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Mixed spin $S = 1$ and $S = \frac{1}{2}$ layered lattice in Cu_2F_5

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The electronic and magnetic structure, including the Heisenberg model exchange interaction parameters, was explored for the recently proposed novel cuprate Cu_2F_5. Using the DFT+U calculation, it is shown that the compound is formed by two types of copper ions with d^9 and d^8 electronic configurations. We have found a very stable antiferromagnetic ordering with strong anisotropy of exchange interaction that results in the appearance of an unusual 2D-magnetism: within the (100)-plane the exchange between the $S = 1$ and $S = 1/2$ Cu ions has almost the same strength as between the two $S = 1$ ions. The interplane magnetic interaction is five times weaker than the in-plane one.

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I. INTRODUCTION

Low-dimensional spin lattices exist in a plethora of forms such as spin ladders [1–3], plaquettes [4], dimers, and zig-zags [5,6]. The compounds possessing these magnetic structures demonstrate unusual magnetic excitation spectra, including the appearance of a spin gap. In the present paper, we have found an unusual type of 2D spin lattice in Cu_2F_5—a stable copper fluoride Cu_2F_5 predicted theoretically in our recent paper [7]. Here we analyze its electronic and magnetic structure in detail, relying on the known crystal structure.

Copper fluorides Cu_2F_5 and CuF_3 predicted earlier [7] have structural and electronic similarity with high-T_c cuprates, such as La_2CuO_4 and with prototypical correlated perovskite compound $KCuF_3$. Following the analogy to the mentioned compounds, one can assume the existence in Cu_2F_5 of AFM ordered spin lattice of the Cu ions moments. At the same time, the type of ordering and dimensionality of the spin lattice is unclear and should be obtained in calculations until experimental data appear.

The proposed analogy between Cu_2F_5 and La_2CuO_4 inspires us to analyze the spin state of Cu ions in Cu_2F_5 and to determine the orbital content of the electronic states right below the Fermi level. We have also explored the magnetic exchange interactions within the Cu_2F_5 crystal to find 2D magnetic structures.

The theoretically predicted [7] (using DFT) crystal structure of Cu_2F_5 has monoclinic C2/m symmetry and contains Cu ions with two types of coordination (see Fig. 1). The first type of Cu ions (Cu1) is in the center of a slightly distorted octahedron with three pairwise Cu-F distances (1.98, 1.96, 1.89 Å) and only one F-Cu-F angle equal to 91.3° (other F-Cu-F angles are 90°). Another type of Cu ions (Cu2) is in the center of a square formed by four F ions with two different Cu-F distances (1.83 and 1.86 Å). All F-Cu-F angles within such square plaquette are equal to 90°. Cu1 and Cu2 ions alternate along *a* and *b* crystal axes and form chains of the same type ions along the *c* axis.

If one neglects (not in calculations, but for simplicity of interpretation) the deviation of the F-Cu1-F angle from the 90° value then the Cu1 ion type has the D_{4h} point group symmetry. It means that the Cu *d* level splits into the t_{2g} (d_{zx}, d_{zy}, d_{xy}) and e_g ($d_{x^2-y^2}$, $d_{3z^2-r^2}$) subshells. For the Cu2 type of ions the square-planar surrounding splits the *d* level into (from highest to lowest): $b_{1g}(d_{x^2-y^2})$, $b_{2g}(d_{xy})$, $e_g(d_{zx}, d_{zy})$, and $a_{1g}(d_{3z^2-r^2})$ subshells.

To interpret our results in terms of Cu *d* orbitals, we have defined the local coordinate system (LCS) for each Cu ion as shown in Fig. 6 with the *z* direction perpendicular to the plaquette plane for the Cu2 ion and the *z* direction along with the crystal *b* vector for the Cu1 ion. Below, analyzing densities of states, hopping integrals, exchange interaction, etc., we will refer to the *d* orbitals defined in this LCS.

II. METHODS

All calculations were performed using Quantum-ESPRESSO [8] package with pseudopotentials from pslibrary set [9]. The exchange-correlation functional was taken to be in Perdew-Burke-Ernzerhof [10] form. The energy cutoff for plane-wave wave functions and charge-density expansion has been set to 50 Ry and 400 Ry, respectively. Integration in the reciprocal space was done on a regular 8 × 8 × 8 *k*-points mesh in the irreducible part of the Brillouin zone.

In Sec. III we first explore the electronic structure within DFT and then, keeping in mind the partially filled *d* shell of the Cu ions, continue with the DFT+U approximation. The DFT+U method is a compromise between the ability to describe correlated *d* states and computational cost of the

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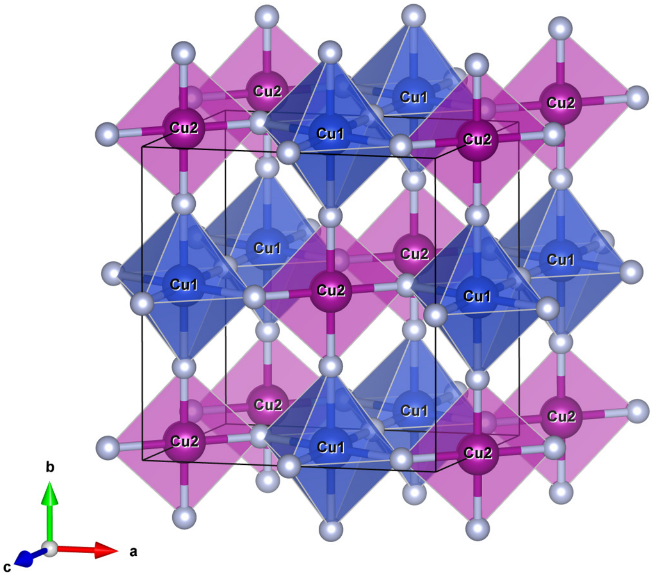

FIG. 1. Crystal structure of Cu_2F_5. Blue spheres denote Cu ions inside the ligand's octahedron, magenta spheres denote Cu ions in the center of plaquettes, grey spheres denote F ions.

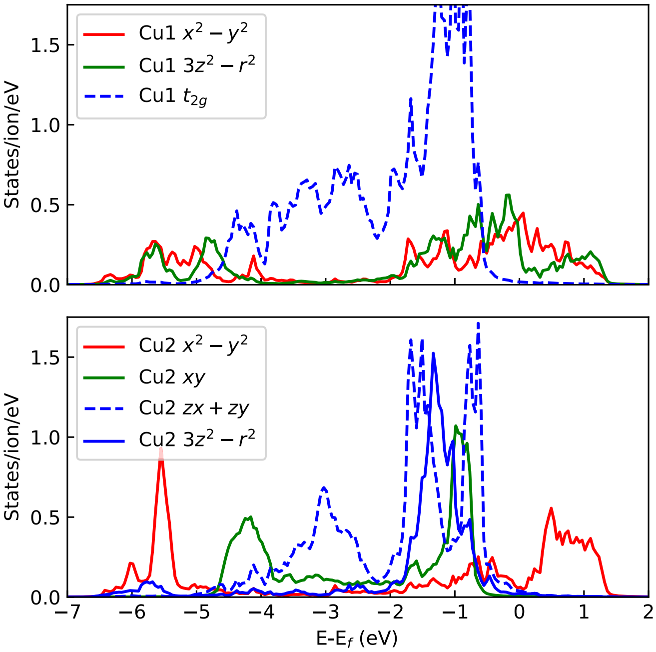

FIG. 2. Partial densities of states for Cu_2F_5 obtained within spin-unpolarized DFT calculation.

calculations. At each value of Hubbard's U parameter we relaxed the crystal structure. At the same time, Hund's parameter J was kept fixed at 0.9 eV in all DFT+U calculations; The relation between crystal field splitting of the e_g level of Cu1 ion and J parameter could, in principle, affect the stability of the $S = 1$ magnetic configuration, but we do not expect such a case because the splitting of e_g levels is small. $J = 0.9$ eV is typical for cuprates [11,12]. As soon as experimental crystal structure of Cu_2F_5 will become available, it will be intriguing to calculate the U and J parameters with the constrained DFT [13] or linear response [14] methods and investigate the electronic structure of this compound with a more advanced approach such as DFT+DMFT [15,16].

The convergence criteria used for the crystal cell relaxation within DFT+U are: total energy $<10^{-6}$ Ry, total force $<10^{-3}$ Ry/Bohr, pressure <0.5 kbar.

III. RESULTS

Partial densities of states (pDOSes) obtained within spin-unpolarized DFT calculation are shown in Fig. 2. For the Cu1 ions, there is the filled t_{2g} energy band with the width ≈4.5 eV. The same three orbitals (d_{xy}, d_{zx}, and d_{zy},) are filled for the Cu2 ions too, and the corresponding energy bands are located in the same energy region.

The situation is different for the other two d states. Both e_g states of the Cu1 ions are partially filled, their energy bands cross the Fermi level, and the occupations (from DFT) are 0.8 e and 0.74 e. Contrary, the $d_{3z^2-r^2}$ orbital of the Cu2 ion (in the center of the flat plaquette) is almost filled, and the corresponding peak of DOS is located ≈1.2 eV below the Fermi level. And the $d_{x^2-y^2}$ orbital of the Cu2 ions is partially filled with the occupation 0.62 e.

Keeping in mind the existence of partially filled d states, one should consider possible magnetic configurations. Also, the strong electronic correlations between the Cu electrons better be taken into account. We have compared the total energies of the Cu_2F_5 cell calculated for ferromagnetic (FM) and two types of antiferromagnetic (AFM) orderings (shown in Fig. 3). Since this compound has not yet been made in an experiment, and it is not known whether it is metallic or insulating, we used various values for the Hubbard U parameter from 2 to 8 eV. The AFM G-type of ordering is always favorable and has the total energy ≈300 meV lower than the other two phases.

The partial densities of states for AFM-G ordered magnetic phase of the Cu_2F_5 calculated within the DFT+U approach are shown in Fig. 4. For each value of the U parameter, the cell volume and atomic positions were relaxed to obtain the ground-state crystal structure. Starting from $U = 4$ eV the Cu_2F_5 is an insulator. The band gap at $U = 4$ eV is 0.48 eV and it broadens with increasing of the U parameter. For this U value it is an antiferromagnetic insulator with the top of the valence band formed by $x^2 - y^2$ states of the Cu2 ion. The increase of U results in the shifting of the occupied Cu-d

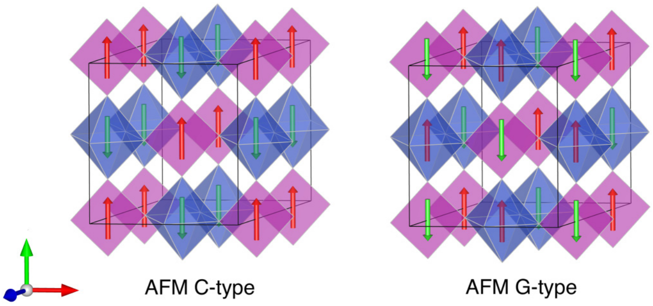

FIG. 3. Two types of considered AFM orderings of Cu ions magnetic moments in Cu_2F_5. Dark blue octahedra are CuF_6 octahedra, light-magenta rhombuses are CuF_4 plaquettes.

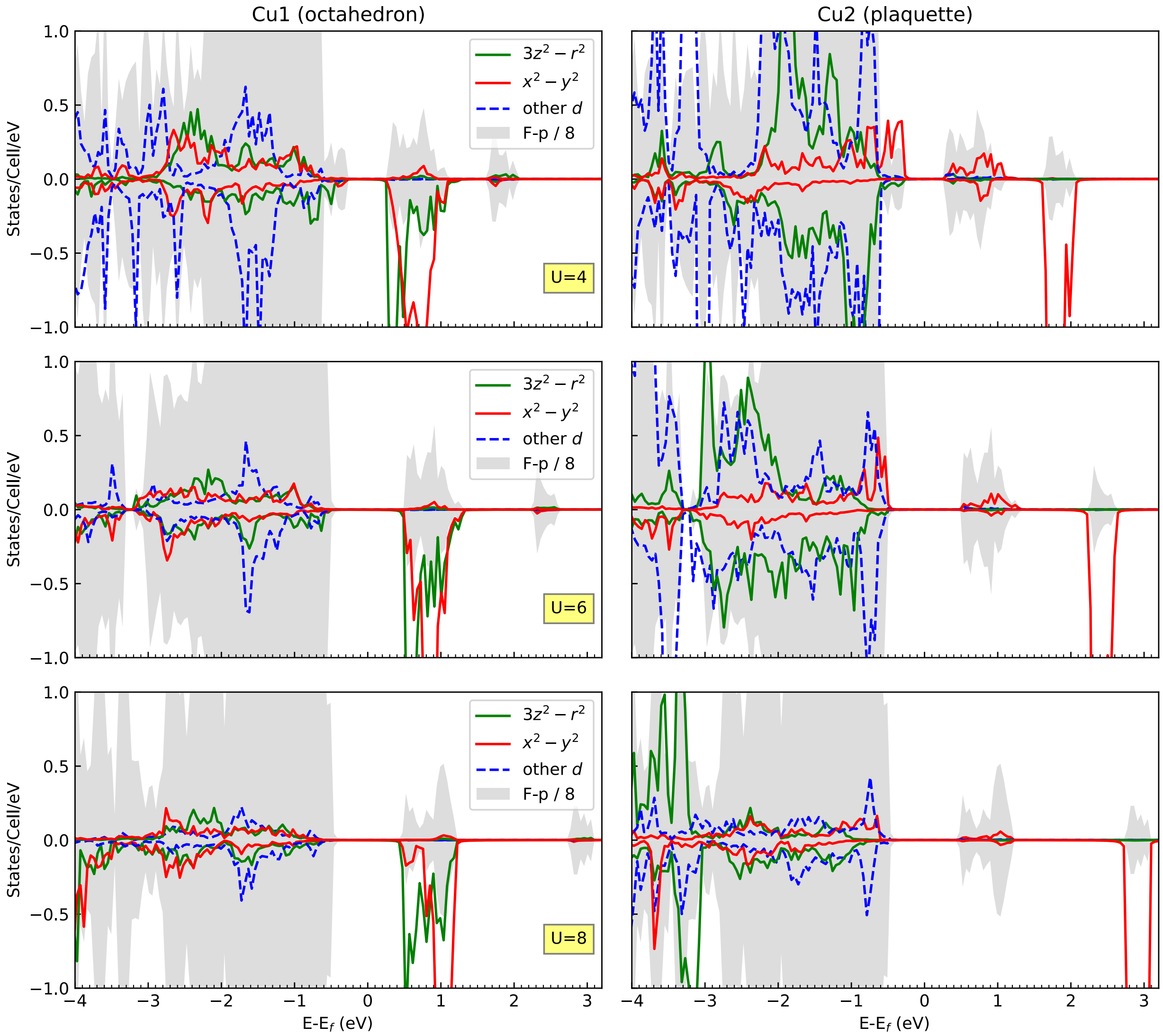

FIG. 4. Partial densities of states for Cu_2F_5 obtained within DFT+U for the AFM-G ordered phase. Positive/negative pDOSes correspond to spin-up/down states respectively.

states into the fluorine band. For $U = 6$ and 8 eV, Cu_2F_5 is a charge-transfer insulator and its band gap equals to 0.9 eV.

From the left panel of Fig. 4, it is seen that the Cu ion inside the fluorine octahedron (Cu1 ion) has unusual Cu^{3+} valence with electronic configuration d^8. The two peaks in spin-down DOSes for $3z^2 - r^2$ and $x^2 - y^2$ orbitals at +0.9 eV should be interpreted as an empty e_g states of Cu and the t_{2g} states are filled. The second type of Cu ion (in the center of fluorine plaquettes) has the d^9 electronic configuration with an empty spin-down $x^2 - y^2$ orbital located at 2–3 eV above the top of the valence band. Consequently, there is S = 1 spin state for Cu1 ion and S = 1/2 spin state for the plaquette-centered Cu ion. The position of the bottom of the conduction band is only slightly affected by the electron-electron interaction strength due to strong hybridization between the F-p and Cu-d states in the corresponding energy interval.

Using Green's function method based on magnetic-force linear response theory [17] we computed the Heisenberg exchange interaction between Cu ions up to the 9th nearest neighbor. The model Hamiltonian has the form:

$$H = -\sum_{\langle ij \rangle} J_{ij} \mathbf{e}_i \mathbf{e}_j, \tag{1}$$

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.

The obtained J_i values are presented in Table I (only values larger than 1.2 meV are included). The spatial illustration of the exchange interaction directions is shown in Fig. 5.

TABLE I. Calculated values of exchange interaction parameters within the (100) layer (J_{2D}^b and J_{2D}^c) and between these layers ($J_\perp$).

U	J_{2D}^b (meV)	J_{2D}^c (meV)	$J_\perp$ (meV)
4 eV	−32.5	−34.2	−6.8
6 eV	−34.5	−40.2	−6.9
8 eV	−32.7	−42.8	−6.3

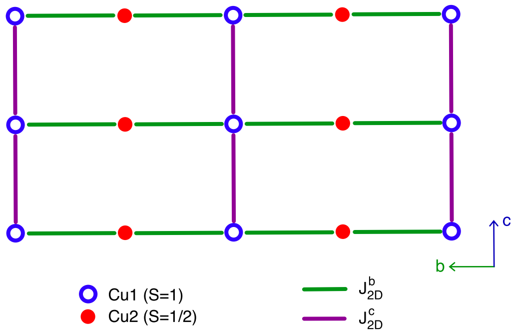

FIG. 5. The pattern of the exchange interaction within the (100) layer of Cu ions. Open circles denote Cu1 ions with S = 1 in the center of CuF_6 octahedron; filled circles are Cu2 ions with S = 1/2 (plaquettes centered). The strongest exchanges are: J_{2D}^b (green lines) and J_{2D}^c (violet lines). The interlayer exchange is $J_\perp$ is five times smaller than intralayer ones. Other exchange interactions are negligible. Fluorine ions are not shown for clarity.

All J values have the same sign that corresponds to the AFM exchange. Both the Cu1-Cu2 interaction along the b axis (J_{2D}^b) together with Cu1-Cu1 interaction along the c axis (J_{2D}^c) are five times larger than the exchange interaction along the a crystal axis ($J_\perp$). The superexchange interaction along the b crystal axis (J_{2D}^b) is provided by the hopping of electrons between the half-filled Cu1 $3z^2 - r^2$ orbital, the p orbital of fluorine (located between the Cu ions), and the half-filled Cu2 $x^2 - y^2$ orbital as illustrated in Fig. 6. The second half-filled e_g orbital of the Cu1 ion - ($x^2 - y^2$) maintains Cu1-F-Cu1 superexchange interaction along the c crystal axis (J_{2D}^c). In both interactions described above the Cu-F-Cu angle is 180°. This bond angle defines the p-d orbitals overlap, consequently, it determines the exchange strength. The Cu1-F-Cu2 along a angle is only 129°. That sets the much weaker exchange interaction in the direction of the crystal a axis ($J_\perp$). As for the Cu2-Cu2 exchange along the c axis, it is negligible because no fluorine ions are providing the superexchange path.

A strong superexchange anisotropy in Cu_2F_5 thereby exists in a way when the in-plane magnetic interactions are significantly larger than the interplane one. The absolute values of the exchange parameters are comparable with the superexchange in 2D [18,19], ladder cuprates [19], and 1D chain cuprates [19,20]. The unusual thing is that the exchange energy between Cu ions with S = 1 is almost the same as between the S = 1 and S = ½ ions.

One can suggest that doping of Cu_2F_5 with electrons would result in filling the Cu1 $3z^2 - r^2$ orbital since the bottom of the conduction band is formed by these states according to Fig. 4. That will shift the Cu1 ion from the d^8 configuration and from the half-filled e_g subshell. According to the Goodenough-Kanamori rule [21], it will suppress the J_{2D}^b AFM superexchange mechanism illustrated in the upper panel of Fig. 6. As a result, 1D magnetic chains could arise along the c crystal axis.

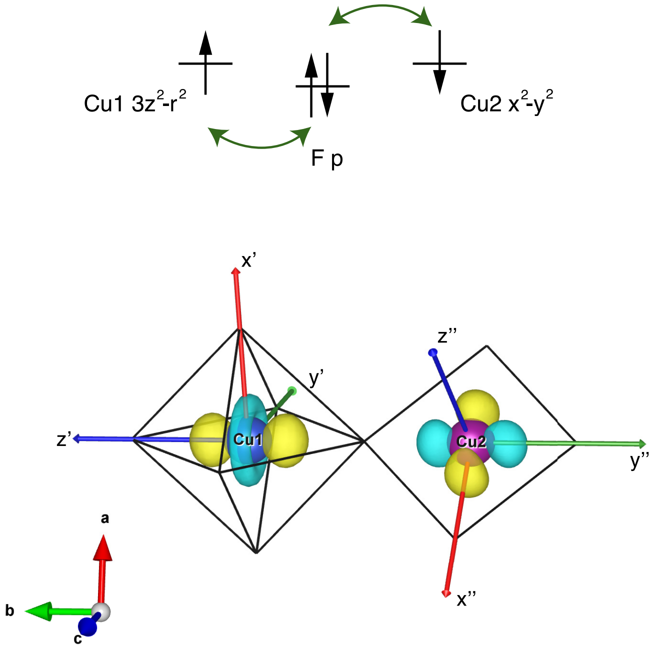

FIG. 6. Upper panel: The scheme of the half-filled Cu $d_{3z^2-r^2} \rightarrow$ F-p $\rightarrow$ the half-filled Cu $d_{x^2-y^2}$ superexchange mechanism. Lower panel: Two half-filled d orbitals providing the AFM superexchange interaction along the b crystal axis (J_{2D}^b). The d orbitals are defined in own local coordinate systems for the octahedron (x'y'z') and plaquette (x"y"z"). The fluoride p orbital, that mediates the superexchange interaction, located between the d orbitals is not drawn for picture simplicity.

In conclusion, we have presented a DFT+U study of the electronic and magnetic structure of the novel copper fluoride. The Cu ions in this compound have two different valences: 2+ for Cu ion in the square coordination and 3+ for Cu in octahedral coordination. We have tested various Hubbard interaction parameters U for Cu_2F_5 and showed that the compound becomes an insulator starting from $U = 4$ eV. The value of the energy gap depends only slightly on the U value.

Calculated values of superexchange interaction parameters indicate that the significant magnetic interaction anisotropy exists in Cu_2F_5. The new 2D spin lattice is obtained: the exchange interactions between Cu ions in the (100) planes are five times larger than along the a crystal axis, and within the layer, the exchange between ions with different spins (S = 1 and S = ½) has the same magnitude.

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