one electron from a $\sqrt{2} \times \sqrt{2} \times 1$ supercell corresponding to 1/8 doping.

Raman Scattering. Raman spectra shown in Fig. 3 and SI Appendix, Fig. S7 were acquired on a dry quartz capillary filled with $\text{AgF}_2$ in the 180° scattering geometry. The capillary was prefluorinated with F$_2$ and the crystal structure of ref. 26. The band structure was obtained for the experimental lattice (26) using a Monkhorst-Pack mesh of $26 \times 26 \times 26$ k points and a 500-eV plane wave cutoff. A smaller mesh of $8 \times 8 \times 8$ k points has been used for the projection onto maximally localized Wannier functions. Polarized calculations were done with the HSE06 functional (61), which is a hybrid functional mixing PBE with 25% of Hartree–Fock exchange energy. For the phonon assignments, dynamical matrix interatomic force constants and polarizabilities (macroscopic dielectric tensors) for computing IR and Raman intensities were obtained from the density functional perturbation theory scheme with $6 \times 6 \times 7$ k-point mesh (including 64 irreducible points) and cutoff = 520 eV using PBEsol functional in combination with Hubbard U for $\text{Ag}^{2+}$ ions with one unpaired electron (electronic configuration $3d^3$) within the DFT + U scheme as implemented in the VASP package (59). The Hubbard $U_{\text{Ag}}$ (23) was set to 5 eV, and $J_{\text{F}}$ was set to 1 eV. The $1\pi$-vibrational frequencies were calculated by diagonalizing the dynamical matrix for the fully converged structural $\text{AgF}_2$ model. IR intensity of $\text{AgF}_2$ has been expressed within dipole approximation in terms of atom-born effective charges and corresponding phonon eigenvectors using the formula for modal oscillator strengths (62, 63) as implemented in ref. 64. Intensity of each Raman mode was calculated in ref. 65. The electronic and ionic convergence was restricted to $10^{-8}$ and $10^{-7}$ eV, respectively. The atomic forces were converged to a maximal value of 0.02 meV/A. For the polaron configurations, we added or removed one electron from a $\sqrt{2} \times \sqrt{2} \times 1$ supercell corresponding to 1/8 doping.
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