On the mechanism for orbital-ordering in KCuF$_3$

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The Mott insulating perovskite KCuF$_3$ is considered the archetype of an orbitally-ordered system. By using the LDA+dynamical mean-field theory (DMFT) method, we investigate the mechanism for orbital-ordering (OO) in this material. We show that the purely electronic Kugel-Khomskii super-exchange mechanism (KK) alone leads to a remarkably large transition temperature of $T_{\text{KK}} \sim 350$ K. However, orbital-order is experimentally believed to persist to at least 800 K. Thus Jahn-Teller distortions are essential for stabilizing orbital-order at such high temperatures.

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In a seminal work $^1$ Kugel and Khomskii showed that in strongly correlated systems with orbital degrees of freedom many-body effects could give rise to orbital-order (OO) via a purely electronic super-exchange mechanism. Orbital-ordering phenomena are now believed to play a crucial role in determining the electronic and magnetic properties of many transition-metal oxide Mott insulators. While it is clear that Coulomb repulsion is a key ingredient, it remains uncertain whether it just enhances the effects of lattice distortions $^2$ or really drives orbital-order via superexchange $^1$.

We analyze these two scenarios for the archetype of an orbitally-ordered material, KCuF$_3$ $^1$. In this 3$d^9$ perovskite the Cu $d$-levels are split into completely filled three-fold degenerate $t_{2g}$-levels and two-fold degenerate $e_g$-levels, occupied by one hole. In the first scenario Jahn-Teller elongations of some Cu-F bonds split the partially occupied $e_g$-levels further into two non-degenerate crystal-field orbitals. The Coulomb repulsion, $U$, then suppresses quantum orbital fluctuations favoring the occupation of the lower energy state, as it happens in some $t_{2g}$-perovskites $^3,4$. In this picture the ordering is caused by electron-phonon coupling; Coulomb repulsion just enhances the orbital polarization due to the crystal-field splitting $^5,6$. In the second scenario the purely electronic super-exchange mechanism, arising from the $e_g$-degeneracy, drives orbital-ordering, and Jahn-Teller distortions are merely a secondary effect. In this picture electron-phonon coupling is of minor importance $^1$.

The key role of Coulomb repulsion is evident from static mean-field LDA+$U$ calculations, which show $^6,7$ that in KCuF$_3$ the distortions of the octahedra are stable with an energy gain $\Delta E \sim 150 - 200$ meV per formula unit, at least an order of magnitude larger than in LDA $^6,8$ and GGA $^5,8$: recent GGA+DMFT $^8$ calculations yield very similar results, suggesting in addition that dynamical fluctuations play a small role in determining the stable crystal structure of this system. However, these results might merely indicate that the electron-phonon coupling is underestimated in LDA or GGA, probably due to self-interaction, rather than identifying Kugel-Khomskii super-exchange as the driving mechanism for orbital-order. This is supported by ab-initio Hartree-Fock (HF) calculations which give results akin to LDA+$U$ $^4$. Moreover, in the superexchange scenario it remains to be explained why $T_{\text{OO}} \sim 800$ K $^10$, more than twenty times the 3D antiferromagnetic (AFM) critical temperature, $T_N \sim 38$ K $^{11,12}$, a surprising fact if magnetic- and orbital-order were driven by the same super-exchange mechanism.

![FIG. 1: (Color online) Left: Crystal structure and orbital-order in $a$-type $^{12}$ KCuF$_3$. Cu is at the center of F octahedra enclosed in a K cage. The conventional cell is tetragonal with axes $a$, $b$, $c$, where $a=b$, $c=0.95a\sqrt{2}$. The pseudo-cubic axes are defined as $x=(a+b)/2$, $y=-(a+b)/2$, and $z=c/2$. All Cu sites are equivalent. For sites 1 the long (short) bond $l$ ($s$) is along $y$ ($x$). Vice versa for sites 2. Orbital $|1\rangle$ (see table I), occupied by one hole, is shown for each site. Right: Jahn-Teller distortions at sites 1, measured by $\delta=(l-s)/(l+s)/2$ and $\gamma = c/a\sqrt{2}$. $R$ is the experimental structure, $R_5$ and $I_5$ two ideal structures with reduced distortions, and $I_0$ is cubic.](image-url)
In this Letter we study the Kugel-Khomskii mechanism at finite temperature and identify the origin of orbital-ordering in KCuF$_3$. We will show that super-exchange alone leads to orbital-order with $T_{KK} \sim 350$ K, less than half the experimental value. Thus Jahn-Teller distortions are essential for driving orbital-order above 350 K.

KCuF$_3$ is a tetragonal perovskite made of Jahn-Teller distorted CuF$_6$ octahedra enclosed in an almost cubic K cage [13, 14]. The Jahn-Teller distortion amounts to a 3.1% elongation/shortening of the CuF distances in the $xy$-plane. The tetragonal distortion reduces the CuF bond along $z$ by 2.5%, leaving it of intermediate length. The long ($l$) and short ($s$) bond alternate between $x$ and $y$ along all three cubic axes ($a$-type pattern) [12]. At each site one hole occupies the highest $e_g$-orbital, $\sim |s^2 - z^2\rangle$, i.e., the occupied orbitals ($\sim |x^2 - z^2\rangle$ or $\sim |y^2 - z^2\rangle$) alternate in all directions. This ordering and the crystal structure are shown in Fig. 1.

As a method for studying the electronic structure of KCuF$_3$ and the super-exchange mechanism we adopt the LDA+DMFT approach [16]. Following the procedure presented in Ref. [3], we first calculate the LDA bandstructure using the $N^{th}$-order muffin-tin orbit method (NMTO). We find filled O-bands divided by a gap of $\sim 39$ eV and a Mott gap of about 2.5 eV for $U_{t2g}$ states are completely filled, do not hybridize with the $e_g$-levels and thus are likely unimportant for orbital-ordering [17]. For the active states we construct a basis of localized $e_g$ NMTO Wannier functions [3]. The corresponding $e_g$ Hubbard model is

$$H = H^{LDA} + \sum_{im} U_{m,m'}n_{i,m}\bar{n}_{i,m'} + \frac{1}{2} \sum_{im(i\neq m')\sigma\sigma'} (U_{m,m'} - J\delta_{\sigma,\sigma'}) n_{i,m\sigma} \bar{n}_{i,m'\sigma},$$

where $n_{i,m\sigma} = c_{i,m\sigma}^\dagger c_{i,m\sigma}$ and $c_{i,m\sigma}^\dagger$ creates an electron with spin $\sigma$ in a Wannier orbital $|m\rangle \approx |x^2 - y^2\rangle$ or $|3z^2 - 1\rangle$ at site $i$; the direct and exchange [18] terms of the screened on-site Coulomb interaction are $U_{m,m'} = U - 2J(1 - \delta_{m,m'})$ and $J$. We solve [19] using dynamical mean-field theory in the single-site approximation (DMFT) [19] and its cluster extension (CDMFT) [20], using quantum Monte Carlo [21] as impurity solver and working with the full self-energy matrix $\Sigma_{m,m'}$ in orbital space [3]. We obtain the spectral matrix on the real axis by analytical continuation [22]. We use as parameters $J = 0.9$ eV and vary $U$ between 7 and 9 eV. These values are close to the theoretical estimates based on constrained LDA [3].

In the paramagnetic phase, single-site DMFT calculations yield a Mott gap of about 2.5 eV for $U = 7$ eV, and 4.5 eV for $U = 9$ eV. The system is orbitally ordered, and the OO is $a$-type as the distortion pattern; static mean-field (LDA+$U$, HF) calculation [1, 2, 23] give similar orbital-order, however also antiferromagnetism. We define the orbital polarization $p$ as the difference in occupation between the most and least occupied natural orbital (diagonalizing the $e_g$ density-matrix). It turns out that to a good approximation $p$ is given by the difference in occupation between the highest (|2\rangle) and the lowest (|1\rangle) energy crystal-field orbital, defined in table I. In Fig. 3 we show $p$ as a function of temperature. We find that the polarization is saturated ($p \sim 1$) even for temperatures as high as 1500 K. We obtain very similar results in two-site CDMFT calculations.

Using second-order perturbation theory, we calculate the exchange-couplings constants for the orbitally ordered state found with DMFT, and obtain [24]

$$J_{i,j,i',j'}^{\delta_{i,j}} \sim \frac{4|t_{i,j}^{i',j'}|^2(U + \Delta)}{(U + \Delta)^2 - J^2} - \frac{|t_{i,j}^{i',j'}|^2 + |t_{2,1}^{i,j'}|^2}{U + \Delta - 3J} 2J,$$

where $t_{i,j}^{i',j'}$ are the hopping integrals from site $i$ to site $i'$, and $j, j' = 1, 2$ are the $e_g$ crystal-field states. As shown in table I, the calculated exchange couplings are in very good agreement with experimental findings. Thus our method gives both the correct orbital-order and the correct magnetic structure.

To understand whether this orbital-order is driven by the exchange coupling or merely is a consequence of the crystal-field splitting, we consider hypothetical lattices with reduced deformations, measured by $\gamma = c/\sqrt{2a}$ (tetragonal distortion) and $\delta = (l - s)/(l + s)/2$ (Jahn-Teller deformation). To keep the volume of the unit cell at the experimental value, we renormalize all lattice vectors by $(\gamma/0.95)^{-1/3}$. We calculate the Hamiltonian for a number of structures reducing the distortion of the real crystal [15] with $\gamma = 0.95$ and $\delta = 4.4\%$ to the ideal cubic structure $\gamma = 1$ and $\delta = 0$. The bands for some
### TABLE I: Hopping integrals $t_{i,i'}^{\alpha}$ in the crystal-field basis $(j,j')$ from a site $i$ of type 1 to a neighboring site $i'$ of type 2 in direction $l+qy+mz$. $J_{SE}$ are the magnetic superexchange couplings for the experimental structure and some representative orbital-superexchange couplings for the ideal cubic structure \[24\]. The crystal-field states are \[1\] $|1\rangle = \cos \theta (3f^2 - 1) + \sin \theta s^2 - z^2$ and \[2\] $|2\rangle = -\sin \theta (3f^2 - 1) + \cos \theta s^2 - z^2$ where $s(l)$ is the direction of the short (long) bond ($s=x$, $l=y$ for a site 1). The crystal-field splitting and $\cos \theta$ are given for all structures. All energies are in meV.

| Structure          | $t_{1,1}$ | $t_{1,2}$ | $t_{2,1}$ | $t_{2,2}$ | $J_{SE}^{zz}$ | $J_{SE}^{z\pm l \pm l'}$ |
|--------------------|----------|----------|----------|----------|-------------|----------------|
| LDA+DMFT           | 0.09     | 0.08     | 0.09     | 0.08     | 0.03        | 0.02          |
| LDA+DMFT           | 0.09     | 0.08     | 0.09     | 0.08     | 0.03        | 0.02          |

We use the notation $R_3$ for structures with the real tetragonal distortion $\gamma = 0.95$ and $I_5$ for ideal ($\gamma = 1$) structures. The distortions affect the hopping integrals, both along $001$ and in the $xy$-plane, as shown in table I. The main effect is, however, the crystal-field splitting $\Delta_{2,1}$ which decreases almost linearly with decreasing distortion, as expected for a Jahn-Teller system. For each structure we obtain the Hamiltonian $H^{LDA}$ for the $e_g$-bands and perform LDA+DMFT calculations for decreasing temperatures. At the lowest temperatures we find a-type OO with full orbital polarization for all structures (see Fig. 3). At 800 K, the situation is qualitatively different. Orbital polarization remains saturated when reducing $\delta$ from 4.4% to 1%. For smaller distortions, however, $\delta$ rapidly goes to zero: For $\delta = 0.2\%$ and $\gamma = 1$, $p$ is already reduced to $\sim 0.5$, and becomes negligible in the cubic limit. Thus super-exchange alone is not sufficiently strong to drive orbital-ordering at $T \gg 800$ K.

From the temperature dependence of the orbital polarization we can determine the transition temperature $T_{KK}$ at which the Kugel-Khomskii superexchange mechanism would drive orbital-ordering, and thus disentangle the super-exchange from the electron-phonon coupling. For this we study the ideal cubic structure, introducing a negligible (1 meV) crystal-field splitting as an external-field to break the symmetry. We find a phase transition to an orbitally-ordered state at $T_{KK} \sim 350$ K. The hole orbitals at two neighboring sites are $\sim |y^2 - z^2|$ and $\sim |x^2 - z^2|$, in agreement with the original prediction of Kugel and Khomskii \[1\]. This critical temperature is sizable, but significantly smaller than $T_{OO} \sim 800$ K \[10\].

Since the screened Coulomb repulsion $U$ is hard to calculate, it is crucial to identify the range of plausible values of $U$ and to estimate how $T_{KK}$ varies in this range. For the experimental structure, $U \sim 5$ eV yields a tiny gap in DMFT and $U \sim 6$ eV a semiconducting gap of 1.3 eV, while KCuF$_3$ is a good insulator \[13\]. It seems therefore unrealistic that $U$ is smaller than 7 eV. It could, however, be larger. In Fig. 8 we show the results for $U = 9$ eV. We find a reduction to $T_{KK} \sim 300$ K, reflecting the decrease in the super-exchange coupling. Thus we can conclude that, within single-site DMFT, $T_{KK} \sim 300 - 350$ K, sizable but at least a factor two smaller than $T_{OO} \sim 800$ K.

The ordering temperature $T_{KK}$ might be even overestimated by the single-site DMFT approximation, as is common for mean-field theories \[27\]. To investigate the effects of short-range correlations, we therefore perform two-site CDMFT calculations for the cubic structure. We use a supercell containing 8 formula units, with axis $a' = 2x$, $b' = 2y$, $c' = 2z$ and a two-site cluster which averages the cubic directions, i.e., imposing $\sum_{\tau} i_{\tau} = \sum_{\tau} i_{\tau + x} = \sum_{\tau} i_{\tau + z}$ for nearest neighbors $i$ and $i'$ in the supercell. For $U = 7$ eV we find that the polarization starts to increase around 300-350 K, somewhat below the single-site transition.

To compare these results with super-exchange theory, we calculate the orbital super-exchange coupling assuming that no long-range magnetic order is present \[24\]. Two representative couplings are

$$J_{SE}^{zz} = \sum_{\tau,\tau'} (-1)^{\tau + \tau'} 2 |t_{\tau,\tau'}| \frac{2U + 6J}{U - 3J},$$

$$J_{SE}^{z\pm l \pm l'} = \sum_{\tau,\tau'} 2 |t_{\tau,\tau'}| \frac{2U}{U - 3J} \left( \frac{2 |t_{\tau,\tau'}|^2}{U - J} + \frac{2 |t_{\tau,\tau'}|^2}{U - 3J} \right),$$

where we adopt the pseudospin description of the orbital states \[1\], with $\tau = 1/2$ corresponding to $|z^2 - 1|$ and $\tau = -1/2$ to $|x^2 - y^2|$. These couplings, shown in table I, are very anisotropic, with the largest about three times the magnetic exchange coupling along $z$. Again this suggests that $T_{KK}$ should be larger than $T_N = 38$ K, but certainly smaller than $T_{OO} \sim 800$ K.

All this indicates that in KCuF$_3$ the driving mechanism for orbital-ordering is not pure superexchange. Further support comes from an accurate re-analysis of LDA+$U$ results. To do this we first perform LDA+$U$ calculations for the cubic and distorted structure \[3\], and obtain results in agreement with previous literature \[1\] \[23\]. For the undistorted KCuF$_3$ we find a fully orbitally polarized solution, and the occupation matrix only slightly
differs from that obtained for the experimental structure. This shows that the energy gain due to the distortions, $\Delta E \sim 180$ meV per formula unit, cannot be ascribed to the orbital polarization itself, but rather is an estimate of the electron-phonon coupling, enhanced by self-interaction correction [1]. In order to estimate the energy gain due to orbital polarization, we performed several LDA+U calculations for the cubic structure with different (fixed) occupation matrix. We find that the energy gain [1] is $\sim 90$ meV, only half of $\Delta E$.

In conclusion, we have calculated the Kugel-Khomskii transition temperature for KCuF$_3$ and find a remarkably large $T_{\text{KK}} \sim 350$ K. Nevertheless, the super-exchange mechanism is not sufficiently strong to explain $T_{\text{OO}} \sim 800$ K: at such a transition both super-exchange and electron-phonon are of comparable importance. The assignment $T_{\text{OO}} \sim 800$ K [10] is however based on the temperature dependence of the orbital peak intensity signals measured by resonant x-rays scattering [10]. A direct measurement of the evolution of the distortions with temperature would be highly desirable. Should orbital-order persist till melting, the electron-phonon coupling contribution would be the dominant mechanism.

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