Orthorhombic fulleride (CH$_3$NH$_2$)$_2$K$_3$C$_{60}$ close to Mott-Hubbard instability: *Ab initio* study

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We study the electronic structure and magnetic interactions in methylamine-intercalated orthorhombic alkali-doped fullerene (CH$_3$NH$_2$)$_2$K$_3$C$_{60}$ within the density functional theory. As in the simpler ammonia intercalated compound (NH$_2$)$_2$K$_3$C$_{60}$, the orthorhombic crystal-field anisotropy $\Delta$ lifts the $t_{1u}$ triple degeneracy at the $\Gamma$ point and drives the system deep into the Mott-insulating phase. However, the computed $\Delta$ and conduction electron bandwidth $W$ cannot alone account for the abnormally low experimental Néel temperature, $T_N = 11$ K of the methylamine compound, compared to the much higher value $T_N = 40$ K of the ammonia one. Significant interactions between CH$_3$NH$_2$ and C$_{60}$ are responsible for the stabilization of particular pseudo-Jahn-Teller fullerene cage distortions and the ensuing low-spin $S = 1/2$ state. These interactions also seem to affect the magnetic properties, as interfullerene exchange interactions depend on the relative orientation of pseudo-Jahn-Teller distortions of neighboring C$_{60}$ molecules. For the ferro-orientational order of CH$_3$NH$_2$-K$^+$ groups we find an apparent reduced dimensionality in magnetic exchange interactions, which may explain the suppressed Néel temperature. The disorder in exchange interactions caused by orientational disorder of CH$_3$NH$_2$-K$^+$ groups could further contribute to this suppression.

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I. INTRODUCTION

The alkali-doped cubic fullerenes ($A_{3-x}A'_x$C$_{60}$, $A$, $A'$ = Na, K, Rb, Cs) are prominent members of a rapidly growing family of $\pi$-electron organic superconductors with superconducting transition temperature, $T_c$, as high as 38 K$^{1,2}$ In the early days of fullerene research the observed monotonic increase of $T_c$ as a function of unit cell volume was attributed to the increased density of states at the Fermi level, within a standard Bardeen-Cooper-Schrieffer (BCS) theory.$^3$ Due to the three-fold degeneracy of the $t_{1u}$-derived bands at the $\Gamma$ point, preserved in cubic structures, and to the well-established vibron coupling, the Jahn-Teller (JT) effect is believed to participate actively in the superconducting pairing mechanism.$^4$ However, since the conduction electron’s bandwidth ($W$) and the on-site Coulomb repulsion energy ($U$) are comparable it was also argued that fullerenes must be very close to a Mott-Hubbard transition.$^5$ Phase transitions from a superconducting to a Mott insulating state were indeed demonstrated long ago upon intercalation-induced lattice expansion in compounds such as (NH$_2$)$_2$K$_3$C$_{60}$ where, similarly to Li$_3$(NH$_2$)$_2$C$_{60}$, expansion increases the repulsion/bandwidth ratio $U/W$ raising the importance of correlations. These notions recently received strong support with the discovery of Cs$_3$C$_{60}$, a cubic fulleride with the largest unit cell and low-spin ($S = 1/2$) antiferromagnetic Mott-insulating ground state at ambient pressure conditions$^{2,9,13}$ and where high-temperature superconductivity is revived under hydrostatic pressure with no structural symmetry change. Strikingly, under pressure here $T_c$ displays a dome-like unit-cell volume dependence typical of unconventional superconductors$^{14}$—frankly inexplicable within BCS, Migdal-Eliashberg and related weakly-interacting models. Conversely, precisely such a nonmonotonic behavior of $T_c$ had been predicted by dynamical mean field theory (DMFT) for the unconventional superconducting phase bordering a Mott-insulating state at large unit cell volumes in a simple three-band Hubbard model incorporating, besides a JT electron-vibron coupling, strong on-site electron correlations, caused both by the Coulomb repulsion $U$ and by Hund’s rule exchange, $J_H$.$^{15,16}$ That success not only highlights the unconventional interplay of strong correlations and phonons in these systems: it also brings expanded alkali-doped fullerenes at the forefront of the strongly-correlated electron systems and superconductors, where good understanding of one model system may help shed more light on the entire highly controversal field.

In search for higher transition temperatures, earlier approaches toward expanded unit cells had been by means of co-intercalation of inert ammonia (NH$_3$), e.g. NH$_3$K$_3-x$Rb$_x$C$_{60}$ ($x = 0, 1, 2, 3$)$^{16,17}$ and in Li$_3$$(NH_2)_x$C$_{60}$ or of methylamine (MA) molecules, in (CH$_3$NH$_2$)$_2$K$_3$C$_{60}$ (MAK$_3$C$_{60}$)$^{16}$ These molecules operate as spacers between C$_{60}$ molecules and are believed to have negligible direct influence on the electronically active $t_{1u}$ molecular orbitals of C$_{60}^{-3-}$ anions. However, their presence breaks the original cubic symmetry resulting in orthorhombic crystal structures and effectively lift-
ing the three-fold degeneracy of the $t_{1u}$-derived bands at the $\Gamma$ point. This splitting reduces the critical value for $U/W \geq 0.5$ immediately pushing non-cubic fullerides over the metal-insulator transition (MIT) boundary. We stress that these anisotropic compounds would still be metals, presumably also BCS superconductors, if strong on-site electron correlations were not present. They are thus important model systems for investigations of correlation effects in metals where the splitting of the originally degenerate narrow bands can be tuned through the anisotropy field.

At low temperatures $\text{NH}_3\text{K}_3\text{x-Rb}_x\text{C}_{60}$ compounds order to an antiferromagnetic insulating state with Néel temperature, $T_N$, ranging from 40 K to the maximum of 80 K for $x = 0$ and $x = 2$, respectively. $\text{MAK}_3\text{C}_{60}$, on the other hand, orders to an antiferromagnetic state at remarkably lower $T_N = 11 \text{ K}$. Assuming that the electronic properties depend mainly on the unit-cell volume one would anticipate $T_N$ to be $\sim 80 \text{ K}$, i.e. similar to that of $\text{NH}_3\text{K}_3\text{Rb}_2\text{C}_{60}$. Such profoundly different magnetic response to different co-intercalands is unexpected and implies that in addition to direct interfullerene electronic overlap also other degrees of freedom play a role in non-cubic fullerides. We first note that the $c/a$ lattice parameter ratio is smaller in $\text{MAK}_3\text{C}_{60}$ than in $\text{NH}_3\text{K}_3\text{Rb}_2\text{C}_{60}$ where it is closer to unity. Therefore, the difference between the two orthorhombic compounds may arise from the different orthorhombic anisotropy field, $\Delta$. In other words, properties of $\text{MAK}_3\text{C}_{60}$ and $\text{NH}_3\text{K}_3\text{x-Rb}_x\text{C}_{60}$ compounds are fine-tuned by the closeness to the Mott-Hubbard boundary on the $(U, \Delta)$ Manini-Santoro-Dal Corso-Tosatti (MSDT) phase diagram for fullerides. While it is well established that $\text{NH}_3\text{K}_3\text{C}_{60}$ lays very close to this boundary, the precise position of $\text{MAK}_3\text{C}_{60}$ is yet to be determined.

In cubic fullerides the high crystal symmetry prevents ordering of the $t_{1u}$ molecular orbitals, i.e. it is believed that cubic $A_2\text{C}_{60}$ are in an orbitally liquid state at least above the antiferromagnetic Néel temperature. In the non-cubic fullerides, however, one expects that crystal field will select a particular $\text{C}_{60}$ cage distortion and thus would also affect the inter-fulleride hopping integrals. Since MA molecule is rather large compared to available octahedral space in the fulleride structure a strong interaction - presumably even the formation of a weak hydrogen bond - between MA-K$^+$ group and the nearest $\text{C}_{60}$ was proposed. $\text{MAK}_3\text{C}_{60}$ thus offers a unique opportunity to investigate the role of symmetry breaking on the JT effect in strongly-correlated electron systems. Stimulated by these open issues we decided to carry out a systematic ab initio study of $\text{MAK}_3\text{C}_{60}$ by the density functional theory (DFT) in the local density approximation (LDA), where even if strong correlations are treated only at the mean-field level, the detailed chemical bonding and crystal-field strengths can be assessed. We show that the crystal-field anisotropy of $\text{MAK}_3\text{C}_{60}$ is larger compared to $\text{NH}_3\text{K}_3\text{C}_{60}$, thus placing it deeper in the insulating region of the phase diagram. The whole electron-hopping structure is found to be significantly affected by the MA insertion. We find evidences for the presence of strong $\text{C}_{60}^3$ pseudo-JT effect that may lead to a reduced dimensionality in magnetic exchange interactions and explain suppressed $T_N$.

## II. METHODS

We execute DFT calculations using the Quantum Espresso software package (pwscf program). Ultrasoft pseudo potentials appropriate for the Perdew-Zunger exchange-correlation (LDA) are used. The pseudo Bloch functions are expanded over plane waves with an energy cutoff of 50 Ry on a $5^3$ Monkhorst-Pack $k$-space mesh, such that the total energy is within 250 meV of its converged value, while the conduction bands are within 0.1 meV of their converged value. The Fermi surface is smeared with a “temperature” parameter of 2 meV. The density of states (DOS) is evaluated with the tetrahedron method, sampling $k$-space with a uniform $8^3$ mesh. For the relaxation of the atomic positions, we adopt a damp (quick-min Verlet) procedure on a $2^3 k$-space mesh and plane-waves’ energy cutoff of 30 Ry. The maximally-localized Wannier orbitals are obtained using the Wannier90 package. The three Wannier orbitals are computed in the $t_{1u}$ energy window, using $5^3 k$-points on Monkhorst-Pack grid with Bloch phases as initial projections. All three Wannier orbitals are positioned on the central $\text{C}_{60}$ molecule and have a similar spread of $\sqrt{T} \sim 0.4 \text{ nm}$. The projected DOS (PDOS) on the three Wannier orbitals were evaluated using the Gaussian smearing method with a “temperature” parameter of 8 meV. The use of two different methods for evaluation of DOS and PDOS gives rise to a slight mismatch between the two. The mismatch does not affect the conclusions of this work.

## III. RESULTS AND DISCUSSION

### A. Phase diagram

The $\text{MAK}_3\text{C}_{60}$ compound grows in the face-centered orthorhombic (space group $F\text{mmmm}$) crystal structure with the room-temperature unit-cell parameters: $a = 15.2027 \text{ Å}$, $b = 15.1800 \text{ Å}$ and $c = 13.5032 \text{ Å} (V = 779.057 \text{ Å}^3)$. $\text{MAK}_3^+$ groups situated only in the large octahedral sites were found to be dynamically disordered between eight equivalent orientations at high temperatures. Below the structural phase transition at $T_s = 220 \text{ K}$ $\text{MAK}_3^+$ groups become static and probably ordered in an (anti)ferro-orientational order similar to $\text{NH}_3\text{K}_3\text{C}_{60}$. Since the details of the low temperature structure are not known yet we base all our band-structure calculations on the experimental room-temperature structure. We select a single $\text{MAK}_3^+$ orien-
The three metallic $t_{1u}$ bands are well isolated from the other molecular orbital-derived bands as is the case with every fullerene compound. The band gap between $C_{60}$ HOMO (h$_{u}$-derived bands) and $C_{60}$ LUMO (t$_{1u}$-derived bands) is 0.96 eV, while the separation between $C_{60}$ LUMO and $C_{60}$ LUMO + 1 (t$_{1g}$-derived bands) is 0.59 eV. For comparison, we refer here to the corresponding gaps of 1.16 eV and 0.38 eV computed for cubic K$_3$C$_{60}$ and to the experimental values, roughly 1.8 eV and 1 eV respectively. The underestimation of the band gaps, standard for LDA calculations, is fortunately of little consequence in our case. The neat separation of the different band groups allows us to focus entirely on $t_{1u}$-derived bands close to the Fermi energy (Fig. 1). Not surprisingly, bare DFT-LDA nonmagnetic calculations yield for MAK$_3$C$_{60}$ a metallic ground state with a half-filled $t_{1u}$ band. However, several experiments proved that MAK$_3$C$_{60}$ is an insulator, clearly suggesting that the mean-field DFT metallic state is driven to a Mott-Hubbard insulating state by electron correlations. Since the phase diagram for non-cubic fullerenes has already been calculated within DMFT with included electron correlations, it is sufficient at this stage to continue the characterization of MAK$_3$C$_{60}$ in the non-correlated limit and then treat electron correlations, e.g., within the established MSDT phase diagram.

Orthorhombic crystal symmetry is reflected in the band-structure [Fig. 1(a)] by (i) the removal of the threefold degeneracy at the $\Gamma$ point [Fig. 1(b)]; and (ii) the inequivalence of Y and X points. At the $\Gamma$ point we compute an energy splitting between the first and the second and between the second and the third $t_{1u}$ energy levels of $\delta = 71$ meV and $\Delta = 140$ meV, respectively. For comparison, the corresponding energy splittings for NH$_3$K$_3$C$_{60}$ are $\delta \approx 30$ meV and $\Delta \approx 150$ eV. In general, $\Delta$ reflects the major orthorhombic crystal-field anisotropy and $\delta$ tracks the smaller anisotropy in the $ab$ plane. Surprisingly, band-structure anisotropies of the two systems are very much comparable despite some obvious crystallographic differences, like for instance the ratio c/a, which is 0.89 and 0.91 for MAK$_3$C$_{60}$ and NH$_3$K$_3$C$_{60}$, respectively. In order to position MAK$_3$C$_{60}$ on the MSDT fulleride ($U, \Delta$) phase diagram we need to evaluate $W$, which is deduced directly from the computed band-structure. The resulting total $t_{1u}$ density of states (DOS), roughly shaped in three peaks, and shown in Fig. 1(a) resembles that of NH$_3$K$_3$C$_{60}$. We note that the apparent disagreement between DOS’s width and the band-structure splitting at the X point is due to a small number of states at extreme values and it can thus be seen only in the zoomed view for small DOS values. We obtain a quite large DOS at the Fermi energy, $N(E_F) = 17$ states/eV/C$_{60}$, which is a result of expanded lattice structure and the resulting smaller bandwidth $W = 0.5$ eV. For comparison, we refer here to the $W \approx 0.6$ eV reported for NH$_3$K$_3$C$_{60}$ and K$_3$C$_{60}$, which are characterized by smaller unit cells.

The above results bring forward two interesting aspects of the MA co-intercalation. The first is the position of MAK$_3$C$_{60}$ on the MSDT ($U, \Delta$) phase diagram. Manini et al. used $\Delta/W$ as a measure of the anisotropy, which also defines the distance to the MIT boundary in non-cubic fullerenes. Based on $\Delta/W \approx 0.25$ NH$_3$K$_3$C$_{60}$ is quite close to both 2- and 3-band metallic phases. It is thus expected that under pressure NH$_3$K$_3$C$_{60}$ would almost instantly end up in one of these two metallic states. We find MAK$_3$C$_{60}$ to be slightly more anisotropic, judging from $\Delta/W = 0.29$, thus deeper in the Mott-insulating phase and further away from the 3-band metallic phase.

Application of a hydrostatic pressure, a standard experimental method for increasing $W$ and thus pushing systems across the metal-insulator boundary, has yet to be tried in this system to verify our calculations. However, based on the above observation, we predict that larger pressures will be needed in MAK$_3$C$_{60}$ to access metallic and possibly superconducting states. To estimate the required metal-insulator transition pressure in MAK$_3$C$_{60}$ we compute the bandwidth as a function of decreasing unit-cell volume, mimicking the effect of an external pressure. The pressure dependence of the unit-cell parameters was taken from the high-resolution X-ray data measured under hydrostatic conditions. To prevent unphysical contact between C$_{60}$ and MA groups we carried out a structural optimization for each volume. The bandwidth increases monotonically with decreasing unit-cell volume, or increasing pressure, with the slope of $dW/dP = 100$ meV/GPa (inset Fig. 2).
of pressure could be reduced only to a pressure dependence of $W$, we would predict a steep increase of $T_N$ in the insulating phase as a function of pressure, estimating for instance $T_N(1 \text{ GPa})/T_N(0) \sim (W/W_0)^2 = 1.44$. At higher pressures insulator-metal instability is expected to occur. If we take critical ratio $(U/W)_c = 1.35$ as appropriate for the orthorhombic structure and a typical value for fullerenes $U = 1 \text{ eV}$, we predict that this transition should take place at around $p_{\text{MT}} = 2.3 \text{ GPa}$. Nonlinear effects on compressibility may push this critical pressure slightly higher.

Contrasted with the metal-insulator transition, magnetic ordering cannot be understood purely in terms of overall properties such as the bandwidth or crystal-field anisotropy. In particular, the abnormally small $T_N = 11 \text{ K}$ of MAK$_5$C$_{60}$ as compared with $T_N = 40 \text{ K}$ for NH$_3$K$_2$C$_{60}$ can hardly be justified by the fairly small differences either in the bandwidth or in the orthorhombic anisotropy. Accordingly, the lattice expansion alone cannot explain the small $T_N$: the antiferromagnetic ordering must be controlled by other degrees of freedom such as the interaction between co-intercaland molecules and C$^3$$_{60}$ anions and the related stabilization of a particular JT deformation. We will test this hypothesis in the following sections.

B. The Jahn-Teller effect

Let us focus first on JT effect of C$^3$$_{60}$ anion, which has been predicted but has been experimentally much more elusive in fullerene systems. Orthorhombic crystal structures should provide a fertile ground for JT effect investigations. In order to isolate JT effect we consider an artificial enlarged face centered orthorhombic C$^3$$_{60}$ structure using the room-temperature MAK$_5$C$_{60}$ lattice parameters multiplied by a factor of 1.5. To ensure charge neutrality, we add a uniform positive background in the DFT calculation. This positive background is not contributing to the orthorhombic crystal field, therefore any removal of $t_{1u}$ degeneracy at the $\Gamma$ point should arise solely from the JT effect on top of the weak residual crystal field from the periodically replicated C$^3$$_{60}$ ions. The positions of C$_{60}$ carbon atoms were relaxed in order to obtain molecular distortions. The C$^3$$_{60}$ ion deforms spontaneously into a structure with $D_{2h}$ symmetry [Fig. 3(a)]. This is the expected symmetry for $t_{1u} \otimes H_g$ JT coupling involving $H_g$ vibrational modes. Distortions are small with the maximum value of 2 pm. We estimate the energy scale for deformation by realizing that the relaxed structure has $\Delta E_t = 170 \text{ meV}$ lower total energy than the starting structure with undistorted icosahedral C$_{60}$. Former threefold $t_{1u}$ degeneracy of the LUMO is now removed, with $t_{1u}$ levels split equally by $\sim 50 \text{ meV}$. The lowest $t_{1u}$ orbital is doubly occupied, while the third electron goes into the central $t_{1u}$ orbital, pinned at the Fermi level. The highest $t_{1u}$ orbital is empty. The total energy difference, $\Delta E_t$, has several contributions: the JT effect, the crystal-field effect and bond-length correction due to LDA approximation. To estimate only the JT energy scale we compare the above $\Delta E_t$ with the one obtained for a structural relaxation with equal and fixed occupations of the $t_{1u}$ bands, which effectively hinders the JT effect. The difference in the total energy between these two calculations is 57 meV, a typical value for the JT effect. Proper energy scale, typical size of deformations, the right symmetry of C$^3$$_{60}$ the splitting and occupation of $t_{1u}$ orbitals are strong indications that the observed distortion is indeed a result of the JT effect.

The residual crystal field of C$^3$$_{60}$ ions is immediately seen for smaller lattice parameters, i.e. when room-temperature MAK$_5$C$_{60}$ lattice parameters are for instance multiplied by a smaller factor of 1.25. Using the same procedure as above, the structural relaxation ended up with the same deformation of the C$^3$$_{60}$ molecule. The only difference is that the axis of JT deformation accidentally rotated from the crystal $z$- to $y$-direction. This indicates that we are dealing in both cases with the JT effect and that the change in the JT deformation axis is due to the existence of several equivalent minima of the lowest JT adiabatic potential energy surface (APES). These minima become nearly degenerate for large lattice expansions. On the other hand, when lattice parameters are reduced down toward experimental MAK$_5$C$_{60}$ values the orthorhombic crystal field starts to play a role by making some of the APES minima deeper, thus promoting one specific JT deformation.

Adding potassium atoms to the C$^3$$_{60}$ structure results in an artificial orthorhombic K$_3$C$_{60}$ where even stronger orthorhombic crystal field due to the close contact between the K$^+$ and C$^3$$_{60}$ ions are expected. The structural optimization of the C$_{60}$ carbon positions when starting from the JT distorted C$^3$$_{60}$ atomic positions [Fig. 3(a)] leads...
to deformations of the $C_{60}$ molecule shown in Fig. 3(b). Molecular deformations are slightly different because the crystal field additionally lifts the $t_{1u}$ degeneracy, hence producing pseudo-JT effect. Nevertheless, the resulting symmetry remains $D_{2h}$ and the maximal distortions of 2.3 pm are similar to the previous cases. The same holds for the total-energy lowering, $\Delta E_t = 140$ meV. The JT effect is obviously still dominant over orthorhombic crystal field, which represents a smaller contribution to the total energy. The important message of this part is thus that the energy scale of the JT effect is $E_{JT} \approx 60$ meV and that for the experimental unit-cell volumes a comparably weak crystal field favors a particular $C_{60}$ pseudo-JT deformation.

C. Methylamine - $C_{60}$ interaction

In the MAK$_3$C$_{60}$ structure, methyl protons of the MA-K$^+$ groups approach $C_{60}^{3-}$ anions to very short distances and, based on this observation, suggestions about the weak hydrogen bond were formulated in the literature. Such close contacts are expected to lead to rather strong crystal fields and, according to the above discussion, to also affect strongly the pseudo-JT effect. It is not a priori clear which of the two effects is dominant in this structure. Therefore, $C_{60}^{3-}$ deformations are now investigated in the room-temperature MAK$_3$C$_{60}$ structure where only $C_{60}$ carbon atoms are allowed to relax. As expected, the presence of MA molecules has a dramatic effect on the $C_{60}$ shape [Fig. 4(a)]. The maximal cage distortions are significantly larger than in the previous cases - they reach up to 3.4 pm and the total energy is reduced by $\Delta E_t = 303$ meV during the structural optimization. In addition, even the $D_{2h}$ symmetry of the distorted $C_{60}$ molecule is lost. The maximal distortions are found for carbons facing methyl protons, at a closest-approach distance of 226 pm. Dramatically larger distortions compared to those obtained for $C_{60}^{3-}$ or even for orthorhombic K$_4$C$_{60}$ structure indicate that the additional crystal field produced by MA-K$^+$ groups plays a dominant role over the JT effect in MAK$_3$C$_{60}$.

We also address the possible hydrogen-bond formation
by relaxing all atomic positions, including those of MA-
K$^+$ groups. Hydrogen-bond traces can be detected on
the tiny deformation of MA where C-H bond lengths of
the CH$_3$ group are 110.3 pm, 110.4 pm and 110.6 pm,
the last one corresponding to the hydrogen with the clos-
est contact to the fullerene molecule. However, with the
structural relaxation, the MA-K$^+$ group rotates slightly
away from the fullerene molecule, increasing the nearest
H-C$_60$ distance to 228.5 pm, i.e. by 2.7 pm longer than
in the experimental structure [Fig. 4(b)]. This distance
still remains in the typical hydrogen-bond length range,
but the C$_60$ - methyl proton contact elongation indicates
that such bond must be very weak, if it exists at all.

D. Magnetic interactions

The above analyses point toward pseudo-JT effect and
strong crystal fields in the MAK$_3$C$_{60}$ arising from the
MA-C$_60$ interactions. The remaining question to be ad-
dressed is how these effects influence the low-temperature
magnetic properties. The appropriate starting point is
to construct an effective tight-binding model for the $t_{1u}$
bands and then relate the transfer integrals to the ex-
change coupling constants. To do so, we proceed by
switching to the maximally-localized Wannier orbitals
(WO).

Setting the energy window to the range around
the DFT $t_{1u}$ band (Fig. 1) we obtain three WOs, each
one localized on the same C$_{60}$ molecule. Close to the
fullerene cage, a typical WO (Fig. 5) has the character-
istic look of an appropriate combination of carbon
2$p_z$ orbitals. The orbital of Fig. 5 resembles the DFT elec-
tron density obtained at the $\Gamma$ point. The distribution of
2$p_z$-like orbitals complies with the expected $t_{1u}$ symme-
try. The other WOs (not shown) have a similar shape,
but different orientations. Based on these WOs, we com-
pute their on-site energies and transfer integrals between
eighboring C$_{60}$ from the Kohn-Sham Hamiltonian as

$$t_{\alpha\beta}(\mathbf{R}_i) = \langle w(0, \alpha)|H_{KS}|w(\mathbf{R}_i, \beta)\rangle.$$  

Here $w(\mathbf{R}_i, \alpha)$ is a $\alpha$-th WO and $\mathbf{R}_i$ is a lattice translation
vector. For $\mathbf{R}_i = 0$ Eq. (1) gives the on-site WO energies
and for $\mathbf{R}_i \neq 0$ Eq. (1) yields nine transfer integrals for
each pair of neighboring C$_{60}$ molecules. By diagonaliz-
ing the tight-binding model, we verify that the obtained on-
site energies and transfer integrals reproduce correctly
the DFT electronic band structure as shown by red solid
line in Fig. 1a.

We note that the computed on-site tight-binding
Hamiltonian has non-zero off-diagonal elements, indicat-
ing hybridization within the obtained set of WOs. By
changing basis to an equivalent one where the on-site
Hamiltonian becomes diagonal, we derive a new set of
WOs with well-defined on-site energies. There are two in-
dications that the new set of WOs is appropriate for our
purposes: (i) the new WOs still reproduce band struc-
ture and (ii) in the Mott-insulating limit such WOs are
a good approximation for the localized $t_{1u}$ electronic or-
bitals with well-defined on-site energies, in our case sepa-
rated by 32 and 67 meV.

To estimate the exchange coupling constants we fo-
cus only on the transfer integrals of the second WO, the
half-filled one at intermediate energy. The neglect of the
other (inter-band) hopping elements between neighbor-
ing C$_{60}$ sites amounts to neglecting inter-band transi-
tions. This selection can be justified by noting that (i)
the retained WO is mainly responsible for the DOS at
the Fermi level [see Fig. 1(a)] and (ii) in a picture where
the Coulomb repulsion is the dominating interaction, the
intermediate orbital hosts the unpaired spin in the spin-
1/2 state of each C$_{60}$ molecular unit, with lower fully
occupied and upper empty orbital. Within this approxi-
mation we estimate the interfullerene exchange coupling
constants with Hubbard’s expression $J_{ij} = 4t_{ij}^2/U$, where
we take $U = 1$ eV. For the considered MAK$_3$C$_{60}$ struc-
ture the strongest exchange couplings $J_3 = J_4 = 1.9$ meV
are found for nearest C$_{60}$ neighbors along the (0 1 1) and
(1 0 -1) directions. We stress that these $J’s$ are of the
right order of magnitude as estimated from the measured
Curie-Weiss temperature $\Theta = 86$ K. All other exchange
constants are much weaker, not exceeding 0.12 $\cdot$ $J_3$, see
Table I.

The obtained exchange network indicates a quasi-two-
dimensional magnetic structure of MAK$_3$C$_{60}$. Low di-
imensionality could account for the reduced experimen-
tal Néel temperature. However, although this is cer-
tainly a viable possibility, we stress that this conclusion
is based on the high-temperature crystal structure. Since
we proved that the interaction between MA and C$_{60}$ is
the governing factor for pseudo-JT effect, we stress at this
point that the low-temperature exchange network may in
fact be different. How sensitive interfullerene exchange
interactions are on the precise position of MA-K$^+$ groups
TABLE I. Exchange coupling constants for the experimental room-temperature structure [Fig. 4(a)] and the relaxed structure [Fig. 4(b)]. See text for details.

| Neighbors | J_{Exp. structure} (meV) | J_{Relaxed} (meV) |
|-----------|--------------------------|-------------------|
| 1: (1 1 0) | 0.03                     | 0.06              |
| 2: (1 0 1) | 0.02                     | 0.02              |
| 3: (0 1 1) | 1.94                     | 0.01              |
| 4: (1 0 -1)| 1.89                     | 3.07              |
| 5: (0 1 -1)| 0.00                     | 0.73              |
| 6: (-1 0)  | 0.22                     | 0.72              |

becomes immediately evident when we consider relaxed DFT structure with a slightly rotated MA-K⁺ groups [Fig. 4(b)]. For this structure the strongest exchange is \( J_4 = 3 \text{ meV} \), but now along (1 0 -1). The quasi low-dimensional picture seems to still hold since the next two strongest interactions are much weaker, i.e. \( J_3 = 0.23 \cdot J_4 \) (0 1 -1), and \( J_6 = 0.23 \cdot J_4 (1 -1 0) \). All other exchange interactions are negligible (Table I). We stress that in all these structures the considered MA-K⁺ order is ferro-orientational. Any deviation from this MA-K⁺ configuration, for example antiferro-orientational MA-K⁺ order as the candidate for the low-temperature MAK₃C₆₀ structure, could significantly change the quasi low-dimensional character of our system. Moreover, if a certain degree of disorder in MA-K⁺ orientations is present, then one would anticipate also a distribution of exchange coupling constants, and an even smaller ordered moment. That would explain the static magnetic order with a broad distribution of local magnetic fields also measured in \( \mu \)SR experiment, for instance. We conclude that this pseudo-JT effect should be responsible for the suppression of \( T_N \). Calculations based on the high-temperature structure with imposed ferro-orientational order of MA-K⁺ groups suggest low-dimensionality in magnetic exchange; however other explanations such as a disorder in pseudo-JT cannot be excluded at this stage. Further progress in understanding of magnetic properties of MAK₃C₆₀ would be possible only when the low-temperature crystalline structure of MAK₃C₆₀ is known.

IV. CONCLUSIONS

Antiferromagnetic Mott-Hubbard insulating MAK₃C₆₀ had been studied by means of DFT calculations. We found the pronounced orthorhombic crystal field anisotropy in the electronic structure and judging from \( \Delta / W = 0.29 \) MAK₃C₆₀ should be deep in the insulating part of the phase diagram. Comparisons between different orthorhombic structures demonstrate that the JT effect is present and that its energy is around 60 meV. However, the interaction between cointercalated MA molecules and \( C_{60}^- \) anions is comparatively strong in MAK₃C₆₀, leading to a strong crystal field and pseudo-JT effect stabilized at ~300 meV. The presence of strong pseudo-JT effect should be responsible for the suppression of \( T_N \). Calculations based on the high-temperature structure with imposed ferro-orientational order of MA-K⁺ groups suggest low-dimensionality in magnetic exchange; however other explanations such as a disorder in pseudo-JT cannot be excluded at this stage. A similar interplay of Mott and JT physics is believed to play an important role in the superconductivity of underdoped cuprates. In the present study we emphasize the similar importance of JT effect in strongly correlated \( C_{60}^- \) structures and setting it as one of the most important parameters for the high-temperature superconductivity in fulleride salts.

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