Mechanism of structural phase transitions in KCrF$_3$

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We study the origin of the cubic to tetragonal and tetragonal to monoclinic structural transitions in KCrF$_3$, and the associated change in orbital order, paying particular attention to the relevance of super-exchange in both phases. We show that super-exchange is not the main mechanism driving these transitions. Specifically, it is not strong enough to be responsible for the high-temperature cubic to tetragonal transition and does not yield the type of orbital order observed in the monoclinic phase. The energy difference between the tetragonal and the monoclinic structure is tiny, and most likely results from the interplay between volume, covalency, and localization effects. The transition is rather driven by Slater exchange than super-exchange. Nevertheless, once the monoclinic distortions are present, super-exchange helps in stabilizing the low symmetry structure. The orbital order we obtain for this monoclinic phase is consistent with the magnetic transition at 80 K.

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I. INTRODUCTION

The Mott insulator KCrF$_3$ is iso-electronic to LaMnO$_3$, the mother compound of colossal magnetoresistance materials, but differently from LaMnO$_3$ it exhibits a series of structural and magnetic phase transitions. At temperatures higher than 973 K it is a cubic perovskite, between 973 and 250 K it is tetragonal and finally below 250 K it becomes monoclinic. The tetragonal and monoclinic structures are shown in Fig. 1. As the temperature varies between 973 and 250 K it is tetragonal and finally below 250 K it becomes monoclinic. The tetragonal and monoclinic structures are shown in Fig. 1. At the 973 K transition, with the lowering of the symmetry from cubic to tetragonal a cooperative Jahn-Teller (JT) distortion develops. It is of G-type (short and long CrF bonds alternate in all directions), while in LaMnO$_3$ the order is instead of C-type (short and long bonds alternate in the ab plane and repeat along the c direction). Thus below 973 K the system is orbitally ordered. Finally, KCrF$_3$ becomes magnetic below $T_N \sim 80$ K; the ordering vector is $(1/2 \pm \delta, 1/2 \pm \delta, 0)$, corresponding to an antiferromagnetic A-type order with an incommensurate component $\delta$ which disappears at 46 K. The phase transitions of KCrF$_3$ have been intensively investigated but their nature, and in particular the role played by the purely electronic super-exchange mechanism in the structural transitions, is to date not fully understood.

In recent years we have studied the origin of G- and C-type Jahn-Teller distortions in KCuF$_3$, LaMnO$_3$, and rare-earth manganites. We have shown that, although Kugel-Khomskii (KK) many-body super-exchange is very large, it appears to have little influence on the high-temperature orbital-order to orbital disorder transition observed experimentally in the full series of rare-earth manganites. However, in particular in LaMnO$_3$, super-exchange effects turned out to be so strong that, if hypothetically the static Jahn-Teller distortion was absent, it could alone explain an orbital-order transition at temperatures as large as 500 K. Remarkably, KCrF$_3$ exhibits a change in the co-operative Jahn-Teller distortion around 250 K; in the monoclinic phase the orbital order acquires a small C-type component in the yz plane, where the pseudocubic z and y axes are defined as $(a + b)/2$ and $(a - b)/2$ (see Fig. 1). Thus, super-exchange could play an important role for the tetragonal to monoclinic structural phase transition, or in similar low temperature phase transitions observed in other systems. In this work we want to clarify if that is the case.

The paper is organized as follows. In section II we discuss the methods and models used. In section III we present our results. In section III.A we discuss the electronic structure, obtained using density-functional theory (DFT) in the generalized-gradient approximation (GGA). In section III.B we focus on the super-exchange mechanism for orbital order; by using the density-functional theory + dynamical mean-field theory (DFT+DMFT) method we calculate for each structure the transition temperature, as well as the occupied orbitals. We use the technique introduced in Ref. [6]. We study both the cubic to tetragonal and tetragonal to monoclinic structural phase transitions. In section III.C we investigate the effect of the changes in volume by using density-functional theory in the GGA as well as the GGA+$U$ approach. In section III.D we discuss the origin of the magnetic structure in the monoclinic phase. Finally, section IV gives our conclusions.
II. MODEL AND METHOD

We calculate the electronic structure in the different phases and optimize the structures *ab-initio* using the projected augmented plane-wave technique as implemented in the ABINIT code\textsuperscript{20,21} and in the VASP package.\textsuperscript{22} We construct Wannier functions via the Marzari-Vanderbilt localization procedure (Wannier90 code\textsuperscript{22}) as well as via the first-principles downfolding approach based on the Nth-order muffin-tin orbital (NMTO) method.\textsuperscript{22}

To study the effects of the Kugel-Khomskii super-exchange mechanism we use *ab-initio* minimal many-body models. The Cr $d$ bands split into half-filled $t_{2g}$ and 1/4-filled $e_g$ bands. The Hund’s rule interaction between $t_{2g}$ and $e_g$ electrons yields a magnetic coupling of the $e_g$ electrons to the effective spin of $t_{2g}$ electrons, $S_{t_{2g}}$. The latter acts as an effective magnetic field $h = JS_{t_{2g}}$, and, in the paramagnetic phase, yields a band-renormalization factor accounting for $t_{2g}$ spin-disorder.\textsuperscript{23} Thus the minimal model is

\[
H = \sum_{i\sigma} \sum_{i'\sigma'} t_{i,i'}^{\sigma\sigma'} c_{i\sigma}^\dagger c_{i'\sigma'} + \frac{1}{2} \sum_{i\sigma\sigma'} (U - 2J - J_\sigma) n_{i\sigma} n_{i\sigma'}.
\]

In this model $c_{i\sigma}^\dagger$ creates an electron with spin $\sigma = \uparrow, \downarrow$ in a Wannier orbital $|m\rangle = |x^2 - y^2\rangle$ or $|3z^2 - r^2\rangle$ at site $i$, and $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$. $\delta_{\sigma,\sigma'}$ indicates the $e_g$ spin parallel (antiparallel) to the $t_{2g}$ spins on the same site. The matrix $u$ accounts for the orientational disorder of the $t_{2g}$ spins, $u_{i\sigma,i'\sigma'} = 2/3$ for $i \neq i'$, $u_{i\sigma,i\sigma'} = \delta_{\sigma,\sigma'}$. The parameter $t_{i,i'}^{\sigma\sigma'}$ is the hopping integral from orbital $m$ on site $i$ to orbital $m'$ on site $i'$. The on-site terms $t_{m,m'} = \delta_{m,m'}$ give the crystal-field splitting. $U$ and $J$ are the direct and exchange terms of the screened on-site Coulomb interaction. The Wannier basis provides us with *ab-initio* values of the hopping integrals and crystal-field splittings. We calculate the average Coulomb interaction\textsuperscript{13,24} $U_{av} - J_{av}$ using the linear-response approach.\textsuperscript{25} We find that $U_{av} - J_{av}$ varies from $\sim 3$ eV in the tetragonal phases.
We have recently shown that the exchange orbital-ordering transition temperature \( T_{KK} \) and spin-flip and pair-hopping terms do not affect the superconducting transition temperature \( T_s \). Thus we use the theoretical estimate for \( T_s \) of 7 eV for LaMnO\(_3\). This approach leads to \( T_s \) being large enough to yield the correct Hund’s rule multiplet structures. We use as impurity solver both the Hirsch-Fye technique \( 27 \) and SGGA+U technique \( 28 \), where SGGA stands for spin-polarized GGA. We perform calculations for different volumes, \( V \) varying from 4 up to 9 eV. Finally, we calculate the magnetic coupling and the magnetic anisotropy by combining many-body perturbation theory \( 29 \) with ab-initio hopping parameters and Coulomb integrals \( 30 \) and direct first principles SGGA+U calculations. 

### III. RESULTS

#### A. Electronic structure

We find that the overall bandwidth of the \( e_g \) and \( t_{2g} \) bands remains about the same in all the structures, \( W_{\text{av}} \approx 1 \text{ eV}, \ W_{\text{av}} \approx 2.3 \text{ eV}, \) perhaps \( W_{\text{av}} \) slightly decreases and \( W_{\text{av}} \) slightly increases reducing the symmetry. The bands themselves are, however, sizably deformed by the distortions, as can be seen in Fig. 2.

We calculate the hopping integrals and crystal-field parameters for the \( e_g \) bands by constructing \( e_g \) Wannier functions by projection. The most important hopping integrals are listed in Tab. I. This table shows that the Jahn-Teller crystal-field splitting progressively increases in the series of phase transitions, while the main hopping integral, the hopping along the \( z \) direction, de-

![FIG. 2. (Color online) Dark lines: GGA band structure for the cubic (C), tetragonal (T) and monoclinic (M) phase. The Fermi level is set at the energy zero. Light lines: \( e_g \)-like bands from maximally-localized Wannier functions plotted on top of the GGA bands. The remaining bands are the Cr \( t_{2g} \) bands, crossing the Fermi level and partially filled, and the empty Cr 4s bands.](image)

| \( \ell m n \) | Cubic \( t_{\ell^m n} \) | Tetragonal \( t_{\ell^m n} \) | Monoclinic \( t_{\ell^m n} \) |
|----------------|----------------|----------------|----------------|
| 100           | -223 124 -80 -171 157 -95 -164 121 83 72 |
| 010           | -223 -124 -80 -171 -109 -95 -163 -87 -167 67 |
| 001           | -9 0 -294 47 -73 292 33 -72 52 -253 |
| \( \varepsilon_{\ell^m n} \) | \( \varepsilon_{211} \) | \( \varepsilon_{111} \) | \( \varepsilon_{212} \) |
| 000           | 0 0 0 0 310 390 0 466 414 |
| \( \lambda_0 \) | 7 15 34 |
| \( \lambda_{\perp} \) | 2 3 4 |

TABLE I. Nearest neighbor hopping integrals \( t_{\ell^m n} \) and crystal-field matrix elements \( \varepsilon_{\ell^m n} \) in the \( e_g \)-like basis, with \( |1\rangle = |x^2 - y^2\rangle \) and \( |2\rangle = |3z^2 - r^2\rangle \). All energies are in meV. For the crystal-field levels we take \( \varepsilon_{111} \) at site 1 as energy zero. The spin-orbit coupling constants \( \lambda_0 \) and \( \lambda_{\perp} \), with \( H_{SO} = \lambda_{0} L_{z} S_{z} + \frac{3}{2} \lambda_{\perp} (L_{+} S_{z} + L_{-} S_{z}) \), are also given. The directions \( (\ell m n) \) are defined \( b = m y + n z \) where \( x, y \) and \( z \) are the pseudo-cubic axes defined in Fig. 1.
creases. Thus, contrarily to naive expectations, the hopping integrals do not increase as the volume shrinks, because the lattice distortions increase as well, leading to a reduction of the matrix elements due to Slater-Koster factors. In the monoclinic case two neighboring Cr sites are inequivalent and have different splitting. We define the lowest energy crystal-field state as $|\theta_{CF}\rangle = \cos \frac{\theta_{CF}}{2}|3z^2 - r^2\rangle + \sin \frac{\theta_{CF}}{2}|x^2 - y^2\rangle$. Our calculations yield $\theta_{CF} = \theta_{CF}^2 \sim 111^\circ = -\theta_{CF}^1$ in the tetragonal phase, where $\theta_{CF}^i$ is the angle for site $i$. In the monoclinic phase we find $\theta_{CF}^i \sim -120^\circ$ and $\theta_{CF}^o \sim 112^\circ$. The sites and the pseudo-cubic axes are defined in Fig. 1.

**B. Kugel-Khomskii super-exchange mechanism**

First we analyze the purely electronic Kugel-Khomskii super-exchange mechanism. We calculate $T_{KK}$, the Kugel-Khomskii critical temperature for the transition cubic to tetragonal, by using the approach of Ref. 6. Starting from the experimental tetragonal structure we progressively reduce the Jahn-Teller and tetragonal crystal-field splitting to zero and perform DFT+DMFT calculations for the corresponding idealized structures, decreasing the temperature to search for the orbital order phase transition. In the zero crystal field limit the transition is due to super-exchange only and occurs at a temperature $T_{KK}^T$. We find that $T_{KK}^T \sim 400$ K, i.e., a value similar to the result we have previously obtained for KCuF$_3$. When we define the DMFT occupied state as $|\theta\rangle = \cos \frac{\theta}{2}|3z^2 - r^2\rangle + \sin \frac{\theta}{2}|x^2 - y^2\rangle$, we find $\theta = -\theta_1 = \theta_2 \sim 90^\circ$, where $\theta_i$ is the angle for a site of type $i$ (see Fig. 1). The transition temperature $T_{KK}^T$ is too small for super-exchange being responsible for the high-temperature cubic to tetragonal cooperative Jahn-Teller distortion above 900 K. Furthermore, the tetragonal crystal-field works against super-exchange, leading to an occupied state with $\theta \sim 180^\circ$ once the tetragonal lattice distortions are taken into account. This is in line with the results for KCuF$_3$ and REMnO$_3$ systems. Nevertheless, $T_{KK}^T$ is sizably higher than the tetragonal to orthorhombic transition temperature, 250 K, and thus well below $T_{KK}^T$ super-exchange could win and even rotate the angle defining the occupied orbital. To verify if this is the case we perform a two-site cluster DFT+DMFT calculations, allowing for inequivalent neighboring Cr sites, i.e., for the lower symmetry of the monoclinic phase. Surprisingly, we find that the orbital-order transition occurs at $T_{KK}^M \sim 400$ K, i.e., at temperatures very similar to the critical temperature $T_{KK}^T$. Furthermore, we find that down to 200 K the two sites have occupied orbitals defined by the angles $\theta = -\theta_1 \sim \theta_2 \sim 90^\circ$. Remarkably, there is no actual difference between the sites, suggesting that super-exchange alone cannot account for the two inequivalent sites in this material. We also find a homogeneous solution in the presence of a tetragonal or a full (tetragonal and Jahn-Teller) crystal field.

![Graph](image-url)

**C. Volume effect**

A very different mechanism to which tilting and rotations in perovskites can be ascribed is the volume reduction with decreasing temperature; perhaps the tetragonal to monoclinic transition and the associated changes in the cooperative Jahn-Teller distortion can be explained by this phenomenon alone, without invoking strong correlation effects. Cation covalency can further help the
stabilization of lower symmetry structures. To clarify whether the 250 K transition is volume- and covalency-driven we compare the total energy of the different structures as a function of the volume. In Fig. 4 we show the total energy curves obtained in GGA and SGGA. The GGA solutions are metallic. Having the largest hopping matrix elements of the three structures, the cubic structure is lowest in energy. The equilibrium volume is quite small as bringing the atoms closer together increases the hopping. Allowing for spin-polarization the situation changes drastically. Exchange effects open a gap and lower all energy curves by about $\sim 2 \text{ eV}$. More importantly, in SGGA the cubic structure is now energetically above the other structures. In the absence of a crystal-field splitting the orbital polarization, and hence the gain in exchange energy, is smaller than in the low-symmetry phases. To confirm this effect, we study the different structures in GGA+$U$, changing the volume by uniformly scaling the unit cell. As shown in Fig. 4 with increasing $U$ the cubic structure becomes less and less favorable, as the orbital polarization of the insulating solution increases. We also observe that the position of the minimum in the energy curves shifts with increasing $U$ to larger volumes. The reason is that for larger $U$ the $d$-electrons tend to spread out to reduce their Hubbard energy. Thus the effective radius of the Cr ion, and therefore also the Cr–F equilibrium distance, increases with $U$. On the other hand, the effective K and F ionic radii, not involving any $d$ electrons, do not change much. Consequently, with increasing $U$ the tolerance factor decreases, favoring the tilting of the octahedra. I.e., with increasing $U$ the monoclinic structure becomes more and more favorable. Overall, for a given volume, the tetragonal and monoclinic structure are very close in energy; in GGA the difference in energy $\Delta E_V = E_M(V) - E_T(V)$ is positive and $\sim 30-40 \text{ meV}$ for volumes $V$ in the region between the GGA minima and the experimental volumes; $\Delta E_V$ becomes even smaller in GGA+$U$.

To clarify this to the super-exchange energy-gain associated with orbital order, $-\Delta E_{KK} \sim k_B T_{KK}/2 \sim 20 \text{ meV}$, with the energy differences between the various structures shown in Fig. 4 calculated in GGA. First we consider the energy difference between the tetragonal/monoclinic structures on the one hand and the cubic structure on the other; $|\Delta E_{KK}|$ is an order of magnitude smaller than this energy difference, which is about (in absolute value) $200-300 \text{ meV}$. Thus $|\Delta E_{KK}|$ alone cannot stabilize the tetragonal/monoclinic with respect to the cubic structure. This energy gain is rather associated with the static crystal field splitting, which is $\sim 840 \text{ meV}$ in the tetragonal case, and the associated gain in exchange energy from orbital polarization. Next, we consider the GGA energy difference between the monoclinic and the tetragonal structure, $\Delta E_V$. We have to compare it with the difference in orbital-order energy gain of the monoclinic structure with respect to the tetragonal structure, $\delta \Delta E_{KK}$. Our results show that $|\delta \Delta E_{KK}|$ is sizably smaller than $|\Delta E_V|$; it even has the wrong sign, i.e., $\delta \Delta E_{KK}$ is positive rather than negative because $T_{KK}^M$ is slightly smaller than $T_{KK}^T$, and therefore would rather stabilize the tetragonal than the monoclinic structure. Thus Fig. 4 makes clear that it is rather the degree of localization and the corresponding change in the equilibrium Cr–F distance which controls the relative stability of the monoclinic and tetragonal structures.

If we also allow for spin-polarization, we obtain the SGGA+$U$ results shown in Fig. 5. Other than in the preceding calculations we do no longer rescale the unit cell, but optimize all cell parameters that, given the space group, can be varied. Consequently, we now find that the structure with the higher symmetry is always above the structure with a lower symmetry. All spin-polarized calculations yield an insulating ground state for all consid-

FIG. 4. Energy per formula unit versus volume from GGA+$U$ for increasing $U$. The energy zero corresponds in each case to the lowest energy point. The labels $V_T$ and $V_M$ indicate the experimental volume in the tetragonal and monoclinic structure. Circles: Monoclinic structure. Triangles: Tetragonal. Squares: Cubic. At $U \sim 9 \text{ eV}$ the monoclinic structure becomes the lowest in energy. The volume is changed by uniformly scaling the unit cells.

FIG. 5. Energy per formula unit versus volume from SGGA+$U$ calculations. The ground state is shifted at zero energy. The SGGA+$U$ calculations are for $U = 6 \text{ eV}$. Circles: Monoclinic structure. Triangles: Tetragonal. Squares: Cubic. The vertical lines indicate the experimental volumes. For each structure all structural parameters are optimized.
to a temperature difference appears to affect hardly this energy balance. Even a difference of the order of 200 K, whereas our results indicate that it is strongly enhanced by the Coulomb repulsion; this can further stabilize the low-symmetry structures with respect the cubic one. The \( e_g \) crystal-field splitting is modified from \( \sim 840 \) meV in the tetragonal structure to \( \sim 950 \) meV (site 1) and \( \sim 680 \) meV (site 2). Our DMFT calculations show that, in the presence of such crystal-field splittings, the occupation at a temperature as high as 550 K is already basically complete for both the tetragonal and for the monoclinic structure, differently than in GGA. Our cluster DMFT results indicate that there is no sizable charge disproportionation, despite the difference in crystal-field splitting between sites of type 1 and 2.

TABLE II. Largest nearest neighbor hopping integrals \( t_{\mu \nu}^{\prime} \), and crystal-field matrix elements \( \varepsilon_{m,m} \) in the \( t_{2g}\)-like basis, with \( |1\rangle = |xy\rangle, |2\rangle = |yz\rangle \) and \( |3\rangle = |xz\rangle \). All energies are in meV. For the crystal-field levels we take \( \varepsilon_{1,1} \) at site 1 as energy zero. The directions \( x = (100), y = (010) \) and \( z = (001) \) are defined in the caption of Fig. 1.

| Imn | Cubic \( t_{11}^{r,r} \) | Cubic \( t_{12}^{r,r} \) | Cubic \( t_{13}^{r,r} \) | Tetragonal \( t_{2}^{r,r} \) | Tetragonal \( t_{3}^{r,r} \) | Monoclinic \( t_{11}^{r,r} \) | Monoclinic \( t_{2}^{r,r} \) | Monoclinic \( t_{3}^{r,r} \) |
|-----|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 100 | -102 | -43 | -113 | 0 | -132 |
| 010 | -102 | -43 | -113 | -75 | -88 | 0 |
| 001 | -43 | -113 | -75 | -88 | 0 |
| 000 | 0 | 0 | 0 | -70 | -96 | -123 | -29 | -3 |

As we have seen, orbital many-body super-exchange appears to affect hardly this energy balance. Even a difference in energy as small as \( 10 \) meV would correspond to a temperature difference \( T_{KK}^{T} - T_{KK}^{M} \approx 2 \delta \Delta_{KK}/k_B \) of the order of 200 K, whereas our results indicate that the super-exchange transition temperature is about the same in the monoclinic and tetragonal phase, and furthermore the incorrect sign \( \delta \Delta_{KK} > 0 \). The difference \( \delta \Delta_{KK} \) could increase if the screened Coulomb repulsion integral \( U \) would be very different for the monoclinic and tetragonal phase. Even if the Coulomb repulsion is slightly different in the two phases, however, it is unlikely that it is reduced by 50\% in the monoclinic phase, as would be required to explain a monoclinic ground state within super-exchange. Furthermore our \textit{ab-initio} estimates of \( U \) indicates that this parameter is slightly larger in the monoclinic than in the tetragonal phase; such a difference would lead again to a positive rather than negative \( \delta \Delta_{KK} \), reinforcing the conclusion that super-exchange alone does not explain the tetragonal to monoclinic transition.

On the other hand, in the presence of static distortions a redistribution of orbital occupations follows, and it is strongly enhanced by the Coulomb repulsion; this can further stabilize the low-symmetry structures with respect the cubic one. The \( e_g \) crystal-field splitting is modified from \( \sim 840 \) meV in the tetragonal structure to \( \sim 950 \) meV (site 1) and \( \sim 680 \) meV (site 2). Our DMFT calculations show that, in the presence of such crystal-field splittings, the occupation at a temperature as high as 550 K is already basically complete for both the tetragonal and for the monoclinic structure, differently than in GGA. Our cluster DMFT results indicate that there is no sizable charge disproportionation, despite the difference in crystal-field splitting between sites of type 1 and 2.

D. Magnetic superexchange

In this last section we analyze the magnetic structure. The aim is to verify if the change in orbital order resulting from our calculations for the experimental structure can explain the observed magnetic order in the monoclinic phase. To do this we calculate the magnetic coupling using super-exchange theory in the basis of the Wannier functions. The magnetic coupling has contributions from both the half-filled \( t_{2g} \) shell and the \( e_g \) shell; in a basis of orthogonal Wannier functions we can split the two contributions so that \( J_{\mu \nu}^{i,i'} = J_{\mu}^{i,i'} + J_{\nu}^{i,i'} \). Then, if we neglect spin-flip and pair-hopping terms we arrive at the approximate expressions

FIG. 6. Super-exchange parameters as function of \( 3J/U \) for \( U = 6 \) eV. Triangles: Tetragonal structure. Circles: Monoclinic structure. Full symbols: coupling along the \( z \) axis. Empty symbols: coupling along \( x \) and \( y \). The directions \( x, y \) and \( z \) are defined in the caption of Table I. The two vertical lines indicate realistic values of the \( 3J/U \) ratio. In this range super-exchange yields an A-type antiferromagnetic structure, in agreement with experiments.
\[ J_{c_g}^{i,i'} = \frac{|t_{a,a}^{i,i'}|^2}{U + 3J + e^c_a - e^c_{a'}} + \frac{|t_{b,b}^{i,i'}|^2}{U + 3J + e^c_b - e^c_{b'}} \]

\[ J_{t_{2g}}^{i,i'} = \frac{2|t_{c,c}^{i,i'}|^2 + |t_{d,d}^{i,i'}|^2 + |t_{e,e}^{i,i'}|^2}{U + 3J}. \]

Here we denote with \(|a\rangle\) and \(|b\rangle\) the \(e_g\) crystal-field states and with \(|c\rangle, |d\rangle, |e\rangle\) the \(t_{2g}\) crystal-field states; We find that \(|e\rangle \sim |xy\rangle, |d\rangle \sim |yz\rangle, |c\rangle \sim |xz\rangle\).

Since for the \(t_{2g}\) states we find that the inter-orbital hopping integrals are very small, for simplicity we set them to zero in the formula above; for the same reason we set to zero the energy difference between crystal-field orbitals at different sites, which is at most 120 meV and leads to small corrections of order \((t^2/U)(\Delta e/U)^2\). The calculated exchange couplings (including also the small contributions neglected in the analytic expression above) are shown in Fig. 4. This figure shows that if the tetragonal structure would persist at low temperature, the magnetic structure would be ferromagnetic and isotropic in the \(xy\) plane, and antiferromagnetic along the \(z\) axis. In the monoclinic structure the coupling in the \(xy\) plane remains ferromagnetic, with the ferromagnetic coupling slightly anisotropic, because the inter-orbital \(t_{2g}\) hoppings are small, hence the antiferromagnetic contribution dominates. Remarkably, ferromagnetism in the \(xy\) plane can then be ascribed to orbital-order in the \(e_g\) states alone. On the other hand the \(t_{2g}\) states are essential for the antiferromagnetic order along \(z\). All this is in excellent agreement with experiment. Thus the orbital-order obtained in our calculation supports the experimentally reported magnetic structure. Finally, by comparing crystal-field energies with and without spin-orbit interaction, we obtain the spin-orbit couplings (Tab. I) and find them small in all systems, but larger in the monoclinic than in the tetragonal or cubic structure. Thus we additionally perform SGGA+U magneto-crystalline anisotropy calculations and find that a spin orientation in the \(xy\) plane is favored, in line with experiments1 our results suggest \(y\) as easy axis, but the energy difference between \(y\) and \(x\) is tiny (0.03 meV).

IV. CONCLUSION

We have studied the origin of orbital-order and structural phase transitions in KCrF\(_3\), a system which is iso-electronic to LaMnO\(_3\). We could reproduce the experimental orbital- and spin-order in all phases. We show that the Kugel-Khomskii super-exchange mechanism is not strong enough to drive the high-temperature cubic to tetragonal transition reported at 973 K. The tetragonal to monoclinic transition is more tricky, because the super-exchange transition temperature is larger than the structural transition temperature. By using the cluster DFT+DMFT approach we show, however, that super-exchange does not support the experimental type of orbital order in the monoclinic phase. Next we analyze the stability of the various phases as a function of volume. We show, by using GGA+U and SGGA+U, that the tetragonal phase is favored at larger volumes and the monoclinic at small volumes, in agreement with experiments. The difference in energy is small, \(\sim 10-20\) meV, again in agreement with experiments. The exact volume of the transition from tetragonal to monoclinic depends on \(U\) and the spin polarization. Increasing \(U\) the transition happens at larger and larger volumes. The change in structure is thus helped more by Slater exchange than by super-exchange; a triggering factor could be a slightly larger direct Coulomb repulsion integral \(U\) in the monoclinic structure. Once the distortions are in place, DMFT calculations show that the orbital polarization is enhanced by Coulomb repulsion, likely providing a positive feedback to the stabilization of the distorted structure.

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Using the local-density approximation (LDA) instead of the GGA does not alter our conclusions.

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