Tuning Crystal Field Potential by Orbital Dilution in Strongly Correlated $d^1$ Oxides

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Abstract We investigate the interplay between Coulomb driven orbital order and octahedral distortions in strongly correlated Mott insulators due to orbital dilution, i.e., doping by metal ions without an orbital degree of freedom. In particular, we focus on layered transition metal oxides and study the effective spin-orbital exchange due to $d^3$ substitution at $d^4$ sites. The structure of the $d^3$–$d^4$ spin-orbital coupling between the impurity and the host in the presence of octahedral rotations favors a distinct type of orbital polarization pointing towards the impurity and outside the impurity–host plane. This yields an effective lattice potential that generally competes with that associated with flat octahedra and, in turn, can drive an inversion of the crystal field interaction.

Keywords Spin-orbital order · Octahedral distortions · Orbital dilution · Doped Mott insulator

1 Introduction

Transition metal oxides (TMOs) are fascinating materials where several quantum degrees of freedom (i.e., spin, orbital, charge, lattice) are intertwined, and require to be treated on equal footing both from a fundamental point of view as well as for developing and enhancing applications in the areas of oxide electronics [1].

The competition of different types of ordered states is ubiquitous in strongly correlated TMOs, mainly arising from the complex nature of the spin-charge-orbital couplings where frustrated Coulomb driven exchange competes with the kinetic energy of charge carriers.

A crucial step for accessing the emergent phenomena of correlated TMOs with spin-orbital charge coupled degrees of freedom is the understanding of the undoped regime [2], where the low-energy physics and spin-orbital order are dictated by effective spin-orbital superexchange [3,4,5,6,7,8,9,10,11,12,13,14]. In undoped 3d Mott insulators, for instance, large local Coulomb interactions localize electrons and the coupling between transition metal ions is controlled by a low-energy spin-orbital superexchange introduced first by Kugel and Khomskii [3]. When multi-orbital degrees of freedom are included, the enhanced quantum fluctuations for $S = 1/2$ compounds can result in destroying the long range order [5]. On the other hand, spin-orbital entanglement in superexchange models may lead to exotic novel types of magnetic order [15], or stabilize topological order in the ground state and in excited states [16].

Long range order in both spin and orbital sector develops in perovskite lattices when spin fluctuations are weaker for spin $S$ larger than 1/2. The fate of spin-orbital order is, however, strongly tied to the character of the orbital degrees of freedom that emerges when
atomic spin-orbit coupling. Taking the example of electrons localize, and on the eventual influence of the elongated octahedron.

\[ |\gamma\rangle = \{a\}, \{b\} \]

The potential to modify the valence of the transition metal elements without destroying the insulating state also allows to achieve non-standard regimes of competition between lattice and spin-orbital degrees of freedom. Indeed, specific for the present study is the physical case of the Mott insulating \( \text{Ca}_2\text{RuO}_4 \) whose substitution of Ru with Mn \( [32] \), Cr \( [33] \), Fe \( [32] \), or Ir \( [34] \) atoms, apart from driving a modification of the spin-orbital order, leads to the observation of negative thermal expansion effects, i.e., the increase of the unit cell volume by thermal cooling. These examples suggest that the negative thermal expansion outcomes are strongly linked to the electronic correlations developing in the doped Mott phase.

Fig. 2 Artist’s view of the evolution of orbital order from (a) the undoped (a,b) plane of \( d^4 \) ions in centers of rotated octahedra (arrows) forming a two-sublattice pattern, (b) the plane with a \( d^3 \) ion in the center, and (c) undistorted (elongated) octahedra at (around) the impurity, respectively, shown by gray (orange) color. The undoped state (a) has a uniform ferro-orbital (FO) order with the doublon occupying the \( |c\rangle \) orbital. Panel (d) shows the possible orbital configurations of the doublon at an undoped \( d^4 \) site, see Fig. 1. Finally, the violet circles stand for oxygen sites in the (a,b) plane.

| TM ion | configuration | Orbital Polarization and octahedral distortions |
|--------|---------------|------------------------------------------------|
| Host   | \( t_{2g}(d^4) \) | Flat octahedron |
|        | \( d_{xy}, d_{yz} \) | | |
| Impurity | \( t_{2g}(d^3) \) | Elongated octahedron |
|        | \( d_{xy} \) | | |

| d\textsuperscript{4} substitution |
|-----------------------------------|
| octahedral configuration around TM |
| Host- undistorted |
| Impurity- undistorted |
| Impurity nearest neighbors- elongated octahedron |

| Orbital polarization at host sites |
|-----------------------------------|
| Violet oxygen site |

\( \text{doping path, indeed, makes possible the design of spin-orbital defects that in turn are expected to cause significant deviations from the standard exchange as related to the Goodenough-Kanamori rules } [23,35,36,37]. \) For instance, focusing on a TMO with \( t_{2g} \) orbital degrees of freedom, one can achieve orbital dilu-
tion by doping with orbitally inactive transition metal magnetic ions \cite{23}. Such doping of \( t_{2g} \) sector can be realized by replacing a \( d^4 \) Ru ion with low \( S = 1 \) spin and effective \( L = 1 \) angular momentum with a \( d^3 \) ion corresponding with a local increase of spin to \( S = \frac{3}{2} \) and removal of the orbital degree of freedom (i.e., \( L = 0 \)), see Figs. 1(a) and 1(e). Alternative substitutional doping by \( d^2 \) ions employs both the orbital and charge degrees of freedom and is called charge dilution \cite{36,37}.

Focusing on \( d^3 \) substitution in \( d^4 \) systems, the impurity-host spin-orbital exchange is strongly dependent on the orbital that is doubly occupied in the \( t_{2g} \) sector. Indeed, the impurity can act as an orbital vacancy for weak host-impurity coupling or favor an orbital polaronic configuration with the doublon sitting in the active orbitals along the 3\( d - 4d \) bond \cite{23}. For an \( (a, b) \) plane, the orbital selection of the doublon configuration couples in a different way to the octahedral distortions corresponding to flat or elongated modes, see Figs. 1(b)–1(d). Thus we explore the interrelation between the orbital order developing around the impurity and the character of the compatible octahedral distortions. We find that the rotation of the octahedra is able to pin uniquely the type of orbital order around the impurity (see Fig. 2). This result indicates a strong bias in the induced octahedral distortions. The main outcomes of the present investigation include:

(i) the determination of the effective \( d^3 - d^4 \) superexchange in the presence of octahedral rotations,

(ii) establishing orbital order around the impurity,

(iii) providing a discussion on the way the orbital order is linked to the flat or elongated distortions of the octahedra in the host.

\section*{2 Spin-orbital superexchange in the host}

First we consider the effective spin-orbital superexchange in the host taking the limit of strong local Coulomb interactions \( U_2 \) at Ru ions in \( 4d^4 \) local configurations, i.e., charge excitations \( d_i^+d_i^- \rightarrow d_i^+d_i^\uparrow \), along each bond \((ij)\) generate effective superexchange \cite{21,22,23},

\[
\mathcal{H}_{\text{d}^3-\text{d}^4} = J_{\text{host}} \sum_{\langle ij \rangle \gamma} \left\{ J_i^{(\gamma)} (S_i \cdot S_j + 1) + K_i^{(\gamma)} \right\}. \tag{2}
\]

Here superexchange \( \propto J_{\text{host}} \) involves spin operators for \( S = 1 \) spins and includes on the orbital operators, \( J_i^{(\gamma)} \) and \( K_i^{(\gamma)} \), which depend on the orbital doublet active along the bond direction \( \gamma \) \((\langle ij \rangle \parallel \gamma)\). The superexchange \( \mathcal{H}_{\text{d}^3-\text{d}^4} \) may be obtained from that for vanadium perovskites with \( V^2 \) ions \cite{38,39} by electron-hole transformation, where an empty site (holon) transforms into a doublon for \( d^4 \) ions. The form of \( \{ J_i^{(\gamma)}, K_i^{(\gamma)} \} \) was given in \cite{38,39,40}; \( J_{\text{host}} \) depends on the hopping \( t \) and on Coulomb \( U_2 \) and Hund’s exchange \( J_{\text{host}}^H \) host parameters, and \( \eta_{\text{host}} \equiv J_{\text{host}}^H/U_2 \). An additional aspect which we neglect here is that spin-orbital entangled variables that drive magnetism in ruthenates are influenced by electron-lattice coupling, for instance via pseudo-Jahn-Teller effect \cite{41}, which focuses on the distortions which split the \( t_{2g} \) orbitals.

We consider here a 2D square lattice with transition metal ions connected via oxygen ions as in an \((a, b)\) RuO\(_2\) plane, see Fig. 2, of Ca\(_2\)RuO\(_4\). In this case \(|a|\) \((|b|)\) orbitals are active along the \( b \) \((a)\) axis, while \(|c|\) orbitals are active along both \( a, b \) axes. Finite crystal field (CF) favors doublons in \(|c|\) orbitals, see Fig. 2(a). Below we investigate the effect of orbital dilution shown in Fig. 2(b).

For the host sites we assume AF spin order replacing spin-spin interactions by the correlation function \( \langle S_iS_j \rangle \approx -5/4 \) (here we neglect spin quantum fluctuations) and add the anisotropic spin-orbit coupling term in a form of,

\[
\mathcal{H}_{\text{so}} = \lambda \sum_i (-1)^i h_z L_i^z,
\]

where \( h_z \) is the local staggered magnetic moment assumed to be along \( z \) axis and the orbital \( L_i^z \) operator has a standard form of \( L_i^z = (i a_i^+ b_i + H.c.) \). Altogether, the total host Hamiltonian reads, \( \mathcal{H}_{\text{host}} = \mathcal{H}_{\text{d}^3-\text{d}^4} + \mathcal{H}_{\text{so}} \).

\section*{3 Hybrid bond: Orbital dilution}

In this section we present the results of the derivation of effective \( 3d^3 - 4d^4 \) spin-orbital superexchange as due to the coupling between orbitals of \( 3d \) and \( 4d \) ions through the oxygen \( 2p \) orbitals which build up the \( p - d \) hybridization \( \propto V_{pd\sigma}^2 \). For our purposes, it is sufficient to analyze a pair of atoms forming a bond \((ij)\), as the effective interactions are generated by charge excitations, \( d_i^+d_j^\uparrow \rightarrow d_i^{(n+1)}d_j^{(n-1)} \) along a single bond \( [8] \). In contrast to the reference \( d^3 \) host where both atoms on the bond \((ij)\) are equivalent, a \( d^3 - d^4 \) hybrid bond has explicitly different ionic configurations. The degenerate Hubbard Hamiltonian \( H(i,j) \) \cite{42} includes in general the standard local Coulomb interaction \( H_{\text{int}}(i) \) and the effective \( d - d \) kinetic term, \( H_i(i,j) \); for a representative \( 3d-2p-4d \) bond after projecting out the oxygen degrees of freedom,

\[
H(i,j) = H_i(i,j) + H_{\text{int}}(i) + H_{\text{int}}(j). \tag{3}
\]

The case without octahedral rotation was investigated in \cite{23}. Here we present the superexchange Hamiltonian for a bond \((12)\) along the \( a \) axis between the \( d^3 \) impurity at site \( i = 1 \) and a host \( d^4 \) ion at site \( j = 2 \), in presence
of octahedral rotation by angle $\phi$,

$$
\mathcal{H}_{d^3-d^1}^{(a)}(\phi) = J_{\text{imp}} (S_1 \cdot S_2) \\
\times \left\{ \alpha_1 + \alpha_2 \left( a_2^2 b_2 + b_2^2 a_2 + \alpha_3 a_2 a_2 + \alpha_4 b_2 b_2 \right) \right\} \\
+ \left\{ \beta_1 + \beta_2 \left( a_2^2 b_2 + b_2^2 a_2 \right) + \beta_3 a_2 a_2 + \beta_4 b_2 b_2 \right\},
$$

(4)

Here the coefficients $\{\alpha_i\}$ and $\{\beta_i\}$ are given by the Slater-Koster rules [43], with the property that $\{\alpha_2, \alpha_4\}$ and $\{\beta_2, \beta_4\}$ vanish for $\phi = 0$, so they are generated by the rotation. At $\phi = 0$, the Hamiltonian tends to project out the inactive orbital $a$ along the bond $\langle ij \rangle \parallel a$ axis. With angle $\phi \neq 0$, also the $c$ orbital is disfavored so that only the $b$ orbital is the preferred one. In this way we obtain polarization of the orbitals $\{a, b\}$ towards the impurity — the orbital polarizer mechanism, see Fig. 2.

The exact form of the coefficients $\{\alpha_i\}$ and $\{\beta_i\}$ as function of rotation angle $\phi$ reads as

$$
\alpha_1 = -\frac{2}{9} \gamma + \frac{1}{6} q_5 + \frac{4\gamma + 3}{18} q_3, \\
\alpha_2 = -\sin(2\phi) \left( -\frac{1}{3} + \frac{1}{12} q_5 + \frac{1}{36} q_3 \right), \\
\alpha_3 = (\sin^2 \phi - \gamma) \left( -\frac{2}{9} + \frac{1}{6} q_5 + \frac{1}{18} q_3 \right), \\
\alpha_4 = (\cos^2 \phi - \gamma) \left( -\frac{2}{9} + \frac{1}{6} q_5 + \frac{1}{18} q_3 \right),
$$

(5)

and

$$
\beta_1 = -\frac{2}{3} \gamma - \frac{1}{4} q_5 - \frac{4\gamma + 3}{12} q_3, \\
\beta_2 = -\sin(2\phi) \left( -\frac{1}{3} + \frac{1}{8} q_5 - \frac{1}{24} q_3 \right), \\
\beta_3 = (\sin^2 \phi - \gamma) \left( \frac{2}{3} + \frac{1}{4} q_5 - \frac{1}{12} q_3 \right), \\
\beta_4 = (\cos^2 \phi - \gamma) \left( \frac{2}{3} + \frac{1}{4} q_5 - \frac{1}{12} q_3 \right),
$$

(6)

with dimensionless parameters,

$$
q_i = \frac{1}{\eta_{\text{imp}}}, \quad \gamma = \left( \frac{t_{c,c}^{(a)}}{V_{pd\pi}} \right)^2, \quad \eta_{\text{imp}} = \frac{J_H^2}{\Delta}.
$$

The $d^3-d^1$ superexchange [4], is given by,

$$
J_{\text{imp}} = \frac{4V_{pd\pi}^4}{\Delta}, \quad \Delta = I_c + 3(U_1 + U_2) - 4(J_1^{HF} - J_2^{HF}),
$$

(8)

and is determined by the effective hopping between two neighboring sites in a two-step process $\propto V_{pd\pi}^2$, involving a charge-transfer excitation energy $\Delta_{\text{CT}}$ along the $d$-$p$-$d$-$\pi$ bond. We introduce for convenience the energy, $V_{pd\pi}^2 \equiv V_{pd\pi}^2/\Delta_{\text{CT}}$; Coulomb and Hund’s exchange parameters are: $\{U_1, J_1^{HF}\}$. The hopping amplitudes are given by the Slater-Koster rules [43].

$$
t_{c,c}^{(a)} = -V_{pd\pi}^2 \cos^2(2\phi)
$$

(9)

The impurity disturbs...
the orbitals at its neighbors and generates the effective change of the CF due to correlations at the host sites $i \in \Omega$. As a result, for small $\Delta_i^c$ the doublons occupy directional orbitals pointing towards the impurity, similar to the orbital polarons in manganites [44,45,46].

To estimate the strength of this inverted CF, we put a finite CF $\Delta_i^f$ at nearest neighbor sites of the impurity and find that for large enough $\Delta_i^f$ the doublon orbital changes from $|a|$ or $|b|$ to $|c\rangle$, i.e., to the one along the bond, see [2(b)]. The change of orbital occupation at sites around the impurity at $\Delta_i^f \simeq 0.12J_{\text{host}}$ is shown in Fig. [1]. Remarkably, the bonds along the $a$ and $b$ axes are equivalent and we observe a change of doublons from directional ($\Delta_i^c \leq 0.12J_{\text{host}}$) to planar ($\Delta_i^c > 0.12J_{\text{host}}$) orbitals. The inversion of CF occurs at the same value of $\Delta_i^f$ for the bonds along the $a$ axis ($i = 1, 9$) and along the $b$ axis ($i = 3, 7$), see Fig. [4].

An abrupt change of the doublon orbital is modified to a smooth crossover at finite temperature $T$, see Fig. [5].

Thermal fluctuations generate a rather broad range of CF splitting $\Delta_i^f$, where $\langle \frac{1}{2} - n_{i}^c \rangle \simeq 0$ and this quantity changes close to the value $\Delta_i^c \simeq 0.14J_{\text{host}}$ found before at $T = 0$, see Fig. [5]. Interestingly, we find that the strength of the effective CF potential induced by exchange interaction is weakly dependent on temperature, so that such electronically driven orbital splitting is remarkably robust against thermal fluctuations.

5 Discussion and Conclusions

We have shown that orbital doping in the presence of octahedral rotations around the $c$ axis tends to favor a distinct type of orbital order, with orbital polarization that is preferentially directional and distributed both towards the impurity and out-of-plane (i.e., with either $xz$ or $yz$ orbital symmetry). Remarkably, as already demonstrated in the tetragonal symmetric octahedra [23], the pinning of the orbital order can occur for both an antiferromagnetic and ferromagnetic exchange between host and dopants. Its manifestation depends either on the amplitude of Hund’s exchange coupling or on the relative strength of the host-host to host-impurity exchange interactions. This means that the local orbital order is a generic sign of the $d^3$ dopant in a distorted host with octahedral rotations and is robust to spin fluctuations.

Another relevant and striking consequence of the specific orbital order induced locally by the $d^3$ dopant is that the orbital pattern around the impurity is uniquely compatible with an elongated octahedral configuration, see Fig. 2. Hence, the impurity-host exchange yields an effective crystal field potential that is akin to that obtained when the lattice favors longer out-of-plane transition metal–oxygen bonds than the in-plane ones. On this basis, there are two possible emergent physical scenarios that can occur: (i) If the lattice potential stabilizes an octahedral configuration that is flat, then, the host-impurity exchange tends to compete with it and, depending on their relative strength, can even end up reversing the sign of the crystal field interaction. This is the case we demonstrate in this paper. Such occurrence clearly implies that the optimal local deformation exhibits an effective enhanced volume of the unit cell due to the bond expansion of the octahedra along the $c$ axis that, in turn, can play a relevant role in setting non-standard negative thermal expansion effects once orbital order is achieved at low temperature.

(ii) On the contrary, for a host configuration with elongated octahedra, the effective host-impurity exchange can enhance the distortions around the impurity thus increasing the stiffness of the lattice. In the present paper, the analysis has been motivated by the study of $d^3$ dopants in $d^4$ Mott insulating host with flat octahedra and antiferromagnetic order as it occurs in Mn-doped $\text{Ca}_2\text{RuO}_4$ compound [32]. Hence, we speculate that the outcome of the induced elongated octahedra by Coulomb driven orbital exchange may be relevant for the anomalous volume expansion occurring below the onset temperatures of magnetic and orbital order [32].
troscopy which is element sensitive and has been successfully demonstrated to unveil the character of the ordered ground state and the corresponding spin-orbital excitations in such transition metal oxides [51,52].

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References

1. Coll, M., Fontcuberta, J., Althammer, M., Bipes, M., Boschker, H., Calleja, A., Cheng, G., Cuoco, M., Dittmann, R., et al.: Towards Oxide Electronics: A Roadmap. Applied Surface Science 482, 1-93 (2019)
2. Komskii, D.I.: Transition Metal Compounds. (Cambridge University Press, Cambridge, 2014)
3. Tokura, Y., Nagaosa, N.: Orbital Physics in Transition-Metal Oxides. Science 288, 462-468 (2000).
4. Kugel, K.I., Khomskii, D.I.: The Jahn-Teller effect and magnetism: Transition metal compounds. Usp. Phys. Nauk 25, 621-664 (1982)
5. Feiner, L.F., Oleś, A.M., Zaanan, J.: Quantum Melting of Magnetic Order due to Orbital Fluctuations. Phys. Rev. Lett. 78, 2799-2802 (1997)
6. Feiner, L.F., Oleś, A.M.: Electronic origin of magnetic and orbital ordering in insulating LaMnO₃. Phys. Rev. B 59, 3295-3298 (2005)
7. Khaliullin, G.: Orbital order and fluctuations in Mott insulators. Prog. Theor. Phys. Suppl. 160, 155-202 (2005)
8. Oleś, A.M., Khaliullin, G., Horsch, P., Feiner, L.F.: Fingerprints of spin-orbital physics in cubic Mott insulators: Magnetic exchange interactions and optical spectral weights. Phys. Rev. B 72, 214431 (2005)
9. Normand, B., Oleś, A.M.: Frustration and entanglement in the t₂g spin-orbital model on a triangular lattice: Valence-bond and generalized liquid states. Phys. Rev. B 78, 094427 (2008)
10. Normand, B.: Multicolored quantum dimer models, resonating valence-bond states, color visons, and the triangular-lattice t₂g spin-orbital system. Phys. Rev. B 83, 064413 (2011)
11. Chaloupka, J., Oleś, A.M.: Spin-orbital resonating valence bond liquid on a triangular lattice: Evidence from finite-cluster diagonalization. Phys. Rev. B 83, 094406 (2011)
12. Corboz, P., Lajkó, M., Laüchli, A.M., Penc, K., Mila, F.: Spin-orbital quantum liquid on the honeycomb lattice. Phys. Rev. X 2, 041013 (2012)
13. Oleś, A.M.: Fingerprints of spin-orbital entanglement in transition metal oxides. J. Phys.: Condens. Matter 24, 313201 (2012)
14. Brzezicki, W.: Spin, orbital and topological order in models of strongly correlated electrons. arXiv:1904.11772 (2019)
15. Brzezicki, W., Dziarmaga, J., Oleś, A.M.: Noncollinear magnetic order stabilized by entangled spin-orbital fluctuations. Phys. Rev. Lett. 109, 237201 (2012)
16. Brzezicki, W., Dziarmaga, J., Oleś, A.M.: Topological Order in an Entangled SU(2)⊗XY Spin-Orbital Ring. Phys. Rev. Lett. 112, 117204 (2014)
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17. Daghofer, M., Oleś, A.M., von der Linden, W.: Orbital Polaron versus Itinerant $e_g$ Electrons in Doped Manganites. Phys. Rev. B 70, 184430 (2004)

18. Kovaleva, N.N., Oleś, A.M., Balbashov, A.M., Maljuk, A., Argyriou, D.N., Khaliullin, G., Krämer, B.: Low-energy Mott-Hubbard excitations in LaMnO$_3$ probed by optical ellipsometry. Phys. Rev. B 81, 235130 (2010)

19. Snamina, M., Oleś, A.M.: Spin-orbital model of stoichiometric LaMnO$_3$ with tetragonal distortions. Phys. Rev. B 97, 104417 (2018)

20. Goodenough, J.B.: Magnetism and the Chemical Bond (Interscience, New York, 1963)

21. Cuoco, M., Forte, F., Noce, C.: Probing spin-orbital-lattice correlations in 4$d$ systems. Phys. Rev. B 73, 094428 (2006)

22. Cuoco, M., Forte, F., Noce, C.: Interplay of Coulomb interactions and $c$-axis octahedra distortions in single-layer rhenates. Phys. Rev. B 74, 195124 (2006)

23. Brzezicki, W., Oleś, A.M., Cuoco, M.: Spin-orbital order modified by orbital dilution in transition-metal oxides: From spin defects to frustrated spins polarizing host orbitals. Phys. Rev. X 5, 011037 (2015)

24. Lee, P.A., Nagaosa, N., Wen, X.G.: Doping a Mott insulator: Physics of high-temperature superconductivity. Rev. Mod. Phys. 78, 17-85 (2006)

25. Dagotto, E., Hotta, T., Moreo, A.: Colossal Magnetoresistance: Neutron scattering study. Phys. Rev. B 127206 (2019)

26. Voit, M.: Lattice symmetry breaking in cuprate superconductors: stripes, nematics, and superconductivity. Adv. Phys. 58, 699-920 (2009)

27. Emery, V.J., Kivelson, S.A., Zachar, O.: Spin-gap proximity effect mechanism of high-temperature superconductivity. Phys. Rev. B 56, 6120-6147 (1997)

28. Wröbel, P., Oleś, A.M.: Ferro-Orbitally Ordered Stripes in Systems with Alternating Orbital Order. Phys. Rev. Lett. 104, 206401 (2010)

29. Cuoco, M., Forte, F., Noce, C.: Origin of the optical gap in half-doped manganites. Phys. Rev. B 98, 094427 (2018)

30. Avella, A., Oleś, A.M., Horsch, P.: Defect-Induced Orbital Polarization and Collapse of Orbital Order in Doped Vanadium Perovskites. Phys. Rev. Lett. 122, 127206 (2019)

31. Horsch, P., Oleś, A.M., Khaliullin, G.: Spin Order due to Orbital Fluctuations and the Exotic Magnetic Properties of YVO$_3$. Phys. Rev. B 75, 184434 (2007)

32. Lee, P.A., Nagaosa, N., Wen, X.G.: Doping a Mott insulator: Physics of high-temperature superconductivity. Rev. Mod. Phys. 78, 17-85 (2006)

33. Slater, J.C., Koster, G.F.: Simplified LCAO Method for the Periodic Potential Problem. Phys. Rev. 94, 1498-1524 (1954)

34. Pan, Z., Chen, J., Yu, R., Patra, L., Ravindran, P., Revcolevschi, A., Büchner, B.: Orbital Polaron Lattice Formation in Lightly Doped La$_{1-x}$Sr$_x$MnO$_3$. Phys. Rev. Lett. 95, 236401 (2005)

35. Okamoto, S., Ishihara, S., Maekawa, S.: Orbital ordering in LaMnO$_3$: Electron-electron and electron-lattice interactions. Phys. Rev. B 65, 144403 (2002)

36. Brzezicki, W., Cuoco, M., Oleś, A.M.: Exotic Spin-Orbital Physics in Hybrid Oxides. J. Supercond. Novel Magn. 30, 129-134 (2017)

37. Brzezicki, W., Cuoco, M., Forte, F., Oleś, A.M.: Topological Phases Emerging from Spin-Orbital Physics. J. Supercond. Novel Magn. 31, 639-645 (2018)

38. Brzezicki, W., Oleś, A.M., Cuoco, M.: Spin-orbital model of stoichiometric LaMnO$_3$ with tetragonal distortions. Phys. Rev. B 97, 104417 (2018)

39. Oleś, A.M., Horsch, P., Khaliullin, G.: Orbital Polaron Lattice Formation in Lightly Doped La$_{1-x}$Sr$_x$MnO$_3$. Phys. Rev. Lett. 95, 236401 (2005)

40. Pan, Z., Chen, J., Yu, R., Patra, L., Ravindran, P., Sanson, A., Milazzo, R., Carnera, A., Hu, L., Yamamoto, H., et al.: Giant Negative Thermal Expansion Induced by the Synergistic Effects of Ferroelectrical and Spin-Crossover in PbTiO$_3$-Based Perovskites. arXiv:1902.04757 (2019)

41. Das, L., Forte, F., Fittipaldi, R., Fatuzzo, C.G., Granata, V., Iavaschi, O., Horio, M., Schindler, F., Dantzig, M., Tseng, Y., et al.: Spin-orbital excitations in Ca$_2$RuO$_4$ revealed by resonant inelastic X-ray scattering. Phys. Rev. X 8, 011048 (2018)

42. Porter, D.G., Granata, V., Forte, F., Di Matteo, S., Cuoco, M., Fittipaldi, F., Vecchione, A., Bombardi, A.: Magnetic anisotropy and orbital ordering in Ca$_2$RuO$_4$. Phys. Rev. B 98, 125142 (2018)