Evolution from two- to one-dimensional magnetic interactions in Cu_2F_{5-x} through electron doping by fluoride nonstoichiometry

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The copper fluoride Cu_2F_5 is a compound with two-dimensional (2D) magnetic exchange interactions between the Cu ions in the $S = 1$ and $S = \frac{1}{2}$ spin states. Using *ab initio* calculations, we predict that the existence of 5% vacancies in the fluoride sublattice of Cu_2F_5 results in a drastic transformation of the spin state of all copper ions and the final spin states are $S = \frac{1}{2}$ and $S = 0$. Consequently, the anisotropy of the magnetic interactions increases, and 1D linear chains of Cu d^9, $S = \frac{1}{2}$ ions appear. We also propose a microscopic mechanism of such a transformation of the exchange interaction via CuO_6 octahedra elongation.

I. INTRODUCTION

Cuprates are objects well known for the appearance of low-dimensional magnetism. With such structural building blocks as CuO_6 octahedra and CuO_4 plaquettes, and due to the presence of a copper ion in the d^9 electronic configuration, there is a variety of magnetic structures. In perovskitelike $KCuF_3$ [1,2], whose structure is formed with corner-sharing CuF_6 octahedra, there is a G-type antiferromagnetic ordering of moments with the existence of one-dimensional (1D) magnetic chains of Cu ions. Two-dimensional (2D) antiferromagnetic ladders are realized in $Sr_{n-1}Cu_{n+1}O_{2n}$ [3] and $SrCu_2O_3$ [4] with edge-sharing CuO_4 plaquettes, and the corner-sharing plaquettes in Sr_2CuO_4 [5] and $AgCuVO_4$ [6] lead to the appearance of a one-dimensional chain of $S = \frac{1}{2}$ Cu ions.

The plethora of spin lattices mentioned above exist in copper-oxygen complexes. The stability of the copper-fluoride complex Cu_2F_5 was predicted recently [7]. Structurally it is formed by both blocks: the octahedra (CuF_6) and the plaquettes (CuF_4). Consequently, one can expect that the magnetic anisotropy, similar to the one seen in the cuprates, could appear in the fluoride with or without additional doping with carriers. In our previous work [8], within the Hubbard U corrected density functional theory (DFT+U) calculations, we show that in stoichiometric Cu_2F_5, the Cu ions are in the $S = 1$ and $S = \frac{1}{2}$ spin states (d^8 and d^9 electronic configuration). Additionally, we obtained that the Heisenberg exchange interaction along the a crystal axis is tiny. In the (100) plane there is an antiferromagnetic superexchange between the half-filled d orbitals of the nearest Cu ions through fluoride p states located in between. As a consequence, the 2D spin lattice exists in stoichiometric Cu_2F_5.

One can assume that if an extra electron occupies the half-filled d orbital of the Cu ion in Cu_2F_5, the corresponding Cu $d \leftrightarrow$ F $p \leftrightarrow$ Cu d superexchange interaction will be destroyed. More extra electrons will cause a significant modification of the exchange interactions. Our purpose is to find the conditions under which the one-dimensional magnetic interactions prevail in copper fluoride.

We have produced additional electrons in the cell considering the doped compound Cu_2F_{5-x}. Each fluoride vacancy results in an extra electron that occupies one of the copper d orbitals. As is shown in the following sections, not only the electronic and magnetic, but the crystal structure of the compound also evolves following the doping.

II. METHODS

In this paper, we follow the methodology defined in the previous one, describing Cu_2F_5 [8]. All calculations were performed using the QUANTUM ESPRESSO [9] package with pseudopotentials from the PSLIBRARY set [10]. The exchange-correlation functional was chosen to be in Perdew-Burke-Ernzerhof [11] form. The energy cutoff for the plane-wave functions and charge density expansion were set to 50 and 400 Ry, respectively. Integration in the reciprocal space was done on a regular $8 \times 8 \times 8$ k-point mesh in the irreducible part of the Brillouin zone.

Electronic correlations were treated within the DFT+U method [12] with the Hubbard U value equaling 6 eV. As it was shown for the parent compound Cu_2F_5, even the U value of 4 eV is enough for the band gap to appear. The variation of the U from 4 to 8 eV does not change the electronic structure qualitatively and affects the Heisenberg exchange interaction parameters only slightly. The Hund parameter $J = 0.9$ eV was set to its typical value for cuprates [13,14].

The convergence criteria used for crystal cell relaxation within DFT+U are total energy $< 10^{-6}$ Ry, total force $< 10^{-3}$ Ry/bohr, pressure < 0.1 kbar.
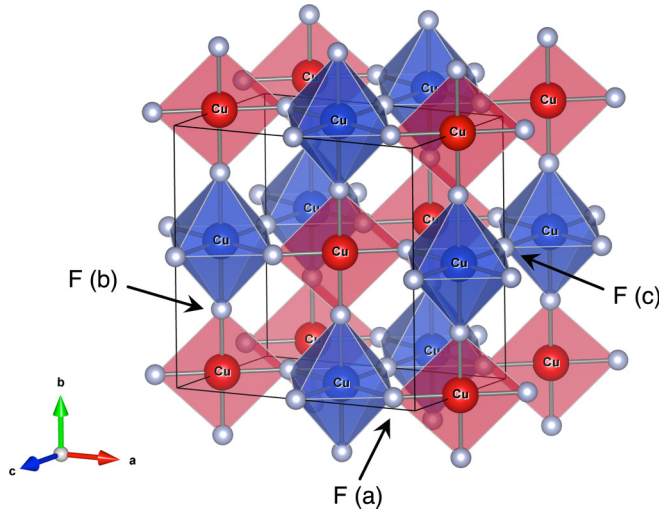
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FIG. 1. Crystal structure of Cu_2F_5 and the three types of fluoride ions that were removed to obtain the structure of Cu_2F_{5-x}. Blue spheres denote Cu ions inside the ligand's octahedron, red spheres denote Cu ions in the center of plaquettes, and gray spheres the F ions. Visualized using VESTA [15].

III. RESULTS

There are three different structural sites for the fluoride ion in Cu_2F_5 that could be substituted by a vacancy: (a) the fluoride shared by the CuF_4 plaquette and CuF_6 octahedron that are placed along the a axis of the cell; (b) the ion shared by the CuF_4 plaquette and CuF_6 octahedron in the direction of the b axis; and (c) the fluoride belonging to the two CuF_6 octahedra along the c axis. The Cu-F-Cu bond angle is $180°$ for the (b) and (c) ions and only $129°$ for the case (a) fluoride ion, which results in a much weaker magnetic exchange interaction in the direction of the a axis. The absence of one of these F ions would naturally lead to a change in the electronic configuration of the nearest Cu ions. With the destruction of the Cu-F-Cu superexchange path, the disappearance of one fluoride ion probably will change the magnetic exchange interaction pattern in Cu_2F_5.

In the Cu_2F_5 crystal cell containing eight Cu ions (see Fig. 1), we removed the F ion in the (a), (b), or (c) position sequentially, as described above, and performed full cell relaxation within the DFT+U approach to obtain a ground state crystal structure. The used cell size corresponds to a 5% concentration of fluoride vacancies ($Cu_2F_{4.75}$), and we are focused on this simplest and most visual case.

After relaxation, we compared the enthalpies of the obtained structures. The lowest enthalpy has a cell where the vacancy is placed instead of the F ion in the (b) position. If F is removed from the (c) position, the enthalpy is +45 meV/formula unit higher and it is +46 meV/formula unit higher for the vacancy in the (a) position. We conclude that the favorable vacancy localization site in Cu_2F_5 is the F ion shared by the CuF_4 plaquette and CuF_6 octahedron in the direction of the b axis. We refer to this particular vacancy position in crystal structure when we are discussing Cu_2F_{5-x} or $Cu_2F_{4.75}$ below in the text.

The vacancy creation results in the crystal structure distortions presented in Table I. A unit cell volume increase

TABLE I. Transformation of crystal structure of Cu_2F_5 with electrons doping via vacancies.

Parameter	Cu_2F_5	$Cu_2F_{4.75}$
Cell volume (Å^3)	369.3	393.6
$Cu_{octa} - Cu_{octa}$ distance along a (Å)	6.98	6.96
$Cu_{octa} - Cu_{octa}$ distance along b (Å)	7.61	8.08
$Cu_{octa} - Cu_{octa}$ distance along c (Å)	7.60	7.52
Average Cu_{plaq}-F bond length (Å)	1.90	1.80
Average Cu_{octa}-F bond length (Å)	1.93	2.04
Average Cu_{octa}-F distance along b (Å)	1.93	2.26

of 6.6% happens from the elongation of the cell along the b lattice vector. At the same time, there is an expansion of the CuF_6 octahedra and a decrease of the average Cu-F bond length within the CuF_4 plaquette in Cu_2F_{5-x}. We refer to the CuF_6 octahedron that lost one of the fluoride ions as a result of vacancy creation and became CuF_5 as $ex-CuF_6$, and the same for the $ex-CuF_4$ plaquette.

The two Cu ions, that had a F ion in between in Cu_2F_5, and have a vacancy site instead in $Cu_2F_{4.75}$, are slightly shifted to each other along the b crystal axis. Hereafter, the Cu-F bonds of the $ex-CuF_4$ plaquette and the $ex-CuF_6$ octahedron are distorted when they lose the shared fluorine ion. For the next-nearest to the vacancy Cu-F octahedra and plaquettes, one can still say that the local environment for the Cu ion remains an octahedron and a plaquette. The structure files for Cu_2F_5 and $Cu_2F_{4.75}$ could be found here [16].

The $Cu_2F_{4.75}$ is an antiferromagnetic insulator with a 0.91 eV band gap. The calculated partial densities of states (PDOS) are presented in Fig. 2. A plausible assumption would be to say that all copper ions inside the fluoride octahedra have very similar PDOS despite the various distortions of CuF_6
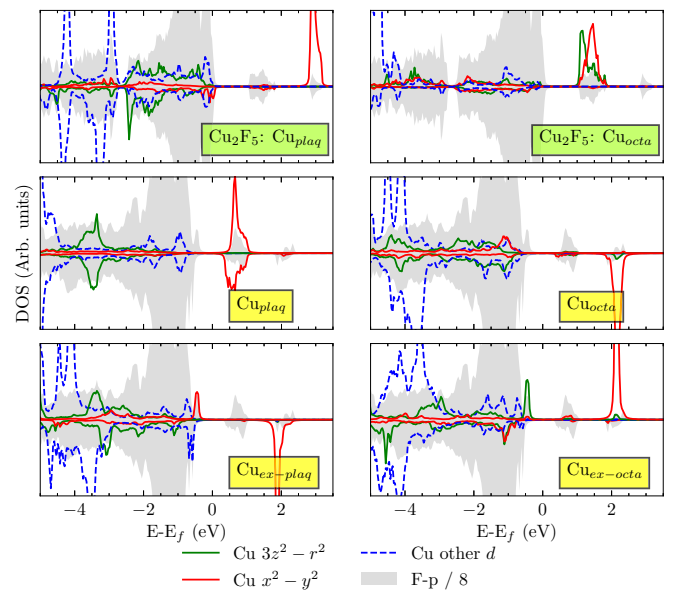

FIG. 2. Partial densities of states (PDOS) for Cu_2F_5 (upper panel) and Cu_2F_{5-x} (middle and lower panels). Positive/negative PDOS correspond to spin-up/spin-down states, respectively.

structures regarding the distance from the vacancy. The same is true for the CuF_4 plaquettes. The corresponding PDOS are marked in Fig. 2 as Cu_{octa} and Cu_{plaq}, respectively. Here and below, we refer to the Cu $3z^2 - r^2$, $x^2 - y^2$, etc., orbitals in terms of the local coordinate system for each Cu ion, where the z direction is perpendicular to the plaquette plane for the Cu_{plaq} ion and the z direction is along with the crystal b vector for the Cu_{octa} ion.

From the analysis of PDOS, one can see that Cu ions in the octahedral environment obtained an additional electron and became Cu^{2+} ions in the d^9, $S = \frac{1}{2}$ electronic configuration: All t_{2g} and $3z^2 - r^2$ orbitals are filled, and the $x^2 - y^2$ orbital is half filled. At the same time, the plaquette-surrounded Cu ions are now in the d^8, $S = 0$ configuration and have negligible magnetic moments. Both $Cu_{ex-plaq}$ and $Cu_{ex-octa}$ ions are in a d^9, $S = \frac{1}{2}$ electronic configuration with the hole at the $x^2 - y^2$ orbital. We started our calculation from the cell containing four Cu_{octa} ions in the d^8, $S = 1$ configuration plus four Cu_{plaq} ions in the d^9, $S = \frac{1}{2}$ configuration plus an electron from the vacancy. At the end we have obtained three Cu_{plaq} ions in the d^8, $S = 0$ plus five Cu ions (three Cu_{octa}, $Cu_{ex-plaq}$, $Cu_{ex-octa}$) in the d^9, $S = \frac{1}{2}$ configuration.

In Cu_2F_5 [8] the lower unoccupied state is the $3z^2 - r^2$ orbital of the Cu_{octa} ions (Fig. 2, upper panel, right graph). We assumed that as a consequence of the doping, the additional electron will occupy some of these orbitals. Consequently, metallization of Cu_2F_5 with electron doping was expected due to the appearance of the partially filled Cu_{octa} $3z^2 - r^2$ states. Surprisingly, we observe an electron transfer from the Cu_{plaq} ions to the Cu_{octa} ions in Cu_2F_5 with doping. We interpret it in the following way. Due to the partial occupation of the Cu_{octa} $3z^2 - r^2$ orbital, the corresponding octahedron elongates in the b direction, which results in the expansion of the cell along the b axis. Consequently, all the CuF_6 octahedra are elongated. Since the Cu-F distances in the b direction within the octahedron become large, the Cu_{octa} $3z^2 - r^2$ orbital turns energetically more favorable than even the Cu_{plaq} $x^2 - y^2$ orbital. Electrons that occupied the Cu_{plaq} $x^2 - y^2$ state in stoichiometric Cu_2F_5 leave it in Cu_2F_{5-x} and fill the Cu_{octa} ions' d shell. As a result, Cu_{plaq} ions that have the d^9 configuration in Cu_2F_5 become d^8 in the doped structure, and Cu_{octa} ions change their configuration in a reverse way.

To confirm such an evolution of the crystal and electronic structure arises from the electronic degrees of freedom, not from interactions between the vacancy states, we modeled the electron doping in stoichiometric Cu_2F_5. The fluoride ion was not removed. We just added one extra electron in the cell and relaxed the crystal structure.

As a result, the same effect was qualitatively reproduced. The cell volume increased by 17.5% with its significant elongation along the b direction (Cu_{octa}-Cu_{octa} distance grows up to 8.08 Å). The CuF_6 octahedra are stretched along the b direction too, with the corresponding average Cu_{octa}-F bond length equaling 2.25 Å. The spin state of the copper ions was also changed as a result of the existence of additional electrons: The Cu_{octa} ions became d^9, $S = \frac{1}{2}$.

We also tightened the limitations on the crystal lattice's relaxation process, permitting solely the modification of the unit cell's volume while keeping the positions of the ions
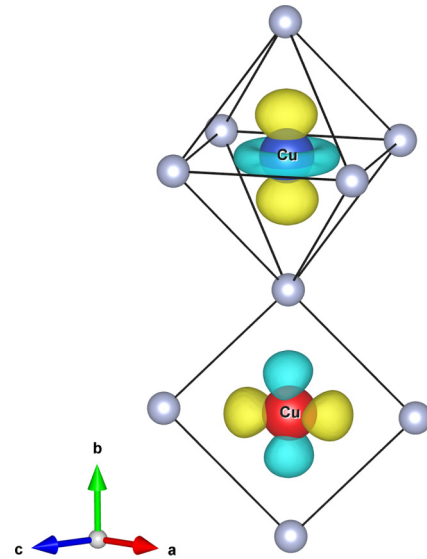

FIG. 3. Two half-filled d orbitals of Cu ions that provide the superexchange interaction via the F p orbital along the b axis in stoichiometric Cu_2F_5. In Cu_2F_{5-x} the $d_{3z^2-r^2}$ becomes fully filled and the superexchange is suppressed.

inside it fixed. However, even with these limitations, adding one additional electron per 4 formula units of stoichiometric copper fluoride resulted in a 13.5% increase in cell volume, primarily along the b-axis direction. The stretching of all CuF_6 octahedra makes the filling of the Cu_{octa} $3z^2 - r^2$ orbital favorable, causing the spin state of the Cu_{octa} ions to change to $S = \frac{1}{2}$.

On the other hand, when stoichiometric Cu_2F_5 is doped in the absence of structural relaxation, it does not result in such a spin-state evolution. Instead, the system becomes metallic, and the $3z^2 - r^2$ orbital remains predominantly unfilled.

We concluded that the electronic configuration and spin state of the copper ions in Cu_2F_5 evolve in the same manner if an extra electron appears regardless of the origin of the extra electron (vacancy or manual increase in the number of carriers within the cell). We continue our presentation and reasoning below for Cu_2F_{5-x} with a vacancy.

In stoichiometric Cu_2F_5 there are only two significant magnetic exchange interactions [8] (Fig. 4, left panel): between Cu_{octa} ions along the c axis and Cu_{octa}-Cu_{plaq} exchange along the b axis. Both interactions are brought about by the superexchange mechanism, i.e., via an electron hopping between a half-filled d orbital of Cu ion↔fluoride p orbital↔half-filled d orbital of the nearest Cu ion. Occupation numbers of d states and the spatial direction of the lobes of corresponding orbitals are critical for the resulting exchange value.

The superexchange interaction path between the Cu_{octa}-Cu_{plaq} ions along the b axis in Cu_2F_5 is shown in Fig. 3. It exists due to an electron hopping between the half-filled Cu_{octa} $d_{3z^2-r^2}$ and Cu_{plaq} $d_{x^2-y^2}$ states via the F p orbital in between. Following our results, the Cu_{octa} $d_{3z^2-r^2}$ orbital is no longer half filled in Cu_2F_{5-x}, consequently the possibility of such a hopping of electrons is suppressed and the corresponding superexchange interaction along the b crystal axis vanishes.
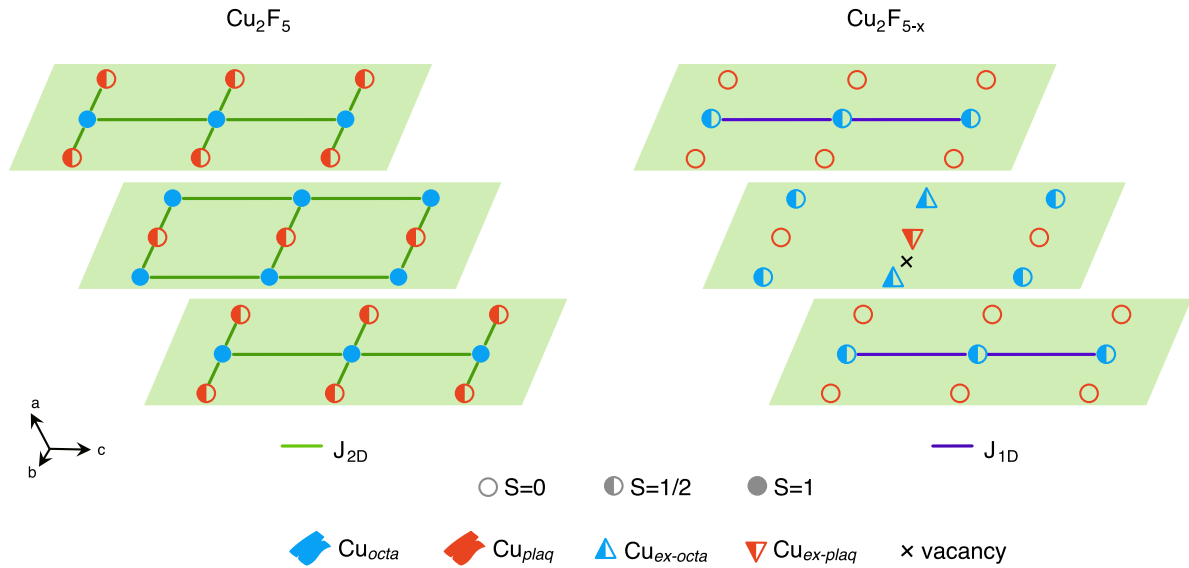
FIG. 4. Evolution of spin states and patterns of the exchange interaction between the Cu ion from Cu_2F_5 (left) to Cu_2F_{5-x} (right). Blue elements denote Cu ions in the surrounding octahedra, and red elements denote Cu ions in the center of the fluoride plaquettes. The blue and red half-filled triangles correspond to $Cu_{ex-octa}$, $S = \frac{1}{2}$ and $Cu_{ex-plaq}$, $S = \frac{1}{2}$ ions, respectively. The solid, half-solid, and open circles denote $S = 1$, $S = \frac{1}{2}$, and $S = 0$ spin states of the ions. The (100) lattice planes are shown with a light green color as a guide for the eye. The vacancy position is shown with a black cross. The strongest exchange interactions are J_{2D} in Cu_2F_5 (green line) and J_{1D} in Cu_2F_{5-x} (violet line). Other exchange interactions are negligible. Fluorine ions are not shown for clarity.

The described evolution of the electronic structure has an outcome that 1D chains of Cu_{octa} ions with a hole on the $d_{x^2-y^2}$ orbital appear. Taking into account the existence of the fluoride ion between such copper ions and following the Goodenough-Kanamori rule [17], the antiferromagnetic superexchange interaction will emerge along the c crystal axis.

Using the Green's function method based on magnetic-force linear response theory [2], we computed the Heisenberg exchange interaction between Cu ions up to the ninth nearest neighbor. The model Hamiltonian has the form $H = -\sum_{\langle ij \rangle} J_{ij} \mathbf{e}_i \mathbf{e}_j$, where $\mathbf{e}_i$ are the unit vectors pointing in the direction of the ith site magnetization, and the summation runs once over each ion pair.

Only one exchange interaction survived under doping. The antiferromagnetic exchange between the Cu_{octa} ions along the c axis is $J_{1D} = -29.5$ meV. The second largest interaction ≈ -3.3 meV is between Cu_{octa} and $Cu_{ex-plaq}$ ions along the [101] direction. The pattern of the 1D magnetic chains stems from such exchanges with the interchain interaction being an order of magnitude smaller than the intrachain one. It is shown in Fig. 4, right panel. The figure illustrates also the evolution of the strongest exchange interactions in Cu_2F_5 that arose from electron doping. The absolute value of the exchange remains almost the same, $J_{2D} \approx -33$ meV in Cu_2F_5, but the dimension of the interaction decreases from 2D to 1D as a result of doping.

We point here to an analogy to the exchange interaction pattern that exists in $KCuF_3$. The potassium copper fluoride is formed with the CuF_6 octahedra, and all copper ions have a hole on the $d_{x^2-y^2}$ orbital [14]. Since there are Jahn-Teller distortions of the octahedra, the lobes of the half-empty d orbitals of the nearest Cu ions are perpendicular to each other in the [001] plane. Consequently, the superexchange via the F p orbitals in the [001] plane is negligible in $KCuF_3$ and the

1D chains of antiferromagnetically ordered moments appear along the c crystal axis. Therefore, despite the different building blocks of the structure in Cu_2F_{5-x} (octahedra and plaquettes) and $KCuF_3$ (octahedra only), there is a similarity in the magnetic interaction picture between these two compounds.

IV. CONCLUSION

Using DFT$+U$ calculations, we explored the influence of the fluoride vacancy on the crystal, electronic, and magnetic structure of Cu_2F_{5-x}. Extra electrons, which resulted from the absence of the fluorine ion, are shown to result in the elongation of the CuF_6 octahedra along the b crystal axis and then the $3z^2 - r^2$ orbital of all Cu_{octa} ions becomes occupied. As a result, all the Cu ions in the center of CuF_6 octahedra obtain an $S = \frac{1}{2}$ spin configuration, and the Cu ions inside the CuF_4 plaquettes become nonmagnetic ($S = 0$). Such a significant effect becomes apparent even when one extra electron per 4 formula units is added. Antiferromagnetic linear chains of copper ions appear along the c axis of the crystal. The interchain exchange interaction is ten times smaller than the largest intrachain one. Our calculations show consistently that Cu_2F_{5-x} can be described as a quasi-one-dimensional $S = \frac{1}{2}$ Heisenberg chain in a good approximation.

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