Orthorhombic crystalline field splitting on orbital and magnetic orders in KCuF$_3$

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I. INTRODUCTION

Three-dimensional pseudocubic perovskite KCuF$_3$ has attracted extensive interest since 1970s for its unusual low-dimensional antiferromagnetic (AFM) and orbital ground state. In this compound the Cu$^{2+}$ ion has 3$d^9$ configuration with the filled $t_{2g}$ orbits and the twofold-degenerate $e_g$ orbits occupied by one hole, the latter leads to the Jahn-Teller (JT) effect. The orbital degree of freedom of the holes interplays with spin and lattice degrees of freedom, which results in the orbital regular occupation in real space, i.e. the orbital ordering. The orbital polarization of the hole is usually depicted by a pseudospin operator, $\vec{\tau} = \sum_{ab} c_{a}^{\dagger} \sigma_{ab} c_{b}$, where $c_{a}^{\dagger}$ creates a hole at orbit $a$, and $\sigma$ denotes the Pauli matrix. $\tau^z = 1/2$ represents the full orbital polarization in $|3z^2-r^2\rangle$ and $\tau^z = -1/2$ the orbital polarization in $|x^2-y^2\rangle$, and $\tau^i = -1/2$ the orbital polarization in $|x^2-y^2\rangle$. The orbital polarization degree ordered by $\langle \tau_i \rangle$ is called the orbitalization. Up to date, the orbital ordering is considered as the essential factor in stabilizing the abnormal magnetic structure in KCuF$_3$, and is observed recently by the resonant x-ray scattering (RXS) experiments.

Though it has been known very early that the combination of the electronic superexchange (SE) interaction and the JT effect is responsible for the orbital ordering in KCuF$_3$, as shown in the following, the uniqueness of the orbital ground state and the magnetic and the orbital experimental results available are not well understood theoretically.

In pseudocubic perovskite KCuF$_3$ the adjacent CuF$_6$ octahedra in (a,b) plane are elongated along the a and b axis alternatively due to the JT distortion. There are two tetragonal crystal polytypes discriminated as type-a by the antiferro-distortion stacking the ab-planes and type-d by the ferro-distortion stacking the ab-planes.

The RXS results showed that in KCuF$_3$ the ground state is the G-type antiferro-orbital (AFO) order for type-a structure; and the C-type AFO arrangement for type-d structure. In these two structures the Cu spins are A-type AFM order below 39 K for type-a and below 22K for type-d; in both situations the averaged magnetic moment of each Cu ion is about 0.49 $\mu_B$ at 4 K. The magnetic couplings in KCuF$_3$ are highly anisotropic, and the magnetic coupling strengths are highly anisotropic, $J_{c}/J_{ab} \approx 26$. These results are in agreement with the experiments, implying that as an orbital selector, the crystalline field plays an essential role in stabilizing the ground state of KCuF$_3$. The 1s-3d resonant X-ray scattering amplitudes in KCuF$_3$ with the type-a and type-d structures are also presented.

More than thirty years ago Kugel and Khomskii proposed a SE model from the pure electron-electron interaction, the so-called K-K model, between Cu 3d electrons to describe the role of orbital degree of freedom in the A-type AFM structure; by comparing the energies of different magnetic structures in the classical approximation, they found the A-type AFM is stable; while for the orbital configuration, the G-AFO ordering is degenerate with the C-type AFO ordering. Further they showed that the anharmonic distortion from the JT effect lowering the lattice symmetry might give rise to the orbital ordering. In fact the orbital part of the K-K model is inherently frustrated. Feiner et al. pointed out that due to quantum spin-orbital wave excitations, this frustrated SE interaction leads to a spin-orbital liquid state; and when a tetragonal crystalline field (CF) splitting, $E_z$, is applied to the K-K model, the ground state is ferro-orbital at large $E_z$. Some other authors emphasized that the phonon-mediated orbital coupling arising from the cooperative JT effect gives rise to the orbital ordering. However, Khomskii and Mostovoy recently pointed out that this effective orbital-orbital interaction is also inherently frustrated, similar to the orbital part in the electronic SE interaction. In this case the JT orbital interaction combining the SE interaction favors the para-orbital or orbital liquid phase since the quantum fluctuations of the pseudospins $\vec{\tau}$ are still very large.

Under the cooperative JT distortion, the low-temperature crystal structure of KCuF$_3$ is tetragonal; meanwhile, the local crystalline field of CuF$_6$ arising from the static Jahn-Teller distortion is orthorhombic.
The effect of the orthorhombic CF splitting on the orbital order and the magnetic order of KCuF$_3$ was seldom taken into account in the past literatures. In the recent \textit{ab initio} study within the LDA+U scheme, Binggeli and Altarelli\cite{Binggeli1993} found that in the type-a JT distorted tetragonal structure, the orbital ordering is G-type AFO and the orbital RXS intensity agrees with the experimental observation; in contrast, Medvedeva \textit{et al.}\cite{Medvedeva2011} found in the absence of the JT distortion, the C-type AFO ground state is degenerate with G-type AFO. Therefore the realistic orthorhombic CF splitting is crucial for the stable orbital-ordered ground state. Nevertheless, the \textit{ab initio} study underestimates the spin and orbital quantum fluctuations and the role of orthorhombic CF splitting on the orbital ordered ground state.

In this paper, after deriving the orthorhombic CF splitting, we study the combination effect of the electronic SE coupling, the effective orbital JT coupling and the CF splitting on the orbital and spin ground state. Utilizing the cluster self-consistent field (Cluster-SCF) approach\cite{Zhao2013}, we demonstrated that the orthorhombic CF splitting plays a key role in stabilizing the orbital ordered phases of KCuF$_3$ in type \textit{a} and type \textit{d} structures: the orbital and spin fluctuations considerably reduce the magnetic moment of Cu spin to 0.49\textmu B, and the strong anisotropy in spin correlation functions and orbital correlation functions results in the ratio of magnetic coupling strengths, $J_c/J_{ab} \approx 26$. The azimuthal dependence of the RXS intensity is also calculated for the 1$s$–3$d$ excitation event. The experimental results could be consistently understood in the present theory. The rest of this paper is organized as follows: in Sec.II we describe the effective Hamiltonian and the Cluster-SCF method; then we present the theoretical results and discuss the role of CF in magnetic and orbital orderings in Sec.III; the azimuthal angle dependence of the RXS intensity is given in Sec.IV; and the last section is devoted to the remarks and summary.

\section{MODEL HAMILTONIAN AND CLUSTER-SCF METHOD}

According to the preceding analysis, the effective Hamiltonian of KCuF$_3$ contains three parts

$$ H = H_{SE} + H_{JT} + H_{CF} $$

The first term $H_{SE}$ represents the electronic SE coupling between two nearest-neighbor (N.N) $e_g$ holes of Cu$^{2+}$ ions derived from the generalized twofold degenerate Hubbard model\cite{Zhao2013},

$$ H_{SE} = \sum_{i \neq j, l=x,y,z} (J_1 \hat{s}_i \cdot \hat{s}_j + J_2 \hat{l}_i^l \hat{s}_j \cdot \hat{s}_j + J_3 \hat{l}_i^l \hat{l}_j^l \hat{s}_i \cdot \hat{s}_j + J_4 \hat{l}_i^l \hat{l}_j^l) $$

where the constants $J_1$, $J_2$, $J_3$ and $J_4$ are the superexchange coupling strengths:

$$ J_1 = 8t^2 \left[ U/(U^2 - J_3^3) - J_H/(U^2 - J_H^3) \right], $$

$$ J_2 = 16t^2 \left[ 1/(U + J_H) + 1/(U + J_H) \right], $$

$$ J_3 = 32t^2 \left[ U/(U^2 - J_H^3) - J_H/(U^2 - J_H^3) \right], $$

$$ J_4 = 8t^2 \left[ (U + 2J_H)/(U^2 - J_H^3) + J_H/(U^2 - J_H^3) \right], $$

respectively. $U$ and $J_H$ are the intra- and inter-orbital Coulomb interactions, and $J_H$ is the Hund’s coupling. Due to the pd hybridization between Cu 3d and F 2p orbitals\cite{Zhao2013}, we take the relationship $U = U + J_H$. The parameters $U = 7.5$ eV and $J_H = 0.9$ eV are adopted from the constrained LDA computation for KCuF$_3$. The hopping integral along the $c$ direction is the largest, $t_{3z^2-r^2}g_{3z^2-r^2} = 4t$, we take $t \approx 0.12$ eV, thus the energy scale of the superexchange coupling is $J = 16t^2/U = 30.7$ meV, $\hat{s}_i$ denotes the spin at site i, while the operator $\hat{l}_i^l = \cos(2\pi m_i/3)\tau_z - \sin(2\pi m_i/3)\tau^l_z$, the index $l$ denotes the direction of a bond, $l = x, y, z$, corresponding to the crystal axes, $a, b$ and $c$; $(i,j)l$ connects site $i$ and its nearest-neighbor site $j$ along the $l$ direction, and $(m_x, m_y, m_z) = (1, 2, 3)$. The orbital pseudospin operators $\tau^l_z$ and $\tau^l_z$ are the components of $\hat{\tau}$.

The second term in Eq.(1) represents the phonon-mediated orbital coupling from the cooperative JT effect. Through eliminating the phonon operator, one can get an effective orbital-orbital interaction $H_{JT}$:\cite{Zhao2013, Sun2011, Zhao2013}

$$ H_{JT} = g_{JT} \sum_{l=x,y,z} \hat{l}_i^l \hat{l}_j^l $$

It has the same form as the orbital part of the last term in Eq.(2), both of them contribute to the orbital frustration and quantum fluctuations. The Jahn-Teller distortion energy $E_{JT} \sim 130$ meV\cite{Zhao2013}, $g_{JT}$ is the same order as $E_{JT}$ in magnitude.

The static JT effect distorts the symmetry of CuF$_6$ octahedra to orthorhombic, in which there are three different Cu-F bonds, the medium length Cu-F bond is along the $z$-axis, the long and short Cu-F bonds alternate along the $x$ and $y$ axes. All of the F-Cu-F angles are $90^\circ$ or $180^\circ$, and no rotation is found\cite{Zhao2013}. Employing the point charge model to calculate the CF splitting, we obtain the orthorhombic CF splitting of the holes,

$$ H_{CF} = \sum_i (V_{iz} \tau^z_i + V_{ix} \tau^x_i) $$

The intermediate compression of the Cu-F bond along $c$-axis implies the sign of $V_{iz}$ is negative for the hole, $V_{iz} < 0$, since the compressed octahedra lifts the $|3z^2-r^2|$ orbit, thus the $|3z^2-r^2|$ orbit is in favor of hole occupation; and the component $V_{ix} z$ mixes the two $e_g$ orbitals at site i. The former favors of the orbital ordering, while the latter tends to destroy the orbital ordering. Using the crystal structure data in Ref.10 we estimate the ratio $|V_{cz}/V_{zx}| \sim 2$, and $V_z$ is the same order in magnitude as the superexchange interaction.

It is a huge challenge to treat the spin-orbital correlations and fluctuations and to find the ground state of such
strongly correlated systems with high accuracy. To study the groundstate properties, we apply the Cluster-SCF approach developed recently to deal with the complicated spin-orbital Hamiltonian (1). This approach combines the exact diagonalization for a central cluster and the self-consistent field for surrounding atoms. The main idea of the approach is described as follows: consider a proper cluster, usually the unit cell of the compounds, in which the 3d electrons interact via Eq.(1). First, we substitute the spin coupling \( \langle \vec{s}_i \cdot \vec{s}_j \rangle \) in the cluster Hamiltonian, \( H \), with the spin correlation functions \( \langle \vec{s}_i \cdot \vec{s}_j \rangle \), here

\[
H = \sum_{l=x,y,z} \left[ F(\vec{r}_i, \vec{r}_j) \vec{s}_i \cdot \vec{s}_j + (J_4 + g_{JT}) I^l_i I^l_j \right] + \sum_i \left( V_{ix} \tau^x_i + V_{ix} \tau^x_i \right),
\]

with

\[
F(\vec{r}_i, \vec{r}_j) = J_1 + \frac{J_2}{2} (I^l_i + I^l_j) + J_3 I^l_i I^l_j.
\]

And then diagonalize the orbital part of the cluster Hamiltonian in the presence of the orbital SCF, hence obtain the orbitalization \( \langle \vec{r} \rangle \) and the orbital correlation functions \( \langle \vec{r}_i \cdot \vec{r}_j \rangle \). Second, substitute the orbital operator, \( \vec{r} \), and their coupling \( \vec{r}_i \cdot \vec{r}_j \) with the orbitalization and the orbital correlation functions obtained, and diagonalize the spin part of the cluster Hamiltonian in the presence of the spin SCF, thus obtain a new set of spin correlation functions. Repeat the above steps iteratively until the groundstate energy, the spin and the orbital correlation functions self-consistently converge to the accuracies. The advantage of the present approach superior to the traditional mean-field method is that the short-range spin and orbital correlations and quantum fluctuations are taken into account. In comparison with the traditional mean-field method, one can obtain more better results for some simple models with large quantum fluctuations, such as the Heisenberg AFM model.

### III. RESULTS AND DISCUSSIONS

In this section we first investigate the ground state of KCuF\(_3\) under the electronic SE interaction and the JT phonon-mediated orbital interaction, then explore the role of orthorhombic CF splitting in the ground state.

#### A. Superexchange and JT Orbital Interactions

For the electronic SE coupling in Eq.(2), the mean-field results suggested the staggered orbital order with \( x^2-y^2 / 3z^2-r^2 \) orbits. However, utilizing the cluster-SCF approach, we find the spin-orbital ground state is composed of numerous degenerate states: such as the Neel AFM order with ferro-orbital structure, in which the hole occupies one of the three orbits among the \( \{|3x^2-r^2\}, \{|3y^2-r^2\}, \{|3z^2-r^2\} \) or the Neel AFM order with the alternating plaquette valence-bond order, in which one plane, for example, the xy-plane, is occupied by the \( \{|3x^2-r^2\} \) orbit and the nearest neighbor ones is taken up with the \( \{|3y^2-r^2\} \) orbit, etc. The degenerate ground state contains the alternating plaquette valence-bond component, in agreement with Feiner et al. results by considering Gaussian quantum fluctuations. This also confirms the validity and the efficiency of our Cluster-SCF approach. In this case, the A-type AFM structure observed in realistic KCuF\(_3\) is not the candidate of the ground state. On the other hand, the nearest-neighbor orbital correlation functions are significantly different from zero. The short-range orbital correlations are strong, indicating that the system with only the electronic SE interaction is a spin-orbital liquid phase.

In such a spin-orbital correlated system, the spin alignment strongly depends on the orbital configuration. In fact one could easily find that the system with the SE interaction is a spin-orbital liquid phase, rather than a spin-orbital ordered state. Due to the spin rotation symmetry, the spin interaction in the SE coupling is Heisenberg-like. After averaging over orbital freedom degree, the spin exchange coupling strength along the l-axis in Eq.(5) reads

\[
J^l_s = \langle F(\vec{r}_i, \vec{r}_j) \rangle = J_1 + \frac{J_2}{2} (I^l_i + I^l_j) + J_3 I^l_i I^l_j,
\]

which is isotropic for the x-, y- and the z-axes, such an interaction does not lead to the anisotropic A-type AFM structure in KCuF\(_3\), unless the orbital symmetry is broken. In the orbital part of the SE interaction in Eq.(2), after averaging over the spin coupling, the orbital part along the l-direction reads,

\[
h^l_o = \frac{J_2}{2} (\vec{s}_i \cdot \vec{s}_j) (I^l_i + I^l_j) + (J_3 \langle \vec{s}_i \cdot \vec{s}_j \rangle + J_4) I^l_i I^l_j,
\]

The first term is similar to a magnetic field, called the orbital field. This orbital field is frustrated for the orbital occupation, which favors either \( \{|3z^2-r^2\} \) or \( \{|x^2-y^2\} \) orbits along the z-axis; while along the x-axis, it favors either \( \{|3x^2-r^2\} \) or \( \{|y^2-z^2\} \) orbits. Unfortunately the orbital interaction part, \( I^l_i I^l_j \), in Eq.(6) is also inherently frustrated: no matter what the coefficient of the second term in Eq.(6) is, negative or positive, this orbital correlation favors a frustrated ground state, as pointed by Khomskii et al. On the one hand, if the coefficient of \( I^l_i I^l_j \) is negative, the orbital exchange coupling favors different ferro-orbital occupations along different directions, in accordance with the frustration of the orbital field mentioned above; on the other hand, if the coefficient is positive, the orbital polarizations in each bond arising from the orbital field are opposite to that arising from the orbital coupling, which enhances the frustration effect.
One notices that if the spin correlation functions are strongly anisotropic, the frustration effect is greatly suppressed. For example, as the spin correlation along the z-axis is so strong that $\langle \hat{s}_i \cdot \hat{s}_{i+1} \rangle \approx -3/4$, while the spin correlation functions along the x, y-axes almost vanish, $\langle \hat{s}_i \cdot \hat{s}_{i+ \pm 1} \rangle \approx 0$, then the orbital part of the SE interaction becomes

$$h_o = J_4 \sum_i [I_i^x I_{i+1}^x + I_i^y I_{i+1}^y - 0.95 I_i^z I_{i+1}^z - 1.78 I_i^+]$$ (7)

the x, y-components of the orbital field approach to zero, leaving a large z-component in Eq.(7). Obviously the strong uniaxial orbital field suppresses the frustration of the orbital exchange coupling, and singles out the $|3z^2 - r^2\rangle$ orbit in each site, forming the ferro-orbital order; our numerical calculation confirms this result. Also it could be shown that strongly anisotropic plaquette-valence-bond correlation of the spins favors the alternating plaquette-valence-bond orbital order. As we will show later, the highly anisotropic magnetic correlation is the consequence of the orbital ordering in KCuF₃.

Neglecting the spin and orbital quantum fluctuations, Kugel and Khomskii found the mean-field solution of the SE interaction is the A-type AFM and G-type/C-type AFO order. In fact, their classical approximation to the spins as the A-type AFM order introduced an orbital order in KCuF₃.

$$\langle \vec{s}_i \cdot \vec{s}_{i+1} \rangle$$

$$\langle \vec{s}_i \cdot \vec{s}_{i+ \pm 1} \rangle$$

the full Hamiltonian, our numerical results show that the presence of the orthorhombic CF breaks the discrete orbital symmetry, suppresses the orbital frustration and quantum fluctuation, and establishes the long-range orbital order in KCuF₃.

B. Role of Orthorhombic Crystalline Field

In perovskite KCuF₃ there exist two kind cooperative JT distortions at low temperatures. With respect to these two different small lattice distortions, KCuF₃ exhibits two slightly different crystalline phases, the type-\(d\) and the type-\(a\) structures. The orbital ground state in the type-\(a\) structure differs from that in the type-\(d\) structure due to different orthorhombic CF splittings of the CuF₆ octahedra.

We first study the orbital components of single Cu atom under the orthorhombic CF. For $|V_x/V_z| = 2$, the orbital wavefunctions always consist of two orbital patterns, a low energy pattern $|a\rangle = 0.851|3z^2 - r^2\rangle \pm 0.526|3x^2 - y^2\rangle$, in which the hole completely occupies this pattern at large $|V_z|$, and a high energy pattern $|b\rangle = 0.526|x^2 - y^2\rangle \pm 0.851|3z^2 - r^2\rangle$; here ‘\(\pm\)’ refer to the two sublattices of the antiferro-distortion in the two crystalline phases. Approximately, $|a\rangle \approx |y^2 - z^2\rangle$ and $|b\rangle \approx |3x^2 - r^2\rangle$ for ‘\(\cdot\)’; and $|a\rangle \approx |x^2 - z^2\rangle$ and $|b\rangle \approx |3y^2 - r^2\rangle$ for ‘\(\cdot\)’. Such combinations are also consistent with the orthorhombic distortions of the CuF₆ octahedra: if the Cu-F bond is elongated along the x-axis, the CF singles out the $|y^2 - z^2\rangle$ orbit, corresponding to ‘\(\cdot\)’; on the other hand, if Cu-F bond is elongated along y direction, the energy of $|x^2 - z^2\rangle$ orbit is lower, corresponding to ‘\(\cdot\)’.

In the lattice case, the orthorhombic CF splitting competes with the SE interaction and the JT orbital coupling, the orbital occupation of Cu 3d holes depends not only on the CF splitting ratio $|V_x/V_z|$, but also on the magnitude of $V_z$. When $|V_z|$ is very small, due to the orbital frustration and large quantum fluctuations, the orbital symmetry is not broken, and the ground state of the system is still an orbital liquid or para-orbital phase. The critical value of $|V_z|$ breaking the orbital symmetry relies on the JT orbital coupling. For large $|V_z|$, the transverse CF splitting $V_x$ alternating in the xy-plane in the type-\(d\) structure gives rise to C-type AFO configuration: as a contrast in the type-\(a\) structure, the staggered transverse CF splitting $V_x$ in the x, y and z directions gives rise to G-type AFO configuration. At $|V_z| = 0.5 J$, the sublattice orbitalization and the orbital correlation functions listed in Table I definitely show the G-type AFO correlation in the type-\(a\) structure and the C-type AFO correlation in the type-\(d\) structure. Some magnetic properties in both structures are also collected in Table I. Therefore the presence of the orthorhombic CF breaks the discrete orbital symmetry, suppresses the orbital frustration and quantum fluctuation, and establishes the long-range orbital order in KCuF₃.

As soon as the orthorhombic CF singles out the orbital structure, it also stabilizes the magnetic structure simultaneously, hence the spin-orbital ground state. Under the full Hamiltonian, our numerical results show that...
the magnetic ground states are the A-type AFM order both for the type-\(a\) and for the type-}\(d\) crystalline phases. And the spin correlations are strongly anisotropic, \(\langle \vec{s}_i \cdot \vec{s}_j \rangle/ \langle \vec{s}_i \cdot \vec{s}_j \rangle_{\text{x,y}} \approx 10\). Furthermore, we obtain the spin coupling strengths \(J_z\) and \(J_{x,y}\), which are 16.6 meV and 0.64 meV, respectively, giving rise to \(|J_z/J_{x,y}| \approx 26\) for \(V_z = -0.5J\), as shown in Fig.1. These results are in agreement with the experimental data in KCuF\(_4\)\(^{1,2,11}\). Such strong anisotropy in spin correlations and magnetic couplings is attributed to the anisotropic regular distribution of the orbital wavefunctions in real space, i.e., the orbital ordering, as we will show later.

Next we focus on the magnetic moment of each Cu spin. We find that the effective magnetic moment of each Cu spin is considerably reduced from 1 \(\mu_B\) to 0.496 \(\mu_B\), the averaged spin of each Cu ion decreases to 0.248, about a half of 1/2, consisting with the neutron scattering experimental data very well\(^{11}\). The theoretical and experimental results are listed in Table I. Obviously such great reduction of the magnetic moment arises from the spin-orbital quantum fluctuations: one possibility is from the low-dimensional AFM spin-wave excitation: the another is from the spin-and-orbital wave excitation in the spin-orbital system\(^{14}\), which causes more spin flipping via the spin-orbital interaction. From Table I, one finds the discrepancy between the present ratio of \(|J_z/J_{x,y}| \approx 26\) and Satija’s experimental fitting data \(|J_z/J_{x,y}| \approx 100\)\(^{22}\), we attribute this discrepancy to the frozen of the orbital excitations in his fitting to the experimental data. According to the spin exchange couplings shown in Table I, we find that in the mean-field approximation, the theoretical Neel temperature of KCuF\(_3\) is about, 37 K, in agreement with the experimental data 39 K in \(type-a\) structure, confirming that our choice to the theoretical parameters \(t, U, J_H, g_{JT}\) and \(V_z\) is appropriate.

In fact the influence of the orthorhombic CF splitting and the JT orbital coupling on the magnetic moment is not monotonously. As shown in Fig.2, the phonon-mediated JT orbital coupling and the orthorhombic CF distortion play distinct roles in the magnetic moments through affecting the orbital quantum fluctuations and the orbital ordering. At small splitting \(|V_z|\) and in the absence of the JT coupling, \(g_{JT} = 0\), the orbital field \(-F_z^a\) in the A-type AFM structure is much stronger than that from the CF splitting, resulting in large orbital polarization with dominant \(|3z^2 - r^2\) orbit; with the increase of the CF splitting, the transverse CF term \(V_x\) mixes the \(|3z^2 - r^2\) orbit with the \(|x^2 - y^2\) orbit, leading to the descent of the sublattice orbitalization, as seen in Fig.2a. Meanwhile the decrease of the orbitalization weakens the low-dimensionality of the spin correlations, the magnetic moment gradually lifts with increasing CF splitting, which can be seen in Fig.2b. At sufficient large \(|V_z|\), the orbital occupation is full polarized at the \(|a\) orbit, and the magnetic moment saturates to 0.61 \(\mu_B\) per site. In this situation, a small CF splitting favoring of the A-type AFM structure produces strong local orbital field and orbital polarization, suppresses the orbital frustration from the superexchange coupling. With the further increase of the CF splitting, the transverse component of the CF splitting \(V_x\) mixes the orbitals \(|3z^2 - r^2\) and \(|x^2 - y^2\)\), the orbital polarization declines and the anisotropy of orbital and spin correlations become weak, hence the ratio of the magnetic couplings \(J_z/J_{x,y}\) decrease with the increase for very large CF splitting, as seen in Fig.1.

When the JT orbital coupling is taken into account, the dependences of the spin coupling, the sublattice orbitalization and the magnetic moment on \(|V_z|\) are different for \(g_{JT}/J = 1\) and for \(g_{JT}/J = 7\). The different behaviors arise from the distinct effects of the CF splitting on the local orbital field and the frustration term. At \(g_{JT}/J = 1\), \(|J_z/J_z|\) is larger than that at \(g_{JT} = 0\), implying the low-dimensional characters of the spin correlations and the spin fluctuations become weak. This leads to large magnetic moment and small anisotropy, as we find in Fig.1 and Fig.2b. The weakness of the anisotropy of the magnetic couplings at \(g_{JT}/J = 1\) arises from the frustration enhancement comparison with that at \(g_{JT} = 0\). Our numerical results show that at \(g_{JT}/J = 1\), the further increase in the CF splitting is almost balanced by the orbital field and the frustrated orbital-orbital couplings, hence the spin and the orbital correlations, the sublattice orbital-
CF splitting, as shown in Fig.1 and Fig.2. Orbitalization and sublattice magnetization and the magnetic coupling almost do not change with the increase of the CF splitting, and sublattice orbitalization (b) on orthorhombic CF splitting in different JT orbitalization

FIG. 2: Dependence of averaged spin (a) and sublattice orbitalization (b) on orthorhombic CF splitting in different JT orbital coupling.

In contrast, the large JT orbital coupling at $g_{JT} = 7J$ leads to strong orbital fluctuation, hence to small sublattice orbitalization and magnetization in Fig.2. In this situation, one would expect more weak anisotropy and large ratio $|J_z/J_x|$; however as shown in Fig.1, one curiously finds that the anisotropy is the most strong, in comparison with $g_{JT} = 0$ and $g_{JT} = J$. We find this strong anisotropy may come accidentally in small orthorhombic CF splitting: in the spin coupling along the $x$-axis, the sign of the constant part $J_1$ is contrary to that from the other terms, which leads to $J_x$ be very small, hence small ratio $|J_z/J_x|$ and large anisotropy. Strong orbital fluctuations also excite spin flipping excitation via the spin-orbital coupling. Thus the magnetic moment critically decreases to 0.49 $\mu_B$ at $|V_z|/J = 0.5$. Further increase of the orthorhombic CF splitting greatly suppresses the orbital and spin fluctuations, and the sublattice magnetic moment and the orbitalization rise a lot. With the further increase of the orthorhombic CF splitting, the anisotropy becomes more weak, and the sublattice magnetization $\langle S \rangle$ and orbitalization $\langle T_z \rangle$ further increase gradually.

IV. RESONANT X-RAY SCATTERING FOR ORBITAL ORDER

The orbital ordering in KCuF$_3$ can be manifested in the RXS peaks utilizing the sensitivity of x-ray scattering to the anisotropic density of orbital ordered electrons.$^{1,2}$ The anisotropy of spatial electronic clouds gives rise to the anomalous tensor component in atomic scattering factor, and the interference of these atomic scattering amplitudes in the presence of long-range orbital order leads to the orbital superlattice reflection at the structural forbidden position. Obviously, it is more directly to identify the orbital ordering using the spectral line shapes of the quadrupole $1s - 3d$ scattering, contrary to the complicated spectra of the $1s - 4p$ dipole scattering which is often used in present experiments.$^{12,21}$ Although the signal enhancement of the quadrupole scattering is weaker than the dipole scattering, we present the azimuthal angle dependence of the $1s - 3d$ RXS intensity to directly demonstrate the character of the orbital order in KCuF$_3$.

For the C-type AFO ordered ground state with type-$d$ structure, the orbital peaks reflect at $(h,k,l) = (odd, odd, even)$, which are forbidden for the structural and magnetic reflections. The sublattice orbital wavefunctions consist of two different components: $|\psi_1\rangle = \alpha_1|3z^2 - r^2\rangle + \alpha_2|x^2 - y^2\rangle$ and $|\psi_2\rangle = \alpha_1|3z^2 - r^2\rangle - \alpha_2|x^2 - y^2\rangle$, here the coefficients $\alpha_{1,2}$ are the functions of the interaction parameters. Then the orbital structural factor is read as:

$$F_{hkl} = f(\Gamma,r_{2,ds},c,\omega) \sqrt{\eta_{k} \eta_{r} \eta_{c}} \alpha_1 \alpha_2 \langle \epsilon_z k_z \rangle$$

$$\left(\epsilon_z' k'_x - \epsilon_y' k'_y\right) + \left(\epsilon_x k_x - \epsilon_y k_y\right) \epsilon_z' k'_z \right)$$

where the function $f(\Gamma,r_{2,ds},c,\omega)$ is the coefficient depending on the lifetime of the intermediate states, $\Gamma$, the radial matrix element $r_{2,ds}$, the velocity of photon $c$ and the incoming photon frequency $\omega$: $\eta_{k} \eta_{r} \eta_{c}$ is the density of the incoming (outgoing) beam of photons with polarization $\epsilon$ and wavevector $k$. The azimuthal angle dependence of the RXS intensity is shown in Fig.3 at $(1,1,0)$ reflection for unrotated $(\sigma')$ and rotated $(\sigma\pi')$ channels for the perfect $\sigma$ polarized incoming beam. As a comparison, we also present the azimuthal angle dependence of the RXS intensity in Fig.4 for the G-type AFO order with type-$a$ structure at $(3,3,1)$ reflection.

Due to the difference of the orbital superlattice for the C-type and the G-type AFO orders, the RXS peaks appear at different orbital reflections with $(odd, odd, even)$ for the C-type orbital order in the type-$d$ structure, and with $(odd, odd, odd)$ for the G-type orbital order in the type-$a$ structure. These sublattice reflections distinguish these orbital orders in different crystalline phases of KCuF$_3$. The azimuthal angle dependence of the RXS intensities exhibits different periods in the type-$d$ and the type-$a$ structures, as seen in Fig.3 and Fig.4. The periods are $\pi$ and $2\pi$ for the $\sigma - \sigma'$ channel in these two structures, respectively; and are $\pi/2$ and $\pi$ for the $\sigma - \sigma'$ channel.
V. REMARKS AND SUMMARY

We notice that in perovskite KCuF₃, the nonresonant magnetic scattering experiments showed that the orbital angular momentum $L$ in the orbital basis wavefunctions $|3z^2-r^2\rangle/(x^2-y^2)$ and any of their combinations is zero. One possibility of such considerable residual orbital moment is attributed to the reduced symmetry of the $t_{2g}$ orbit in KCuF₃ or a small fraction of the $t_{2g}$ orbit mixing with the $e_g$ orbit; another possibility is from the hybridization of the $4p$ orbits with the $e_g$ orbits. In both situations the weak $LS$ coupling in KCuF₃ will not change the spin alignment considerably.

In the numerous literatures on KCuF₃, some authors took the tetragonal CF splitting into account to stabilize the A-type AFM order, but the degeneracy of the G-type and the C-type AFO orders is not lifted, so the ground state under the tetragonal CF is still indefinite. Only in the present theory the full consideration of the orthorhombic CF splitting, $V_x$ and $V_z$, together with the JT orbital coupling and the SE coupling, can we determine the ground state exclusively, and consistently interpret the experimental data. Furthermore, considering many other spin-orbital-lattice interacting compounds, such as manganites, vanadium oxides, and titanium oxides, in which the CF splitting arising from the lattice distortion extensively exists, one may find such a fact that the low-symmetric CF splittings play crucial roles in singling out many degenerate candidates as the sole orbital ordered ground state. Thus a conclusion arrives that the highly degenerate ground state in the correlated electronic system with pure spin-orbital interactions usually stabilizes through distorting to a lower symmetry phase, which is a natural generalization of the Jahn-Teller effect in strongly correlated systems. Detail results will be presented in further study.

In summary, we have performed a systematic study on the roles of the electronic SE interaction, the JT orbital coupling and the orthorhombic CF splitting in the orbital ordering and the magnetic properties in KCuF₃. The SE and effective JT orbital coupling lead to an orbital liquid state due to the inherent frustration and orbital quantum fluctuations. The orthorhombic CF lowers the orbital symmetry, and stabilizes the orbital ordering as the observed in experiment. The orbital ordering results in the strong magnetic anisotropy. Strong spin fluctuation and the orbital frustration considerably reduce magnetic moment of Cu spins.

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