Novel copper fluoride analogs of cuprates†

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On the basis of the first-principles evolutionary crystal structure prediction of stable compounds in the Cu–F system, we predict two experimentally unknown stable phases – Cu2F5 and CuF3. CuF3 comprises two interacting magnetic subsystems with Cu atoms in the oxidation states +2 and +3. CuF3 contains magnetic Cu2+ ions forming a lattice by antiferromagnetic coupling. We showed that some or all of Cu3+ ions can be reduced to Cu2+ by electron doping, as in the well-known KCuF3. Significant similarities between the electronic structures calculated in the framework of DFT+U suggest that doped CuF3 and Cu2F5 may exhibit high-Tc superconductivity with the same mechanism as in cuprates.

1 Introduction

Transition metal fluorides have been thoroughly studied during the last century. Among them, coinage metal fluorides have recently attracted considerable attention: the Cu–F system in the electrochemistry field,3–6 Ag–F as a potential new route to superconductivity,7,8 and Au–F due to the unusual oxidation state of gold. Actually, the Cu–F system contains an old puzzle of crystalline copper fluoride existence and synthesis, which produced a never-ending debate and remained unresolved to date. The first report of the synthesis of CuF with a zinc blende structure was published in 1933.10 It was then argued that the reported CuF is identical to Cu2O, dismissing the previous experimental results.11 Recently, no one succeeded in reproducing the synthesis of CuF, and the earliest studies have met strong criticism,12,13 since it is commonly believed that fluorine, because of its high electronegativity, will always oxidize copper to the oxidation state +2. Even though all attempts to synthesize CuF have been unsuccessful and the very existence of this compound is questionable, studies are ongoing14,15 and the complexes of CuF are already well characterized.16

The computationally guided studies of new transition metal fluorides, and CuF in particular, also continue. Initially, they mainly compared different structure prototypes to find a hypothetical ground state crystal structure17,18 or investigated cluster formation.19 A variety of new structures have been reported using evolutionary crystal structure prediction and assuming CuF stoichiometry.20 On the basis of all previous studies, eventually, it has been shown that all the predicted structures are metastable.18,20

Recently, a computational crystal structure prediction of coinage metal fluorides at different pressures has been done.20 However, the used method works with a fixed stoichiometry, which limits the prediction of new phases in the whole system. Moreover, redoing the same calculations leads to different structures.21 Thus, a detailed and reliable analysis of the whole Cu–F system remains to be carried out.

In this work, we present a first-principles variable-composition evolutionary crystal structure prediction study of all phases in the Cu–F system. We recover the experimentally known structure of CuF2 and report hitherto the unknown stable C2/m-Cu2F5, R3c-CuF3, and Pnma-CuF3 phases. Based on the similarities between the crystal structure of the discovered fluorides and the structure of the parent cuprate high-temperature (high-Tc) superconductor La2CuO4, we explored the possibility of high-Tc superconductivity in doped copper fluorides.

2 Computational methods

Here, the stable phases in the Cu–F system were predicted using the first-principles evolutionary algorithm as implemented in the USPEX package.22,23 The evolutionary search was combined with structure relaxation and energy calculations using density functional theory (DFT) within the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional and employing the projector augmented plane wave (PAW) method25 as implemented in...
the VASP package. We used a plane-wave energy cutoff of 600 eV and \( \Gamma \)-centered \( \xi \)-meshes with a resolution of \( 2\pi \times 0.05 \, \text{Å}^{-1} \) for Brillouin zone sampling, ensuring the excellent convergence of the quantities of interest. During the variable-composition structure search, the first generation of 160 structures was produced using random symmetric and random topological structure generators, with up to 18 atoms in the primitive cell. 70% of the next generation was obtained by applying variation operators (heredity, soft mutation, lattice mutation) to the 70% of the lowest energy structures of the current generation and the other 30% of the generation was produced randomly.

### 3 Results and discussion

#### 3.1 Hitherto unknown compounds in the Cu–F system

Phases located on the thermodynamic convex hull are stable with respect to decomposition into elemental Cu and F or other Cu–F compounds. Moreover, all the values of the chemical potentials, delimiting the fields of stability of compounds, are derived directly from the convex hull. The spin-polarized DFT calculations lead to the convex hull diagram of the Cu–F system as presented in Fig. 1. It contains experimentally known \( P2_1/c \)-CuF, hitherto unknown \( C2/m\text{-}CuF_2 \) and \( R3c\text{-}CuF_3 \), and slightly metastable \( Pnma\text{-}CuF_3 \), which is just 0.001 eV above the convex hull. The successful prediction of \( CuF_2 \), a known compound, and \( R3c\text{-}CuF_3 \), predicted in another theoretical study, indicates the robustness of our methodology for crystal structure prediction. All the obtained potentially stable structures became the subject of an experimental study.

The most energetically favorable structure of CuF, found in our study, is the low-symmetry \( P1\text{-}CuF \), which is even lower in energy than that in previous reports by \( \sim 0.05 \, \text{meV} \) per atom, but its low symmetry and high energy (\( \sim 50 \, \text{meV} \) per atom above the convex hull) indicated its instability and tendency to decompose into Cu + CuF. Thus, we conclude that CuF is unlikely to exist at ambient pressure.

\( CuF_3 \) crystallizes in the monoclinic space group \( C2/m \) with two inequivalent Cu sites, where each Cu atom of the first type is bonded to six pairwise equivalent F atoms forming a \( CuF_6 \) octahedron (Fig. 2a), with the corner-sharing octahedral tilt angles of 0°. In the second site, the Cu atom is in a square planar geometry with four pairwise equivalent F atoms. This arrangement could also be described as a distorted octahedron (see the ESI† for Fig. S3a). While isostoichiometric \( P1\text{-}AgF_3 \) is well-known, hypothesis \( P1\text{-}CuF_3 \) has a higher energy than \( C2/m\text{-}CuF_2 \) by \( \sim 3 \, \text{meV} \) per atom in the spin-polarized DFT solution.

Ground state \( CuF_3 \) has a trigonal perovskite structure with the space group \( R3 \) (Fig. 2b). This structure was also predicted in ref. 9. The Cu atom is bonded with six equivalent F atoms to form an octahedron with the corner-sharing octahedral tilt angles of 29°. Orthorhombic \( Pnma\text{-}CuF_3 \), metastable at 0 K, also has a perovskite structure \( ABX_3 \), with the absence of A cations – ReO\(_2\)-type structure (Fig. 2c), with the corner-sharing octahedral tilt angles of 28°. Metal trifluorides such as FeF\(_3\), CoF\(_3\), RuF\(_3\), RhF\(_3\), PdF\(_3\), and IrF\(_3\) also have a perovskite structure with the space group \( R3c \) whereas AgF\(_3\) and AuF\(_3\) crystallize in a totally different structure with the space group \( P6_3\text{22} \). Hypothetical \( P6_3\text{22}\text{-}CuF_3 \) has a higher energy than the \( R3c \) phase by \( \sim 30 \, \text{meV} \) per atom in the spin-polarized DFT solution. Notably, perovskite-type structures frequently have octahedral tilt instabilities and exhibit phase transition.

#### 3.2 Analogy with cuprates

Discovered Cu fluorides have significant crystal-chemical similarities with high-\( T_c \) cuprates. In both systems, we observe \( Cu^{2+} \) (in square planar coordination, as a consequence of Jahn–Teller distortion in all cuprates and \( CuF_3 \)) and \( Cu^{3+} \) (in \( CuF_3\), \( Cu_2F_6 \), and doped cuprates). As we discuss below, pure parent compounds \( CuF_3\), \( Cu_2F_6 \), and \( La_2CuO_4 \) are antiferromagnetic insulators, but doping with electrons or holes makes them metallic and superconducting (for sure \( La_2CuO_4 \) and most likely for copper fluorides).
The lowest in energy (ESI† considered systems, solutions with antiferromagnetic order are formed by the ligands. Notably, the magnetic exchange interaction is believed to be mediated by spin fluctuations. Doped Cu fluorides can, or perhaps, be superconducting by the same magnetically mediated mechanism.

3.3 The importance of DFT+U

Although DFT sheds light on some premature analogies with cuprates, in principle, this method is pathological since it cannot correctly reproduce the antiferromagnetic insulating state of La$_2$CuO$_4$ because it neglects on-site Coulomb correlations, and more robust results are achieved by taking into account the electronic correlations using the DFT+U method with the Coulomb interaction parameter $U = 8$ eV and the exchange interaction parameter $J = 0.9$ eV. Because we deal with copper in the same divalent and trivalent states, and the energy bands in cuprates and copper fluorides studied here have similar widths (Fig. 3a, c, e and Table 1), we chose the same values of $U$ and $J$ for all the calculations taking into account the on-site Coulomb repulsion between the Cu-3d electrons in CuF$_3$, Cu$_2$F$_5$, and Bamb-La$_2$CuO$_4$. For consistency with DFT calculations, the PBE exchange–correlation functional was also used in DFT+U. Structural information obtained after the relaxation with DFT+U and the values of total energy for ferromagnetic and antiferromagnetic orders are presented in the ESI† (Tables S1 and S2). We note that the calculations at the DFT-PBE level of theory allow us to compare the formation energy of structures on equal footing during the crystal structure prediction step. The inclusion of correlation effects at this step would require some particular $U$, which would be suitable for all compounds in the search. In fact, such $U$ does not exist.

We reproduced the insulating antiferromagnetic ground state of Bamb-La$_2$CuO$_4$ with the DFT+U energy gap of about 2 eV and the magnetic moment of the Cu atoms of 0.65 $\mu_B$, which are in close agreement with the experimentally observed values of ~2 eV and 0.68 $\mu_B$, respectively. The DOS for R3$_c$-CuF$_3$, Cu$_2$F$_5$, and Bamb-La$_2$CuO$_4$ obtained using DFT+U is presented in Fig. 3(b, d and f). The DOS for the Pnma phase is presented in Fig. S2 in the ESI†. For R3$_c$-CuF$_3$ and Pnma-CuF$_3$ in the antiferromagnetic phase, the DFT+U calculations show similarities in the key features of the electronic structures of CuF$_3$ and Bamb-La$_2$CuO$_4$ – they have well-separated Hubbard bands formed by the Cu-d states, whereas the first ionization states have a $p$-symmetry and are formed by the ligands.

In the CuF$_3$ structures, copper has an atypical formal oxidation state of +3, which leads to the 3$d^8$ electronic configuration, whereas in Bamb-La$_2$CuO$_4$ there are Cu$^{3+}$ Jahn–Teller active ions. However, some or all of Cu$^{3+}$ ions in CuF$_3$ can be reduced to Cu$^{2+}$ by electron doping, like in the well-known perovskite-type KCuF$_3$, where all Cu atoms are in the oxidation state +2. CuF$_3$, in fact, can

To compare the electronic properties of copper fluorides and cuprates, we first performed the spin-unpolarized DFT calculations using dense Monkhorst–Pack meshes of $8 \times 8 \times 4$ and $12 \times 12 \times 12$ $k$-points for the distorted orthorhombic low-temperature Bamb-La$_2$CuO$_4$ phase and all fluorides, respectively. Structural information and energies for ferromagnetic and antiferromagnetic orders are presented in the ESI† (Tables S1 and S2). The density of states (DOS) for R3$_c$-CuF$_3$, Cu$_2$F$_5$, and Bamb-La$_2$CuO$_4$ resolved for the Cu-d and ligand-$p$ states using DFT is shown in Fig. 3(a, c and e). In all the systems, the DFT results show that the Cu-3d energy band is located completely inside the $p$ band of the ligands and strongly hybridizes with it. Therefore, the partially filled electronic states of interest are formed by the $d$- and $p$-symmetry states with approximately equal weights, and the usual ionic picture is not applicable for such a band structure. Notably, the magnetic exchange interaction is proportional to the scale of magnetic fluctuations. For all the considered systems, solutions with antiferromagnetic order are the lowest in energy (ESI† Tables S3 and S4).

Since the energy difference obtained from the spin-unpolarized and spin-polarized DFT calculations is quite small (comparable to the thermal energy at room temperature (~26 meV) and vibrational energy of atoms (the highest optical phonon modes have energies of ~75 meV in Cu$_2$F$_5$ and ~65 meV in CuF$_3$ and less than ~0.05 and ~0.1 eV per Cu atom for Cu$_2$F$_5$ and CuF$_3$, correspondingly, and ~10$^{-4}$ eV per Cu atom for $K_{0.75}$CuF$_3$)), one can expect strong spin fluctuations in both types of systems – and we recall that the high-$T_c$ superconductivity of cuprates is believed to be mediated by spin fluctuations. Doped Cu

![Fig. 3](https://example.com/image3.png)

**Table 1** Bandwidth $W$ and charge transfer gap $\Delta_{pd}$ calculated using DFT. Hubbard bands splitting $U_{dd}$, spin $S$, and magnetic moment $M$ obtained using the DFT+U method. The values in parentheses are related to the second type of Cu atoms in the Cu$_2$F$_5$.

| Compound | $W$ (eV) | $\Delta_{pd}$ (eV) | $U_{dd}$ (eV) | $S$ | $M$ (µB) |
|----------|----------|-------------------|----------------|-----|-----------|
| R3$_c$-CuF$_3$ | 8 | 1.7 | 9.5 | 1 | 1.15 |
| Cu$_2$F$_5$ | 8 | 1.42 | 9.5 | 1 (1/2) | 1.17 (0.79) |
| La$_2$CuO$_4$ | 9 | 2 | 10.5 | 1 | 0.65 |
be described as the structure of KCuF₃ with all K atoms removed. Thus, one way to make a superconducting Cu fluoride is to remove the part of K atoms from KCuF₃ (in a vacuum tube) – the result should be a metallic perovskite-type compound with mixed Cu²⁺ and Cu³⁺ states. To clearly show this, we performed a fixed-composition structure search of K₃(CuF₃)₄, which determined that the most stable phase has a perovskite-type structure with the space group Im₃m (ESI, Fig. S3c). This structure is stable with respect to the decomposition into R₃c-CuF₃ and KCuF₃ (~0.05 eV per atom below the decomposition line), which means that potassium ions can be easily extracted from the KCuF₃, forming a mixed-valence compound.

According to the DFT+U solution: each Cu site in the CuF₃ has spin 1; Cu₂F₅ is determined as a compound with mixed Cu²⁺ and Cu³⁺ state and Cu ions with spin 1 and 1/2; Cu ions in the cuprate have spin 1/2. The magnetic moments per atom obtained from the DFT+U calculations for R₃c-CuF₃ are 1.15 μB (1.14 μB in the Pmma phase). These magnetic moment values are smaller by a factor of 0.58 than the formal ionic value of 2 μB for a Cu³⁺ ion compared to the reduction factor of 0.65 for the formal atomic value of 1 μB for a Cu²⁺ ion in the La₂CuO₄.²⁷ For Cu₂F₅, we found that two types of Cu atoms have different formal electronic configurations of d⁰ and d³, and different magnetic moments of 1.17 μB and 0.79 μB. All the predicted copper fluoride structures and Bamb-La₂CuO₄ are charge-transfer insulators with respect to the classification of Zaanan et al.¹⁸ The first energy excitation occurs between the p band of the ligands and the d band of the metal ion. CuF₃ has a small charge transfer gap (an important characteristic of cuprates) Aₚd = 1.7 eV, and Cu₂F₅ also has a small charge transfer gap Aₚd = 1.42 eV, comparable with 2 eV of La₂CuO₄. Though the energy gap depends on the choice of the Hubbard U parameter, the charge-transfer nature of the gap remains the same for a wide range of U values in fluorides. The splitting between the Hubbard bands for CuF₃ and La₂CuO₄ is similar and equal to ~9.5 eV and 10.5 eV, respectively (Fig. 3b and d).

### 3.4 Influence of doping on the electronic structure

Cu₂F₅, CuF₃, and La₂CuO₄ are insulators and can exhibit superconductivity only when properly doped. Consequently, we performed DFT+U calculations of the considered systems doped with holes using the rigid-band shift approximation, with doping amounted to 0.25 holes for each copper atom in the unit cell (Fig. 4a–c). CuF₃ and Cu₂F₅, like La₂CuO₄, undergo a transition from the insulating to the conducting state upon the hole doping, which once again highlights the similarity of their electronic properties. We have also examined a 2 × 2 × 2 R₃c-CuF₃ supercell (64 atoms) with a vacancy on one of the F atoms. This ferrimagnetic structure lies on the thermodynamic convex hull (Fig. 1). This indicates that the formation of non-stoichiometric CuF₃₋ₓ₋₁₋₀ is favorable. The DFT+U solution determines the formation of a peak at the Fermi level for this structure (Fig. 4d). The perovskite-type Im₃m-K₃(CuF₃)₄ also has a metallic solution from the DFT+U study (Fig. 4e).

### 4 Conclusions

In summary, the results of the systematic crystal structure search in the Cu–F system support that CuF is unlikely to exist and have revealed hitherto unknown C2/m-CuF₃ and R₃c-CuF₃, and slightly metastable Pmna-CuF₄. Cu₂F₅ contains Cu ions with oxidation states +2 and +3, which leads to the presence of two magnetic subsystems. In CuF₃, Cu ions have an unusual oxidation state +3, which can be reduced to +2 by appropriate doping. We showed that potassium can be extracted from KCuF₃ forming a metallic state. We showed using DFT+U that all the discovered copper fluorides are strongly correlated compounds and charge-transfer insulators. Since the comparison of CuF₃ and Cu₂F₅ with the classical cuprate La₂CuO₄ shows many similarities, the discovered structures could possibly be a new class of high-Tc superconductors.

### Conflicts of interest

There are no conflicts to declare.

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