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Effects of anharmonic lattice distortion on orbital and magnetic orderings in $KCuF_3$*

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Lattice, magnetic and orbital structures in $KCuF_3$ are self-consistently determined by our cluster self-consistent field approach based on a spin-orbital-lattice Hamiltonian. Two stable structures are obtained and found to be degenerate, which confirms the presence of the coexistent phases observed experimentally. We clearly show that due to the inherent frustration, the ground state of the system only with the superexchange interaction is degenerate; while the Jahn–Teller distortion, especially the anharmonic effect, stabilizes the orbital ordered phase at about 23% in the x^2–y^2 orbit and at 77% in the $3z^2$–r^2 orbit. Meanwhile the magnetic moment of Cu is considerably reduced to $0.56\mu_B$, and magnetic coupling strengths are highly anisotropic, $J_z/J_{xy} \approx 18$. These results are in good agreement with the experiments, implying that the anharmonic Jahn–Teller effect plays an essential role in stabilising the orbital ordered ground state of $KCuF_3$.

Keywords: orbital ordering, $KCuF_3$, Jahn–Teller effect, anharmonic lattice distortion
PACC: 7530E, 7510, 7550

1. Introduction

The perovskite system $KCuF_3$ has attracted extensive interest since the 1960s for its unusual one-dimensional (1D) antiferromagnetism (AFM). In this compound, the Cu^{2+} ion has $3d^9$ configuration with fulfilled t_{2g} orbits and twofold-degenerate e_g orbits occupied by one hole. Under the cubic crystalline field (CF), the twofold degeneracy of the e_g orbits is removed through the spontaneous Jahn–Teller (JT) distortions. The orbital degree of freedom of the holes interplays with those of the spin and lattice, which may result in the orbital regular occupation in real space, i.e. the orbital ordering. The orbital polarisation of the holes is usually depicted by a pseudospin operator, $\boldsymbol{\tau} = (1/2)\sum_{ab} c_a^\dagger \sigma_{ab} c_b$, where $c_a^\dagger$ creates a hole at the orbit a, and σ denotes the Pauli matrix. $\tau_i^z = 1/2$ $(-1/2)$ represents the full orbital polarisation in the $|3z^2 - r^2\rangle$ $(|x^2 - y^2\rangle)$ orbit. Up to date, the electronic orbital ordering is considered as an essential factor in stabilising the abnormal magnetic structure in $KCuF_3$, as manifested in the recent resonant x-ray scattering (RXS) experiments.[1,2] Though it has been known very early that the electronic superexchange (SE) interaction and the JT effect are responsible for the orbital ordering in $KCuF_3$,[3] the uniqueness of the orbital ground state, the magnetic and orbital experimental data available are not well understood theoretically.[3–9]

In $KCuF_3$, the adjacent CuF_6 octahedra in the ab plane are elongated along the a and b axes alternatively due to the JT distortion. The CuF_6 octahedra form two tetragonal crystal polytypes discriminated as type-a structure with the antiferro-distortion stacking the ab planes and type-d structure with the ferro-distortion stacking the ab planes.[10,11] Recent RXS experiments[1,2] showed that in $KCuF_3$, the ground state is G-type antiferro-orbital (AFO) order for type-a structure, and is C-type AFO arrangement for type-d structure. In both structures, the magnetic order is A-type AFM below 39 K for type-a structure and below 22 K for type-d structure. In both situations, the averaged magnetic moment of each Cu ion is about 0.49 μ_B at 4 K.[12] The magnetic couplings in $KCuF_3$ are highly anisotropic, and the neutron scat-

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tering experiments[12,13] give rise to $J_{ab}/J_c \sim -0.01$, suggesting a significant one-dimensional character.

More than thirty years ago, Kugel and Khomskii[3] proposed an SE model, the so-called K–K model, to describe the role of orbital degree of freedom in the magnetic structures based on the 2nd-order perturbation approximation of the pure electron-electron interactions between Cu $3d$ electrons. By comparing the energies of different magnetic structures in the classical approximation, they found the A-type AFM structure is stable; while for the orbital configuration, the G-type AFO order is degenerate with the C-type AFO order. Further, they showed[14] that the anharmonic distortion from the JT effect might give rise to the orbital ordered ground state through lowering the lattice symmetry. In fact, the orbital part of the K–K model is inherently frustrated.[15] Feiner *et al*[16,17] 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 CF splitting, E_z, is applied to the K–K model, the ground state is ferro-orbital at large E_z, or spin–orbital liquid at small E_z. Some other authors[7] emphasized that the phonon-mediated orbital coupling arising from the cooperative JT effect gives rise to the orbital ordering. However, Khomskii and Mostovoy[15] recently pointed out that this phonon-mediated orbital interaction is also inherently frustrated, similar to the orbital part in the electronic SE interaction. As a result, the JT phonon-mediated interaction combining the SE interaction favors the para-orbital or orbital liquid phase, since the quantum fluctuations of the pseudospin $\boldsymbol{\tau}$ are still very large.

Under the cooperative JT distortion, the low-temperature type-a and type-d structures of $KCuF_3$ are tetragonal. The effect of the anharmonic distortion on the orbital order and the magnetic order of $KCuF_3$ was seldom taken into account explicitly in the literatures. Recently, within the *ab initio* LDA+U scheme, Binggeli and Altarelli[18] found that in the type-a JT distorted tetragonal structure, the orbital ordering is G-type AFO and the orbital resonant x-ray scattering (RXS) intensities agree with the experimental observation. In contrast, Medvedeva *et al*[5] found that in the absence of the JT distortion, the C-type AFO ground state is degenerate with G-type AFO. Therefore, the JT effect is crucial for the stable orbital-ordered ground state. Nevertheless, the *ab initio* study[18] underestimates the spin and orbital quantum fluctuations in $KCuF_3$, predicting that the magnetic moment of Cu ion is about 0.9 μ_B, which is much larger than the experimental data, 0.49 μ_B.[12] The quantum fluctuations of the spins and orbitals on the orbital ordering and magnetic properties in $KCuF_3$ deserve to explore in detail.

In this paper, after self-consistently determining the JT distortions, we study the electronic SE coupling as well as the JT effect on the orbital and spin structures, and explore the roles of the quantum fluctuations of the spins and the orbitals. Utilising the cluster self-consistent field (cluster-SCF) approach,[19] we demonstrate that the anharmonic JT distortion plays a key role in stabilising the orbital ordered phases both in type-a and type-d structures; the orbital and spin fluctuations considerably reduce the magnetic moment of Cu spin to 0.56 μ_B, and the orbital correlation functions result in strong anisotropy of the spin correlation functions and the ratio of the magnetic coupling strengths, $J_z/J_{xy} \approx 18$. The present approach provides a systematic and consistent agreement between the experimental data and the theoretical results. The rest of this paper is organised as follows: we describe the effective spin-orbital-lattice Hamiltonian and the cluster-SCF method in Section 2; then we present the theoretical results and discuss the roles of the JT effect in magnetic and orbital orders in Section 3; and the last section is devoted to the remarks and summary.

2. Model Hamiltonian and cluster-SCF method

According to the preceding analysis, the effective Hamiltonian of $KCuF_3$ consists of two parts:

$$H = H_{\rm SE} + H_{\rm QJT}. \tag{1}$$

The first term $H_{\rm SE}$ represents the electronic SE couplings between two nearest-neighbor (N.N) e_g holes of Cu^{2+} ions, which is derived from the generalised twofold-degenerate Hubbard model,[20]

$$H_{\rm SE} = \sum_{i,\alpha=x,y,z} [(J_1 + J_2 I_i^\alpha + J_3 I_i^\alpha I_{i+\alpha}^\alpha)\boldsymbol{s}_i \cdot \boldsymbol{s}_{i+\alpha} + J_4 I_i^\alpha I_{i+\alpha}^\alpha], \tag{2}$$

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

$$J_1 = 8t^2[U/(U^2 - J_{\rm H}^2) - J_{\rm H}/(U_1^2 - J_{\rm H}^2)],$$
$$J_2 = 16t^2[1/(U_1 + J_{\rm H}) + 1/(U + J_{\rm H})],$$
$$J_3 = 32t^2[U_1/(U_1^2 - J_{\rm H}^2) - J_{\rm H}/(U^2 - J_{\rm H}^2)],$$
$$J_4 = 8t^2[(U_1 + 2J_{\rm H})/(U_1^2 - J_{\rm H}^2) + J_{\rm H}/(U^2 - J_{\rm H}^2)],$$

respectively. Here U and U_1 are the intra- and inter-orbital Coulomb interactions, and $J_{\rm H}$ is the Hund's coupling of Cu $3d$ electrons. Due to the pd hybridization between Cu $3d$ and F $2p$ orbits,[18] we take $U = U_1 + J_{\rm H}$. The parameters U=7.5 eV and $J_{\rm H} = 0.9$ eV are adopted from the constrained LDA computation for $KCuF_3$.[4] The hopping integral along the c-direction is the largest, $t_{3z^2-r^2,3z^2-r^2}$=$4t$, with t=0.12 eV. Thus the energy scale of the SE coupling is $J = 16t^2/U = 30.7$ meV. And $\boldsymbol{s}_i$ denotes the spin at site i, while the operator $I_i^\alpha = \cos(2\pi m_\alpha/3)\,\tau_i^z - \sin(2\pi m_\alpha/3)\,\tau_i^x$, here the index α denotes the direction of α bond, $\alpha = x, y$ or z, corresponding to the crystal axes, a, b and c; (m_x,m_y,m_z)=(1, 2, 3).

The JT effect associated with one hole per Cu^{2+} site reads[6]

$$H_{\rm QJT} = g\sum_i(Q_{i2}\tau_i^x + Q_{i3}\tau_i^z) + \frac{K}{2}\sum_i(Q_{i2}^2 + Q_{i3}^2) + G\sum_i[(Q_{i3}^2 - Q_{i2}^2)\tau_i^z - 2Q_{i2}Q_{i3}\tau_i^x], \quad (3)$$

where both the linear and quadratic vibronic coupling terms have been included. The first and second terms describe the linear harmonic JT effect. Here g is the linear JT coupling strength and K is the elastic constant. The third one, i.e., the quadratic coupling, arises from the anharmonic JT effect and contributes to the anisotropic energy.[6] Here Q_{i2} and Q_{i3} are the normal vibration coordinates, defined as

$$Q_2 = (-X_1 + X_2 + Y_3 - Y_4)/2\,,$$
$$Q_3 = (-X_1 + X_2 - Y_3 + Y_4 + 2Z_5 - 2Z_6)/\sqrt{12}$$

with X, Y and Z as the coordinates of the i-th F ions.[21] G is the coefficient of quadratic coupling. For $KCuF_3$, we fix $K = 10$ eV/Å^2 (1 Å=0.1 nm) throughout this paper.

In such a strongly correlated spin-orbital-lattice system, according to Feynman–Hellman theorem, the ground state energy is minimised with respect to Q_{i2} and Q_{i3}, i.e., $\langle\partial H/\partial Q_{i2}\rangle = 0$, $\langle\partial H/\partial Q_{i3}\rangle = 0$. Then one could find the strength of the normal modes critically depends on the orbital polarisation through the following equation:

$$\langle Q_{i2}\rangle = g\frac{K\langle\tau_i^x\rangle + 4G\langle\tau_i^x\rangle\langle\tau_i^z\rangle}{4G^2(\langle\tau_i^x\rangle^2 + \langle\tau_i^z\rangle^2) - K^2},$$
$$\langle Q_{i3}\rangle = g\frac{K\langle\tau_i^z\rangle + 2G(\langle\tau_i^x\rangle^2 - \langle\tau_i^z\rangle^2)}{4G^2(\langle\tau_i^x\rangle^2 + \langle\tau_i^z\rangle^2) - K^2}. \quad (4)$$

Notice that in the absence of the anharmonic JT effect ($G = 0$), $\langle\tau_i^x\rangle = -(K/g)\langle Q_{i2}\rangle$, and $\langle\tau_i^z\rangle = -(K/g)\langle Q_{i3}\rangle$. To obtain the magnetic, orbital and deformation configurations, the spin order, orbital order and amplitude of the lattice distortion should be determined self-consistently. The compression of the Cu–F bond along c-axis implies the sign of Q_3 is negative for the hole, since the compressed octahedra lift the $|3z^2 - r^2\rangle$ orbit. Thus the $|3z^2 - r^2\rangle$ orbit is in favor of hole occupation.

It is a huge challenge to treat the spin–orbital correlations, and fluctuations and to find the ground state of such a strongly correlated system with high accuracy. We apply the cluster-SCF approach[19,22] to deal with the complicated spin–orbital Hamiltonian (1). This approach combines the exact diagonalization (for the cluster) scheme and the self-consistent field (for the surrounding atoms) scheme. The main idea of the approach is briefly described as follows: consider a proper Cu cluster, for $KCuF_3$, the cluster consists of an 8 sites, denoted as the solid balls in Fig.1. In the presence of environmental field, the cluster Hamiltonian, $H_{\rm cluster}$, reads:

$$H_{\rm cluster} = \sum_{i,\alpha=x,y,z}\left[\left(J_1 + \frac{J_2}{2}(I_i^\alpha + I_{i+\alpha}^\alpha) + J_3 I_i^\alpha I_{i+\alpha}^\alpha\right)\boldsymbol{s}_i\cdot\boldsymbol{s}_{i+\alpha} + J_4 I_i^\alpha I_{i+\alpha}^\alpha\right] + g\sum_i(Q_{i3}\tau_i^z + Q_{i2}\tau_i^x) + G\sum_i[(Q_{i3}^2 - Q_{i2}^2)\tau_i^z - 2Q_{i2}Q_{i3}\tau_i^x] + \frac{K}{2}\sum_i(Q_{i2}^2 + Q_{i3}^2) + \sum_i h_i^{\rm scf} \quad (5)$$

with the environmental SCF, $h_i^{\rm scf} = {\rm Tr}_{j'}(\rho_{j'} H_{ij'})$, where i runs over the sites inside the cluster, $\rho_{j'}$ denotes the reduced density matrix of the j'-th environmental site, and $H_{ij'}$ is the SE coupling between an inner site R_i and its environment $R_{j'}$. Now we could solve the cluster Hamiltonian (5) self-consistently. Firstly, with the help of the neutron scattering experiment on the spin configuration, we replace the spin correlations $\boldsymbol{s}_i \cdot \boldsymbol{s}_{i+\alpha}$ with the spin correlation functions $\langle \boldsymbol{s}_i \cdot \boldsymbol{s}_{i+\alpha} \rangle$ in $H_{\rm cluster}$, and diagonalize $H_{\rm cluster}$ in the presence of the orbital SCF.[22] Thereby we obtain the orbital polarization $\langle \boldsymbol{\tau} \rangle$ and the orbital correlation functions $\langle \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_{i+\alpha} \rangle$. Secondly, replace the orbital operators $\boldsymbol{\tau}_i$ and the orbital couplings $\boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_{i+\alpha}$ with $\langle \boldsymbol{\tau}_i \rangle$ and $\langle \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_{i+\alpha} \rangle$, and then diagonalize $H_{\rm cluster}$ in the presence of the spin SCF. Thus we obtain a new set of spin correlation functions. Repeat the above steps iteratively until the ground-state energy, the spin and orbital correlation functions converge to the accuracies. Since the short-range spin and orbital correlations, and quantum fluctuations are taken into account, the present approach is superior to the conventional mean-field method. In comparison with the conventional mean-field method, one can obtain more better results in some simple models with large quantum fluctuations, such as the Heisenberg AFM model.[22]

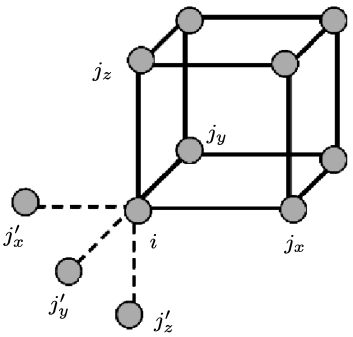

Fig.1. Schematic pseudocubic cluster adopted in our present calculation, one of Cu ions at R_i experiences three nearest-neighbor molecular fields from the surrounding Cu ions at $R_{j'_x}$, $R_{j'_y}$ and $R_{j'_z}$.

3. Results and discussion

In this Section we first investigate the ground state of $KCuF_3$ under the electronic SE interaction, then explore the ground state under the combination of the SE coupling and the JT effect, especially the role of the anharmonic JT effect in the ground state.

3.1. Superexchange interaction

For the electronic SE coupling (2), the conventional mean-field results[3,5] suggested the staggered orbital order with $x^2 - z^2/y^2 - z^2$ symmetry. However, utilizing the cluster-SCF approach, we find that numerous spin-orbital ground states are degenerate: such as the Néel AFM order with ferro-orbital structure, in which the hole occupies one of the three orbits among the $|3x^2 - r^2\rangle$, the $|3y^2 - r^2\rangle$ and the $|3z^2 - r^2\rangle$ orbits; or the Néel AFM order with the alternating plaquette valence-bond order, in which one plane, for example, the ab plane, is occupied by $|3x^2 - r^2\rangle$ orbit and the nearest-neighbor ones are taken up with $|3y^2 - r^2\rangle$ orbit, etc. These degenerate candidates for the ground states contain the alternating plaquette valence-bond component, in agreement with Feiner *et al.*'s result[16] by considering Gaussian quantum fluctuations. This also confirms the validity and the efficiency of our cluster-SCF approach. In this situation, the A-type AFM structure experimentally observed in $KCuF_3$ is not stable. Moreover, the nearest-neighbor orbital correlation functions are significantly different from zero. Such strong short-range orbital correlations indicate that the system only with the electronic SE interaction is a spin-orbital liquid phase, rather than a spin-orbital ordered state.

In the present spin-orbital correlated system, the spin alignment strongly depends on the orbital configuration. Due to the spin rotation symmetry, the spin coupling in the SE interaction is Heisenberg-like and has SO(3) rotational symmetry in the spin space. After averaging over the orbital degree of freedom, the spin exchange coupling strength along the α-axis in Eq.(2) reads

$$J_s^\alpha = J_1 + \frac{J_2}{2}\left(\langle I_i^\alpha \rangle + \langle I_{i+\alpha}^\alpha \rangle\right) + J_3 \langle I_i^\alpha I_{i+\alpha}^\alpha \rangle, \quad (6)$$

which is isotropic for the x-, the 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 α-direction writes

$$h_o^\alpha = \frac{J_2}{2}\langle \boldsymbol{s}_i \cdot \boldsymbol{s}_{j_{i+\alpha}} \rangle \left(I_i^\alpha + I_{i+\alpha}^\alpha\right) + \left(J_3 \langle \boldsymbol{s}_i \cdot \boldsymbol{s}_{i+\alpha} \rangle + J_4\right) I_i^\alpha I_{i+\alpha}^\alpha. \quad (7)$$

The I_i^α term in Eq.(7) is similar to a 'magnetic field', called the orbital field. This orbital field is frustrated, which favors either $|3z^2 - r^2\rangle$ or $|x^2 - y^2\rangle$ orbits along

the z-axis; while it favors either $|3x^2-r^2\rangle$ or $|y^2-z^2\rangle$ orbits along the x-direction. Unfortunately, the orbital interaction part, $I_i^\alpha I_{i+\alpha}^\alpha$, in Eq.(7) is also inherently frustrated: no matter what the coefficient of the second term in Eq.(7) is, this orbital correlation favors a frustrated ground state, as pointed out by Khomskii *et al.*[15]

We notice that when the spin correlation functions are strongly anisotropic, the orbital frustration is greatly suppressed. For example, when the spin correlation along the z-axis is strong as $\langle \boldsymbol{s}_i \cdot \boldsymbol{s}_{i+z}\rangle \approx -3/4$, while the spin correlation functions along the x, y-axes almost vanish, $\langle \boldsymbol{s}_i \cdot \boldsymbol{s}_{i+x,y}\rangle \approx 0$. Then the orbital part of the SE interactions becomes

$$h_o = J_4 \sum_i [I_i^x I_{i+x}^x + I_i^y I_{i+y}^y - 0.95 I_i^z I_{i+z}^z - 1.78 I_i^z]. \quad (8)$$

The x, y-components of the orbital field approach to zero, leaving a large z-component in Eq.(8). The strong uniaxial orbital field obviously 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. It also could be shown that the strongly anisotropic plaquette-valence-bond correlation of the spins favors the alternating plaquette-valence-bond orbital order.

Neglecting the spin and orbital quantum fluctuations, Kugel and Khomskii[3] found that 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 introduces an orbital field $(-\sum_i I_i^z)$. This orbital field lifts the degeneracy of the most orbital ground states, only leaving the G-type and C-type AFO configurations as the candidates. The fourfold rotation symmetry of the spin structure also confines the possible orbital ground state as the G-type or the C-type AFO structure, in agreement with the Goodenough–Kanamori empirical rule.[23] Nevertheless, the orbital field still does not remove the degeneracy of the G-type and the C-type AFO structures, as shown in Ref.[3]. Furthermore, the spin quantum fluctuations in $KCuF_3$ are very strong, as found in the experiments.[12] The magnetic moment of each Cu is about 0.49 μ_B, only a half of the classical expectation. Therefore, the classical approximation to the spins is not appropriate. From another viewpoint, the quantum fluctuations of the spins and orbitals may melt the classical spin-orbital ordered phase.[16] This is why once we take the quantum fluctuations of the spins and orbitals into account, the ground state of H_{SE} is a spin-orbital liquid or para-spin-orbital phase. While, the orbital symmetry in $KCuF_3$ could be broken by the JT distortion, i.e. H_{QJT}.

3.2. Role of the Jahn–Teller effect

In perovskite $KCuF_3$, there exist two kinds of cooperative JT distortion at low temperatures.[10,11] With respect to these two small and different lattice distortions, $KCuF_3$ exhibits two different crystalline phases, the type-d and the type-a structures, see the left inset of Fig.2, which coexist over a large temperature.[10] The orbital ground state in the type-a structure differs from that in the type-d structure due to different JT distortions of the CuF_6 octahedra.

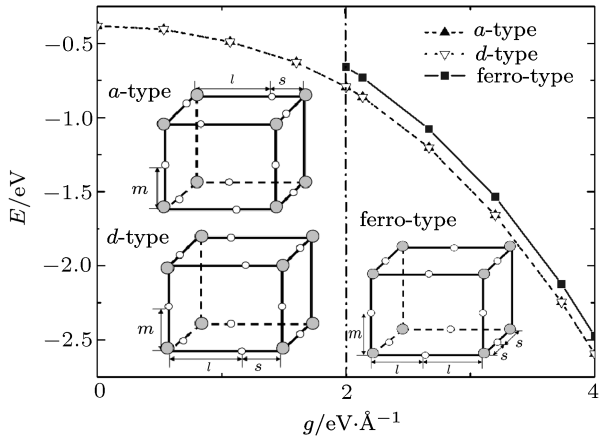

Fig.2. Dependence of ground-state energy on the linear JT coupling strength with anharmonic coupling $G = 0.75g$ eV/Å^2 for a-type, d-type and ferro-type structures in the cluster. The dashed vertical line indicates the appearance of the ferro-type distortion.

3.2.1. Lattice configuration

We then study the possible stable structures in the low temperature of $KCuF_3$ based on our spin-orbital-lattice Hamiltonian (1). The normal coordinates Q_2 and Q_3 of the JT distortions in $KCuF_3$ are obtained self-consistently through Eq.(4). We considered all possible distortions (A: $\pm Q_2$, $\pm Q_3$; B: $\pm Q_2$, $\pm Q_3$) in ab plane, and the antiferro and ferrolike stacking of the ab planes, where the A (B) corresponds to the distortion of the first (second) JT center in the cluster, respectively. The sign of G for $KCuF_3$ is also positive, which is similar to that of $4d^9$ material Cs_2AgF_4.[24] We find that for positive G, the lattice structure obtained in the ground state is either

a-type or d-type. The antiferro and ferrolike stackings of the ab planes with lattice configurations (Q_2, Q_3; $-Q_2$, Q_3), give rise to two different structural polytypes, which is consistent with the results experimentally observed in Refs.[10] and [11]. We find that the total energy of the ferro-type (Q_2, Q_3; Q_2, Q_3) structure is about 150 meV higher than those of the a-type and d-type structures, as seen in Fig.2. And the ferrotype structure as a metastable state only appears in the strong JT region.

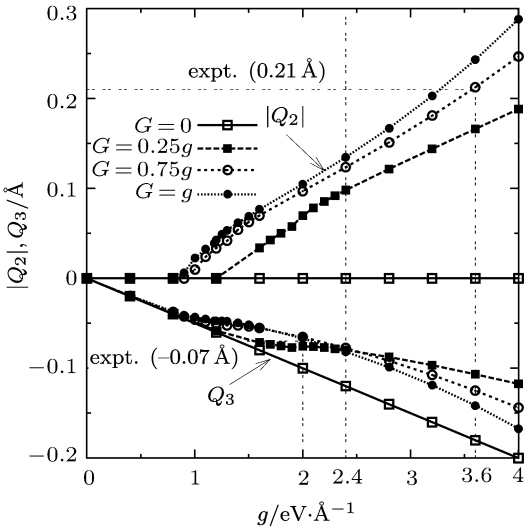

Fig.3. The amplitudes of $|Q_2|$ and Q_3 as functions of the linear JT coupling for different anharmonic coupling G. Two dashed horizontal lines correspond to the experimental values of $|Q_2|$ and Q_3 and the left and right vertical dashed lines are the corresponding linear JT coupling for $G = 0.75g$ eV/Å^2 in $KCuF_3$; and the middle vertical dashed line is plotted at $g = 2.4$ eV/Å.

According to experimental data, one can evaluate the corresponding amplitudes of $Q_2 \sim 0.21$ Å and $Q_3 \sim -0.07$ Å from the observed structural parameters at room temperature[11] and the LDA structural relaxation parameters.[18] Theoretically, we also obtain the dependence of Q_2 and Q_3 distortions on the linear JT coupling g for different anharmonic coupling parameters G, as shown in Fig.3. We find that in the absence of the anharmonic coupling, $G = 0$, Q_2 is nearly zero, which indicates that there is no distortion in the ab plane. In fact, it is the positive anharmonic effect that lowers the lattice symmetry, leading to the compression of the ligand octahedron.[14] $G \geq 0$ leads to a negative Q_3, giving rise to the correct distortion $c/a = 2m/(l+s) < 1$ in $KCuF_3$. On the contrary, the negative G gives a positive Q_3, which is not displayed in Fig.3, resulting in a wrong distortion $c/a = 2m/(l+s) > 1$. The experimental amplitudes of Q_2 and Q_3 identified as the dashed lines in Fig.3 show that $g = 2 \sim 3.6$ eV/Å with $G = 0.75g$ eV/Å^2. We adopt $g = 2.4$ eV/Å and $G = 0.75g$ eV/Å^2 for $KCuF_3$ in the following. Theoretically, at $g = 2.4$, $|Q_2|$ and Q_3 are about 0.14 and –0.075 Å, respectively. The calculated $|Q_2|$ is slightly smaller than the experimental value 0.21 Å. The reason for the small difference between the theory and the experimental data will be discussed in Section 4.

Most recently, Deisenhofer *et al*[25] extracted that the crystal field splitting between the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbits is about 0.69 eV in the optical absorption experiment. In the presence of the Jahn–Teller effect, such a crystal field splitting is not for the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbits. Rather, from Eq.(3), it is the splitting of the two mixed orbits in the single ion. Theoretical splitting is $\Delta_{\rm CF} = g\sqrt{Q_3^2 + Q_2^2} \sim 0.38$ eV in the absence of the anharmonic distortion, or ~ 0.36 eV in the presence of the anharmonic distortion. Both of splittings are comparable with Deisenhofer *et al*'s observation.

3.2.2. Magnetic properties

Once the JT distortion singles out the orbital structure, it stabilises the magnetic structure simultaneously, hence the spin-orbital ground state. Under the full Hamiltonian, our numerical results demonstrate that the magnetic ground states are the A-type AFM order both for the type-a and type-d crystalline phases. And the spin correlations are strongly anisotropic, $\langle \boldsymbol{s}_i \cdot \boldsymbol{s}_{i+z}\rangle / \langle \boldsymbol{s}_i \cdot \boldsymbol{s}_{i+x,y}\rangle \approx 7.1$. Furthermore, we obtain the spin coupling strengths J_z and $J_{x,y}$, which are 34.4 meV and -1.94 meV respectively, giving rise to $|J_z/J_{x,y}| \sim 18$ for $g = 2.4$ and $G = 0.75g$, as shown by the vertical dashed lines in Fig.4. These results are in agreement with the experimental data in $KCuF_3$,[12,13,26] as listed in Table 1. With the JT coupling increasing, the system undergoes a quantum phase transition from a Néel G-AFM ($J_{x,y} > 0$, $J_z > 0$) to an A-AFM ($J_{x,y} < 0$, $J_z > 0$) state. We can clearly see in Fig.4 that in the weak JT region, the magnetic ground state lies in G-AFM phase. Only in the strong JT region, is the A-AFM phase stable. Meanwhile, the positive anharmonic JT coupling is

also responsible for the anisotropic A-type AFM in $KCuF_3$. In the absence of anharmonic effect, i.e. $G = 0$, the magnetic coupling strengths are positive, $J_{x,y} > 0$, in contradiction to the experimental results. Therefore the anharmonic JT coupling plays an essential role in the A-type AFM magnetic ground state.

Notice that the present anisotropic character of the magnetic coupling strengths $|J_z/J_{x,y}| \approx 18$ is not as strong as Satija's experimental data,[13] in which $|J_z/J_{x,y}| \approx 100$. The recent spin dynamics experimental data[26,27] demonstrate a relatively small ratio of $|J_z/J_{x,y}|$, suggesting that the present theoretical values for J_z and $J_{x,y}$ are plausible. The residual discrepancy between the theoretical result and the experimental data[13] can be attributed to the freeze of the orbital excitations in fitting the experimental data, and the numerical error from our cluster-SCF approach. The strong anisotropy in the spin correlations and the magnetic couplings originates from the anisotropic regular distribution of the orbital wavefunctions in real space, i.e., the orbital ordering. Moreover, the large JT distortion Q_2 strongly mixes the $|3z^2 - r^2\rangle$ and $|x^2 - y^2\rangle$ orbits, leading to the declines of the orbital polarization, the anisotropy of orbital and spin correlations. Hence the anisotropy of the magnetic couplings, $|J_z/J_{x,y}|$, is suppressed by the large Q_2 distortion, as seen from the orbital occupancy.

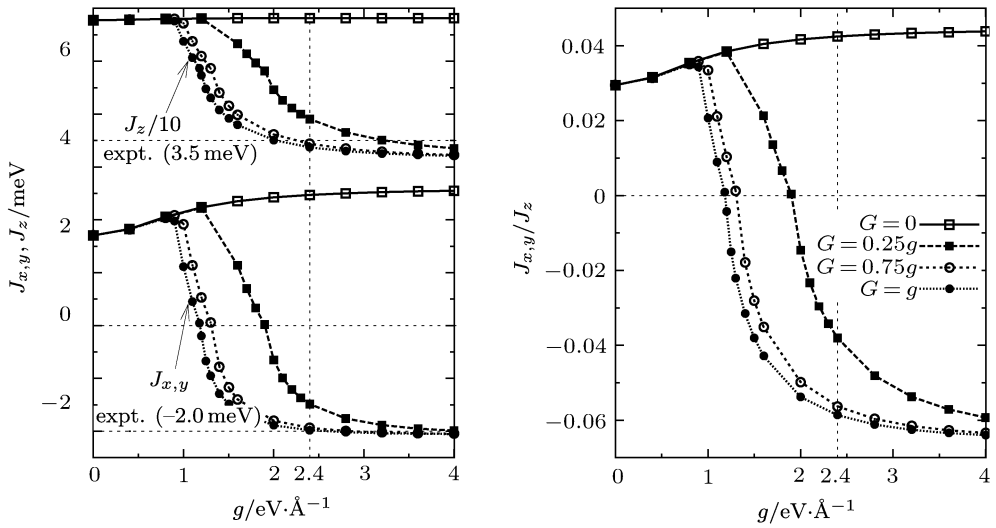

Fig.4. Dependence of the magnetic coupling strengths $J_{x,y}$, J_z (left panel) and $J_{x,y}/J_z$ (right panel) on the linear JT coupling for different anharmonic coupling G. The vertical dashed line indicates $g = 2.4$ eV/Å.

Next we focus on the magnetic moment of each Cu ion. We find that the effective magnetic moment of each Cu ion is considerably reduced from 1 μ_B to 0.56 μ_B, the averaged spin of each Cu ion decreases to 0.28, consisting with the neutron scattering experimental data very well,[12] which can also be seen in Table 1. Obviously, such a great reduction of the magnetic moment arises from the spin-orbital quantum fluctuations: the more the spin waves and the orbital waves are excited arising from the quantum fluctuation in the low-dimensional AFM,[17] the more spin flips and disorder are in the spin-orbital system, which greatly reduces the magnetic moment.

Table 1. Theoretical and experimental averaged spin, magnetic couplings, N.N spin correlations, orbital polarisation, N.N orbital correlations, and the amplitudes of JT distortions. 'a' and 'd' refer to type-a and type-d phases. '±' corresponds to two N.N sublattices. $J_{x,y,z}$ are in units of meV. The theoretical parameters are $g = 2.4$ eV/Å, and $G = 0.75g$ eV/Å^2.

	$\langle s \rangle$	$J_{x,y}$	J_z	$J_z/J_{x,y}$	Q_2	Q_3
calc.	0.286	–1.94	34.4	18	±0.14	–0.075
expt.	0.245[12]	–0.4∼–2.0[13,26]	35.0[13,26]	87.5[13]	±0.21	–0.07
	$\langle \tau_z \rangle$	$\langle \tau_x \rangle$	$\langle \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_{i+x,y} \rangle$	$\langle \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_{i+z} \rangle$	$\langle \boldsymbol{s}_i \cdot \boldsymbol{s}_{i+x,y} \rangle$	$\langle \boldsymbol{s}_i \cdot \boldsymbol{s}_{i+z} \rangle$
calc.^{d}	0.279	±0.415	–0.094	0.250	0.093	–0.659
calc.^{a}	0.279	±0.415	–0.094	–0.092	0.093	–0.659

The influence of the linear JT coupling on the magnetic moment is complicated. It is clearly seen in Fig.5 that with the JT coupling increasing, the magnetic moment sharply decreases as soon as a G-AFM−A-AFM quantum phase transition occurs. However, in the absence of the anharmonic coupling, there is no such a phase transition. With the increase of the anharmonic coupling, the quantum critical point ($\langle s\rangle \to 0$) shifts to the weak JT region. Thus the presence of such a phase transition suggests that the anharmonic JT coupling plays a crucial role in the A-AFM state in $KCuF_3$.

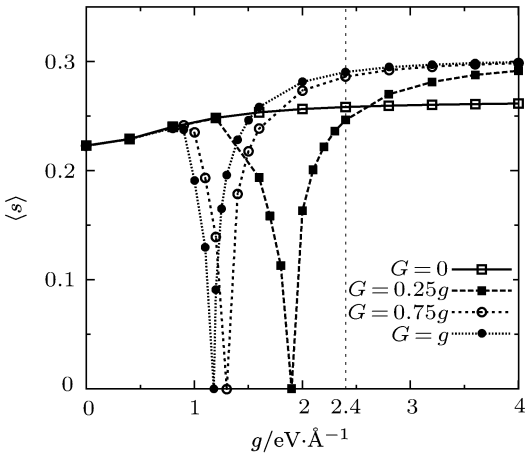

Fig.5. Dependence of the averaged sublattice spin on the linear JT coupling for different anharmonic coupling G. The vertical dashed line is plotted at $g = 2.4$ eV/Å.

3.2.3. Orbital properties

The unusual 1D AFM in $KCuF_3$ is in fact associated with the formation of the long-range orbital ordering. As seen in Fig.6, with the increase of the linear JT coupling g, the orbital polarisation τ_z is suppressed from 0.5 to 0.25. At $g = 2.4$ and $G = 0.75g$, the hole orbital wavefunctions of the Cu site is $|\psi\rangle = 0.877|3z^2 - r^2\rangle \pm 0.480|x^2 - y^2\rangle$, here '±' refer to the two sublattices of the antiferro-distortion, approximately, $|\psi\rangle \approx |y^2 - z^2\rangle$ for '+', and $|\psi\rangle \approx |x^2$–$z^2\rangle$ for '−'. This orbital ordered phase, about 23% in the x^2–y^2 orbit and 77% in the $3z^2$–r^2 orbit in both sublattices, is consistent with the tetragonal distortions of the CuF_6 octahedra: when the Cu-F bond is elongated along the x axis, the CF singles out the $|y^2$–$z^2\rangle$ hole orbit, corresponding to '+'; when Cu-F bond is elongated along the y axis, the energy of $|x^2 - z^2\rangle$ hole orbit is lower, corresponding to '−'.

At $g = 2.4$ and $G = 0.75g$, the sublattice orbital polarisation and the orbital correlation functions are also listed in Table 1, definitely manifesting the G-type AFO correlation in the type-a structure and the C-type AFO correlation in the type-d structure. From Fig.6, we can find that the anharmonic coupling suppresses the orbital polarization greatly. On the contrary, in the absence of anharmonic coupling, the orbital polarization $\langle\tau_z\rangle$ is nearly polarized in the $|3z^2 - r^2\rangle$ orbit. Therefore, the anharmonic JT distortion breaks the orbital symmetry, suppresses the orbital frustration and the quantum fluctuations, and establishes the unusual long-range orbital order, hence the magnetic order in $KCuF_3$.

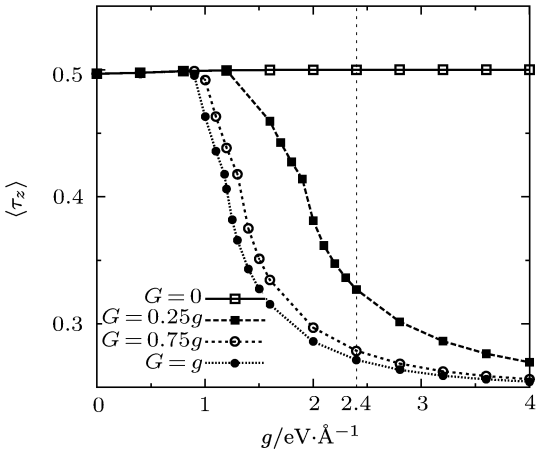

Fig.6. Dependence of the sublattice orbital polarization on the linear JT coupling for different anharmonic coupling G. The vertical dashed line is plotted at $g = 2.4$ eV/Å.

4. Remarks and summary

We notice that the present theoretical magnetic moments are slightly different from the experimental ones. We anticipate that besides the Cu–F pd hybridization, the agreement of the theoretical results with the experimental data will be much better if the L–S coupling in perovskite $KCuF_3$ is taken into account, since the nonresonant magnetic scattering experiment[1] showed that the orbital angular momentum L contributes a finite value to the total magnetic moment, and $L/S \approx 0.29$. Obviously the finite orbital moment does not come from the two e_g orbits, since the expectation of the orbital angular momentum L in these orbital basis wavefunctions $|3z^2$–$r^2\rangle$, $|x^2$–$y^2\rangle$, or any of their combinations is zero. One possibility of the residual orbital moment is contributed from the reduced symmetry of the t_{2g} orbits in $KCuF_3$[28] or a small fraction of the t_{2g} orbit mixing with the e_g orbit; another possibility is the hybridization of the $4p$ orbits with the e_g orbits. In both situations, the weak LS coupling in $KCuF_3$ does not change the spin configuration considerably, while it definitely reduces the magnetic moment of each Cu ion. The theoretical magnetic moment will be more in agreement with the experimental data.

Furthermore, considering many other spin-orbital-lattice interacting compounds, such as CMR manganites,[29−31] vanadium oxides,[32,33] and titanium oxides,[34,35] in which the JT or other distortions extensively exist, one may sum up such a rule that the low-symmetric JT lattice distortions play a crucial role in singling out many degenerate candidates as the orbital ordered ground state. This would be the natural generalisation of the JT effect in strongly correlated systems that the highly degenerate ground state in the correlated electronic system with pure symmetric spin-orbital interactions is usually stabilised to the orbital ordered phase through distorting to a lower symmetric structure. It is also worthy of pointing out that the present cluster-SCF approach is also applicable to many other undoped spin-orbital compounds, such as $LaMnO_3$, $LaTiO_3$, YVO_3, etc.

In summary, the systematic study on the roles of the electronic SE interaction and the JT effect in the lattice distortions, orbital ordering and magnetic properties in $KCuF_3$ showed that the SE interaction leads to an orbital liquid or a disordered state due to the inherent frustrations, the spin and orbital quantum fluctuations. The incorporation of the JT effect, especially the anharmonic coupling, lowers the orbital symmetry, and stabilizes the orbital ordering as the observed ground state. The ordered orbital configuration results in a strong magnetic anisotropy; the spin and orbital fluctuations and the spin-orbital fluctuation induced by orbital frustration lead to a considerable reduction of the magnetic moment of Cu ions.

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