

Charge and Orbital Order in Transition Metal Oxides*

ANDRZEJ M. OLEŚ**

Marian Smoluchowski Institute of Physics, Jagellonian University, Reymonta 4, PL-30-059 Kraków, Poland
and

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

A short introduction to the complex phenomena encountered in transition metal oxides with either charge or orbital or joint charge-and-orbital order, usually accompanied by magnetic order, is presented. It is argued that all the types of above ordered phases in these oxides follow from strong Coulomb interactions as a result of certain compromise between competing instabilities towards various types of magnetic order and optimize the gain of kinetic energy in doped systems. This competition provides a natural explanation of the stripe order observed in doped cuprates, nickelates and manganites. In the undoped correlated insulators with orbital degrees of freedom the orbital order stabilizes particular types of anisotropic magnetic phases, and we contrast the case of decoupled (disentangled) spin and orbital degrees of freedom in the manganites with entangled spin-orbital states which decide about certain rather exotic phenomena observed in the perovskite vanadates at finite temperature. Examples of successful concepts in the theoretical approaches to these complex systems are given and some open problems of current interest are indicated.

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1. Degrees of freedom in transition metal oxides

The physical properties of transition metal oxides are driven by strong electron interactions [1]. It is due to strong local Coulomb interactions that these systems exhibit very interesting and quite diverse instabilities towards ordered magnetic phases when doping x or temperature T is varied — in some cases also with orbital order. These instabilities are observed, *inter alia*, in rapid changes of the transport properties at the metal-insulator phase transitions, or in the onset of superconductivity.

One of the outstanding problems in modern condensed matter theory is the description of strongly correlated electrons in various systems. When local Coulomb interactions are strong, the usual methods used for calculating the electronic structure fail and have to be extended by the terms following from local interactions, either in the framework of the local density approximation (LDA) with Coulomb U , the so-called LDA+ U method [2], or by the self-energy within the dynamical mean-field theory (DMFT) [3], in the LDA + DMFT approach [4]. This latter approach makes use of the local self-energy which becomes exact in the limit of infinite spatial dimension $d = \infty$ [5]. However, even these methods cannot overcome certain shortcomings of the effective one-particle theory which justifies modelling of the transition metal

oxides with Hamiltonians of the Hubbard type, and looking for solutions with methods of quantum many-body theory. The advantage of recent rapid progress in the electronic structure calculations is that such models can use realistic parameters nowadays, which follow from the electronic structure calculations for a given system.

Although the field of strongly correlated electronic systems is very rich, we shall concentrate here on the phenomena observed in transition metal oxides. There are two major classes of systems: either with RMO₃ perovskite structure, or with the layered R₂MO₄ structure, where R stands for a rare-earth ion and M for a transition metal ion. In the latter class the subsequent layers of MO₆ octahedra are displaced, so the electronic properties are well described by two-dimensional (2D) models, see Ref. [1]. In both above structures electron correlations are strong and lead to remarkable consequences, with several degrees of freedom contributing simultaneously to coexisting magnetic, charge and (in some cases also) orbital order. Examples of these complex phenomena are high-temperature superconductivity [6], the colossal magnetoresistance in the manganites [7–9], and the Verwey transition in the magnetite (Fe₃O₄) [10]. Although the charge order occurs typically in doped systems, there are a few systems of formally mixed valence type, where the electron number per one transition metal ion is not an integer but local correlations stabilize charge order, as in the magnetite. The latter problem was recently addressed and the mechanism of the Verwey transition was explained as triggered by the electron-phonon coupling enhanced by local Coulomb correlations [11], so we

* Dedicated to the memory of the late Professor Jan Stankowski.
** e-mail: a.m.oles@fkf.mpg.de

shall not discuss it here but refer an interested reader to another contribution in this issue [12].

The electronic structure of transition metal oxides includes several bands [1, 13], but the properties of the system do depend entirely on the states in the vicinity of the Fermi energy. It is usually sufficient to derive effective M–O–M hopping elements t_σ for σ -bonds and t_π for π -bonds, and next use them in an effective model describing only $3d$ electrons [14]. The respective kinetic energy is described in a perovskite system by

$$H_0 = \sum_{\langle ij \rangle, \alpha\beta\sigma} t_{\sigma, \alpha\beta} a_{i\alpha\sigma}^\dagger a_{j\beta\sigma} + t_\pi \sum_{\langle ij \rangle, \mu\sigma} a_{i\mu\sigma}^\dagger a_{j\mu\sigma}. \quad (1)$$

Here $\{\alpha, \beta\} = \{x, z\}$ are the indices of e_g orbitals,

$$|x\rangle \equiv (x^2 - y^2)/\sqrt{2}, \quad |z\rangle \equiv (3z^2 - r^2)/\sqrt{6}, \quad (2)$$

and this orbital flavor is in general not conserved along the hopping processes — for the basis of Eq. (2) the orbitals may be changed due to $t_{\sigma, xz} \neq 0$ hopping along the bonds in ab planes in the perovskite structure. In contrast, the t_{2g} orbital flavor,

$$|a\rangle \equiv |yz\rangle, \quad |b\rangle \equiv |zx\rangle, \quad |c\rangle \equiv |xy\rangle, \quad (3)$$

is conserved for the hopping along the bonds in all three cubic directions $\gamma = a, b, c$, as indicated by a single diagonal hopping element t_π (for simplicity we assume only nearest neighbor hopping elements), with $\mu = \{a, b, c\}$ labeling t_{2g} orbitals and referring to the cubic axes perpendicular to the planes accommodating the respective orbitals. The latter notation is introduced using an ideal cubic system in which each t_{2g} orbital is perpendicular to a single cubic axis, for instance the $|xy\rangle$ orbital lies in the ab plane and is perpendicular to the c axis.

On-site intraorbital Coulomb interactions are described by a single parameter U (identical for all $3d$ orbitals [15]):

$$H_U = U \sum_{i\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow}. \quad (4)$$

In the simplest approach, the ratio U/W , where W is the bandwidth for the relevant partly filled band, decides whether electrons localize and the electronic structure changes to two Hubbard subbands in a Mott insulator, or the system is metallic, with rather strongly correlated electrons and possibly spin-split heavy effective masses [16] (this happens for the f -electron systems which are addressed in other contributions in this volume). As the hopping elements along π bonds are significantly lower than the ones for σ bonds [14], the t_{2g} electrons in the early transition metal oxides (i.e. in titanium or vanadium oxides) are even stronger correlated than e_g electrons in the RMnO₃ or RNiO₃ perovskites. This resembles the situation in molecular bonds in sp systems, with π bonds being always stronger correlated than σ bonds [17].

A second class of correlated insulators, so-called charge transfer insulators, arises when the oxygen states are within the gap between the two Hubbard subbands [18]. A crucial parameter is the energy difference between the d and p electron (hole) levels, $\Delta = \varepsilon_p - \varepsilon_d$ — here we

use the hole notation which is more convenient for the high- T_c cuprates. When $\Delta > U$ one has a Mott–Hubbard insulator, but when $\Delta < U$, the correlated insulator is of charge transfer type.

The electronic structure of the cuprates does not involve orbital degree of freedom as the CuO₆ octahedra are elongated and the e_g orbital degeneracy is removed by a tetragonal distortion. Therefore, a hole in the d^9 configuration occupies the $|x\rangle \equiv (x^2 - y^2)/\sqrt{2}$ orbital at each Cu²⁺ ion in La₂CuO₄. The resulting charge transfer model for the CuO₂ planes in the cuprates may be thus written as follows [19]:

$$H_{dp} = H_0 + H_{\text{int}}, \quad (5)$$

$$H_0 = \varepsilon_p \sum_i n_{pi} - t_{pd} \sum_{\langle mi \rangle \alpha\sigma} \gamma_{mi} \left(d_{m\alpha\sigma}^\dagger p_{i\alpha\sigma} + \text{H.c.} \right) - t_{pp} \sum_{\langle ij \rangle \alpha\sigma} \eta_{ij} \left(p_{i\alpha\sigma}^\dagger p_{j\alpha\sigma} + \text{H.c.} \right), \quad (6)$$

$$H_{\text{int}} = U_d \sum_m n_{m\uparrow} n_{m\downarrow} + U_p \sum_i n_{pi\uparrow} n_{pi\downarrow}. \quad (7)$$

The parameters of the charge transfer model (5) are: the oxygen hole energy ε_p (we assume that the reference copper hole energy $\varepsilon_d = 0$), the $d - p$ hybridization t_{pd} , and the Coulomb interaction parameters for d and p orbitals, U_d and U_p ; the same parameters describe also other Cu–O systems, as for instance CuO₃ chains in YBa₂Cu₃O_{6+x} [20], or Cu₂O₅ coupled ladders in Sr_{14-x}Ca_xCu₂₄O₄₁ compounds [21]. Here $n_{pi} = n_{pi\uparrow} + n_{pi\downarrow}$ and $n_{pi\sigma} = p_{i\sigma}^\dagger p_{i\sigma}$ are charge density operators, γ_{mi} and η_{ij} are the phase factor for a pair of orbitals along the considered $d - p$ ($p - p$) bond. The parameters for the cuprates which follow from the electronic structure calculations are (all in eV) [22]: $\Delta = 3.6$, $t_{pd} = 1.3$, $t_{pp} = 0.65$, $U_d \approx 10.5$, $U_p \approx 4.0$. Electron correlations are moderate in spite of the large value of U_d [19], but they suffice to localize holes at Cu sites in the undoped system, such as La₂CuO₄ or YBa₂Cu₃O₆. Taking the above parameters, $\Delta \ll U_d$ and these systems are charge transfer insulators, in contrast to the perovskite titanates and vanadates, which are the Mott–Hubbard systems [1].

It is important to realize that the charge transfer gap Δ plays the role of an effective Coulomb parameter $U \equiv \Delta$ in the correlated electronic structure of a charge transfer insulator. When the Cu–O–Cu hopping between two $|x\rangle$ orbitals along a bond in an ab plane is defined as $t \equiv 3t_\sigma/4$ — this leads to the effective Hubbard model [23],

$$H = -t \sum_{\langle ij \rangle, \sigma} (a_{i\sigma}^\dagger a_{j\sigma} + a_{j\sigma}^\dagger a_{i\sigma}) + U \sum_{i\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow}. \quad (8)$$

For the considered case of $|x\rangle$ orbitals the phase factors on each bond $\langle ij \rangle$ are identical. Let us note that t may be deduced from the charge transfer model (5), $t = t_{pd}^2/\Delta = 0.4$ eV, and for the actual ratio $U/t = 10$ the holes are strongly correlated. Hence, the undoped systems La₂CuO₄ or YBa₂Cu₃O₆ are antiferromagnetic (AF) insulators. In general, the derivation of an effec-

tive model from the relevant multiband model is rather tedious — a more complete model includes in addition to Eqs. (5)–(7) next nearest (second) neighbor and third nearest neighbor hopping elements $\{t', t''\}$ and intersite Coulomb interactions [24].

A broad class of phenomena investigated for strongly correlated electron systems are the changes of their physical properties in the vicinity of metal–insulator transitions. As mentioned above, one way of localizing electrons in a correlated insulator is by changing the electron interaction parameter U in Eq. (8) (or the charge transfer gap Δ). Although this may be easily realized only in theory, in certain systems the changes of the electronic parameters are sufficient to induce metal–insulator transitions observed in V_2O_3 [25]. A more common situation, however, is encountered in doped systems, where the carriers are released at certain doping concentration and the system becomes metallic. In contrast to the earlier suggestions, the one-band model is not sufficient to describe the metal–insulator transition in V_2O_3 [26], and doping is not equivalent to varying external pressure [27]. This and other metal–insulator transitions in the oxides are controlled by doping. A very well known example is the colossal magnetoresistance effect in the perovskite manganites [7], another is the superconductivity in doped $La_{2-x}Sr_xCuO_4$ or $YBa_2Cu_3O_{6+x}$ compounds [6]. Other examples can be found, for instance, in the excellent review article by Imada et al. [1].

In this paper we address in particular the phenomena related to magnetic and orbital order in undoped transition metal oxides which follow from strong electron correlations. Charge order arises in doped systems, while the orbital order is common in transition metal oxides with partly filled degenerate orbitals. We begin in Sect. 2 with the stripe phases in the cuprates, where we explain the stabilizing mechanism and show that the charge modulation is the way to optimize total energy in doped systems. While the properties of an undoped cuprate are driven by the AF superexchange, the description of systems with orbital superexchange interactions is more complex as the interactions are intrinsically frustrated [28]. These interactions are exemplified by the so-called compass model [29], see Sect. 3, and may give either highly degenerate ordered ground states, or the disordered orbital liquid. Consequences of the orbital superexchange for the magnetic order are addressed in Sect. 4, where we briefly summarize the structure of the spin-orbital superexchange [30], and demonstrate that spin and orbital degrees of freedom may be separated in the perovskite manganites. In contrast, in the perovskite vanadates spin-orbital entanglement plays a dominating role and decides about their properties at finite temperature, see Sect. 5. Finally, we give examples of coexisting charge-and-orbital order in doped systems in Sect. 6. A summary and some open problems in the field are given in Sect. 7. Figures illustrating the theoretical concepts reviewed in this article will not be reproduced here — they may be found in the cited literature which is far

from being complete and was selected on the criterion of addressing the most important concepts in this field.

2. Stripe phases in the cuprates

A crucial concept in the physics of the superconducting cuprates is the Zhang–Rice singlet [31]. It makes an explicit use of the charge transfer nature of the electronic structure, as a doped hole occupies not one of $Cu(d_x)$ orbitals but a linear combination of p_σ orbitals with $x^2 - y^2$ symmetry around a given Cu^{2+} ion, and forms a singlet together with the hole at that ion. It is this concept which provides a justification for using the t – J model as the effective model describing the physical situation in the cuprates, and plays a prominent role in this class of compounds [32].

The t – J model itself was derived from the Hubbard model in Cracow more than three decades ago [33], using the perturbation theory. A properly chosen canonical transformation leads from the full Hilbert space to an effective low-energy Hamiltonian acting in the restricted space, where only spins and holes occur at different sites. It consists of the kinetic energy $\propto t$ and the superexchange interaction $\propto J$ between $S = 1/2$ spins

$$H_{t-J} = -t \sum_{\langle ij \rangle, \sigma} (\tilde{a}_{i\sigma}^\dagger \tilde{a}_{j\sigma} + \tilde{a}_{j\sigma}^\dagger \tilde{a}_{i\sigma}) + J \sum_{\langle ij \rangle} \left(\mathbf{S}_i \cdot \mathbf{S}_j + \frac{1}{4} \tilde{n}_i \tilde{n}_j \right), \quad (9)$$

with the superexchange interaction,

$$J = \frac{4t^2}{U}. \quad (10)$$

The operators $\tilde{a}_{i\sigma}^\dagger \equiv a_{i\sigma}^\dagger (1 - n_{i\bar{\sigma}})$ ($\bar{\sigma} = -\sigma$) and $\tilde{n}_i = \sum_\sigma \tilde{a}_{i\sigma}^\dagger \tilde{a}_{i\sigma}$ are projected fermion operators and act in the restricted space with no doubly occupied sites. The above t – J model may also be derived directly from the charge transfer model — in this case (realistic for the cuprates) the superexchange includes both the Anderson and charge transfer excitations [34]. For the cuprates one finds $J \approx 0.13$ eV, which is either deduced from the magnetic experiments [35], or derived from the charge transfer model [24] using its parameters [22].

The first intriguing question concerning hole doping is whether a doped hole may propagate coherently in the antiferromagnet. Naively one might argue that a hole creates defects on its way, so it would need to make a hopping along a closed loop to annihilate these defects and to move in the square lattice with a minute dispersion [36]. Actually, this is the only process by which a hole may delocalize in the Ising model. The situation is quite different, however, when a hole is doped into a Heisenberg antiferromagnet — in this case the quantum fluctuations of the AF background may repair the defects created by the hole, and the hole dispersion occurs on the energy scale of J [37, 38]. This concept was confirmed by experiment, and indeed the hole dispersion on the low energy scale of J was observed in the

cuprates [39]. Detailed comparison between the experimental data of angle resolved photoemission (ARPES) experiments and the outcome of the theoretical calculations performed using the self-consistent Born approximation (SCBA) [38] were presented by several groups. Here we mention only the experimental data of high quality obtained for $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ by Wells et al. [40], which fit very well to the theoretical curves obtained with finite next neighbor hopping t' [41]. This demonstrates that the right effective model for the high- T_c cuprates is the t - t' - J model rather than the t - J one.

Higher doping of CuO_2 planes leads to a gradual weakening of AF correlations, which however survive even in the overdoped regime at $x \approx 0.2$ [35]. There are several possibilities concerning the phase diagram of doped cuprates [9], but the commonly accepted point of view now is that doped holes self-organize in form of phases with charge modulation [42]. Such structures with coexisting charge and magnetic order, called *stripe phases*, were first discovered in the theory as an instability of doped antiferromagnets towards AF domains separated by (usually) nonmagnetic domain walls [43]. Only a few years later their existence in the doped cuprates was confirmed in the neutron experiments of Tranquada et al. [44]. The stripe phases are characterized by the coexisting charge and magnetic order, with the charge density varying twice faster than the spin density in the real space [45].

The first question concerning stripe phases is whether they would form as solitonic defects in the AF structure, i.e. in between different AF domains, or instead they are of polaronic nature not disturbing the AF order. Although naively one could argue that the polaronic mechanism could give a better kinetic energy, this argument is misleading. To see this, one can consider a cluster of three sites centered at the domain wall, filled by two electrons [45]. Due to strong correlations with $U \gg t$, the particles are confined in this cluster, although it is just a part of the AF 2D plane. Taking two electrons with either identical spins or with opposite spins, it is straightforward to estimate the ground state energy of two possible configurations: (i) polaronic (E_P) and (ii) solitonic (E_S) one. One finds that the solitonic energy is lower by the superexchange energy J which arises from the three-site hopping terms in this cluster [45], with: $E_P = -\sqrt{2}t$ and $E_S = -\sqrt{2}t - 4t^2/U$. This simple argument explains the experimental finding that charge walls separate AF domains with different phase of the order parameter.

Quantitative results for the stripe phases were first obtained using the Hartree-Fock (HF) approximation [43, 46], and then refined using variational wave functions [47], within DMFT for the stripe phases [48, 49], and slave-boson approach [50]. As usually, the HF serves only as a hint for possible instabilities, and gives remarkably robust stripe structures [46] with rather large amplitude of the charge density between the domain wall and the centers of AF domains, and the filling of half of

doped hole per one stripe charge unit cell, as observed in experiment. These stripes are vertical (or horizontal), meaning that domain walls are along (10) [or (01)] direction, and insulating. Actually, their stability follows from a small gap which opens in the electronic structure. This mechanism is subtle and involves certain additional modulation, either spin or charge density wave, along the domain walls [46], so one has to expect major changes when electron correlations are implemented. However, variational calculations confirmed this quantitative picture to some extent [47], although the question whether the stripes are insulating or not could not be resolved (in fact, following the HF results, it was believed for a long time that the stripes are insulating).

Stable stripes were also found using an exact diagonalization method within the DMFT for the 2D Hubbard model, in the broad doping range $0.03 < x < 0.2$ in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [48]. These calculations allowed also to reproduce the observed crossover from diagonal (11) to vertical (01) site-centered stripes at doping $x \approx 0.05$ [51]. In addition, also the doping dependence of the size of magnetic domains and chemical potential shift $\Delta\mu \propto -x^2$ were found to be in quantitative agreement with the experimental results for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. In this way the paradigm of insulating stripe phases was abolished — the chemical potential was varying with doping within the metallic phase.

The spectral functions obtained within the DMFT [49] show a coexistence of the incoherent states in the lower Hubbard band and a coherent quasiparticle (QP) close to the Fermi energy. The main features of the spectra are: a flat part of the QP band near the $X = (\pi, 0)$ point, and gaps for charge excitations at the $Y = (0, \pi)$ and $S = (\pi/2, \pi/2)$ points in the low-doping regime $x < 1/8$. These gaps are gradually filled up and eventually close under increasing doping, in agreement with the experimental data for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ obtained using angle resolved photoemission [52]. In the range of low temperatures T the obtained spectra have a distinct QP peak at the $X = (\pi, 0)$ point, present just below the Fermi energy μ , and a charge gap and well defined QP at the $S = (\pi/2, \pi/2)$ point [49]. These calculations demonstrated the importance of dynamical correlations which strongly screen the local potentials resulting from on-site Coulomb interactions and lead thus to drastic changes in the distribution of spectral weight with respect to the HF picture. It was also shown that the melting of stripe order is influenced by the next nearest neighbor hopping element t' , which plays also an important role in explaining the observed difference in the spectral properties between $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ [53] and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [52]. At the same time, t' can tip the energy balance between the filled diagonal and half-filled vertical stripes [50], which might explain a change in the spatial orientation of stripes observed in the high T_c cuprates at the doping $x \approx 1/16$.

More insight into the charge and magnetization distribution as well as into the stability of stripe phases could be obtained using a rotationally invariant version of the

slave-boson approach in spin space in the 2D Hubbard model [50]. This approach allowed one to treat strong electron correlations in the stripe phases with large unit cells relevant in the low doping regime, and gave results representative of the thermodynamic limit. It also helped to resolve the longstanding controversy concerning the role played by the kinetic energy in stripe phases. While the transverse hopping across the domain walls yields the largest kinetic energy gain in the case of the insulating stripes with one hole per site, the holes propagating *along* the domain walls stabilize the metallic vertical (01) stripes with one hole per two sites, as found in the cuprates.

Recently observed pattern of unidirectional domains in high- T_c superconductors [54] motivated also search for coexisting charge modulation and d -wave superconductivity. Indeed, half-filled charge domains separated by four lattice spacings were obtained along one of the crystal axes leading to modulated superconductivity with *out-of-phase* d -wave order parameters in neighboring domains [55]. Both renormalized mean-field (MF) theory and variational Monte Carlo calculations yield that the energies of modulated and uniform phases are very close to each other, so modulated phases could easily be stabilized by other effects going beyond the t - J model used in these calculations. Novel doped phases with superconductivity coexisting with charge modulation or even the valence-bond solid order were also reported recently [56].

3. Intrinsic frustration of the orbital superexchange

In the undoped transition metal oxides, however, the physics is frequently not as simple as in CuO_2 planes of high- T_c superconductors, where the superexchange stabilizes the AF long-range order. This happens in particular when the orbital degrees of freedom are active (when degenerate orbitals are only partly filled) and contribute to the magnetic order [57, 58]. The central property of the orbital degrees of freedom is that they are intrinsically frustrated [28, 59], so they may lead to novel (ordered or disordered) phases.

Frustration in magnetic systems may be of geometrical origin if only nearest neighbor interactions are present, or may arise due to competing exchange interactions [60, 61]. For instance, when one considers ferromagnetic (FM) interactions along every second vertical line in the square lattice while all other interactions are AF — then this 2D Ising model is exactly solvable and has a lower critical temperature [62] than the one with isotropic exchange interactions. Frustration for quantum spins acts to enhance the effects of quantum fluctuations, leading to a number of different types of magnetically disordered states, among which some of the more familiar ones are static and resonating valence-bond (VB) phases [61]. However, also ordered phases may emerge in systems with frustrated spin interactions from their disordered manifolds of states, and their mechanism of

stability is nowadays called “order-by-disorder” [60]. Numerous materials are known at present whose physical properties could be understood only by employing microscopic models with frustrated spin interactions in which some of these theoretical concepts are exemplified.

A prototype model to study frustration in pseudospin systems which mimic the directional orbital superexchange [63] is the 2D compass model [29]:

$$\mathcal{H}_{2D} = \sum_{\langle ij \rangle \parallel a} J_x \tau_i^x \tau_j^x + \sum_{\langle ij \rangle \parallel b} J_z \tau_i^z \tau_j^z. \quad (11)$$

In this model the $\tau_i^x \tau_j^x$ interactions $\propto J_x$ for horizontal bonds $\langle ij \rangle$ (along the a axis) compete with the $\tau_i^z \tau_j^z$ ones $\propto J_z$ in the vertical direction (along the b axis). Recently, the structure of eigenstates in this model was investigated by numerical methods [64], and it was shown using quantum Monte Carlo that a phase transition at finite temperature exists in the 2D compass model [65], suggesting that this model is indeed in the 2D Ising universality class. A competition of pseudospin interactions along different directions results here in intersite correlations similar to the anisotropic XY model, and in competition between two types of Ising-like order. This competition culminates in the highly degenerate ground state at the compass point [64] (i.e., when all interactions have the same strength), and generates there a first order phase transition when the anisotropic model with $J_z > J_x$ changes into $J_z < J_x$ through the $J_z = J_x$ transition point [66]. More insights on the nature of the ground state and the phase transition from the Ising-like 2D ground state to the symmetry-broken state at the compass point has been given by two powerful methods recently: (i) the multiscale entanglement renormalization ansatz (MERA), and (ii) the sixth order boson expansion in the spin-wave theory [67].

It is interesting to note that a similar first order quantum phase transition occurs also in the one-dimensional (1D) compass model [68], when both above interactions alternate along the chain ($N' = N/2$ is the number of unit cells)

$$\mathcal{H}_{1D} = \sum_{i=1}^{N'} (J_x \tau_{2i-1}^x \tau_{2i}^x + J_z \tau_{2i}^z \tau_{2i+1}^z). \quad (12)$$

This model was solved exactly in the entire range of $\{J_x, J_z\}$ parameters [68] by mapping onto the exactly solvable quantum Ising model [69] in different subspaces. Equal coupling constants $J_x = J_z = J$ correspond here to the quantum critical point, where the two different types of Ising-like order compete with each other, and the first order transition takes place between them. A similar transition was shown as well by an exact solution of the compass ladder [70].

The compass model is currently under discussion also due to its interdisciplinary character. It can be derived using the symmetry arguments which are necessary for the realization of doubly degenerate states which are protected from external perturbations in a wide class of Hamiltonians [71]. The Hamiltonian with this symme-

try can be physically implemented in the Josephson junctions, and it was argued that these junctions provide fault tolerant quantum bits. Recently magnetic interactions in the Mott insulators with strong spin-orbit coupling were also discussed and it was pointed out [72] that they may provide a realization of the exactly solvable Kitaev model on the honeycomb lattice, which is relevant for quantum computation [73].

4. Spin-orbital superexchange

In several transition metal oxides with active degrees of freedom one finds coexisting magnetic and orbital order, both in the Mott and in charge transfer insulators. Experimental observations give frequently some unexpected properties and the question arises how to explain particular types of observed coexisting spin-and-orbital order. First of all, magnetic interactions in these systems frequently break the cubic symmetry of the perovskite lattice and AF phases with FM interactions along certain directions arise (in contrast to the G -AF phase with isotropic AF interactions). Two of them are quite common: (i) the C -AF phase with FM interactions along the c axis as in LaVO_3 , and (ii) the A -AF phase with FM interactions within the ab planes as in LaMnO_3 [59]. These phases follow from the microscopic models (see below) which justify the complementary behavior of the observed (orbital and magnetic) order postulated by Goodenough for the manganites [74]: alternating orbital (AO) order supports FM spin order, while ferro-orbital (FO) order supports AF spin order. The structure of spin-orbital superexchange described below allows one to understand better the physical mechanism beyond this complementarity, known since long as the Goodenough-Kanamori rules [75].

Realistic superexchange models for transition metal oxides with orbital degrees of freedom contain both spin and orbital operators. They may be derived by considering intersite charge excitations in a Mott insulator employing perturbation theory in a way similar to the derivation of the t - J model from the Hubbard model (and applied to the cuprates), as described in Sect. 2. This task is somewhat involved, so usually one considers an effective model with hopping elements between d orbitals of transition metal ions derived from electronic transitions over the intermediate oxygen orbitals [14], as in Eq. (1). The energy scale for the hopping is set by the largest hopping element t : the $(dd\sigma)$ element in case of e_g systems, and the $(dd\pi)$ element when only π electrons contribute in systems with degenerate and partly filled t_{2g} orbitals. For noninteracting electrons the Hamiltonian H_0 (with crystal-field terms) would lead to tight-binding bands, but in a Mott insulator one is in the regime of large Coulomb interaction $U \gg t$, so charge fluctuations are suppressed and the hopping elements can only contribute via virtual excitations, leading to the superexchange as described below.

The derivation of the superexchange involves virtual charge excitations $d_i^m d_j^m \rightleftharpoons d_i^{m+1} d_j^{m-1}$ between two

neighboring transition metal ions in $3d^m$ configuration each, which have to be included with the correct excitation energies following from the structure of local Coulomb interactions in degenerate d states (a similar expression can also be written for f electrons). These interactions are well known since long [76], but nevertheless simplified expressions can be still found in the literature which in some cases lead to misleading or even qualitatively incorrect conclusions. When only one symmetry class of electrons is involved in charge excitations, e.g. either e_g or t_{2g} electrons in a perovskite system, the interactions read:

$$\begin{aligned} H_{\text{int}} = & U \sum_{i\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + \left(U' - \frac{1}{2} J_{\text{H}} \right) \sum_{i,\alpha<\beta} n_{i\alpha} n_{i\beta} \\ & + J_{\text{H}} \sum_{i,\alpha<\beta} \left(d_{i\alpha\uparrow}^\dagger d_{i\alpha\downarrow}^\dagger d_{i\beta\downarrow} d_{i\beta\uparrow} + d_{i\beta\uparrow}^\dagger d_{i\beta\downarrow}^\dagger d_{i\alpha\downarrow} d_{i\alpha\uparrow} \right) \\ & - 2J_{\text{H}} \sum_{i,\alpha<\beta} \mathbf{S}_{i\alpha} \cdot \mathbf{S}_{i\beta}, \end{aligned} \quad (13)$$

where [76],

$$U' = U - 2J_{\text{H}}. \quad (14)$$

The parameters $\{U, J_{\text{H}}\}$ determine the excitation energies by the corresponding eigenenergies of the local electron-electron Coulomb interaction Hamiltonian (13). The eigenstates have to be derived for each particular situation separately. For instance, if two-hole d^8 excited states are considered in the $d_i^9 d_j^9 \rightleftharpoons d_i^8 d_j^{10}$ transitions for KCuF_3 cuprate, there are triplet ($S = 1$) and singlet ($S = 0$) states when two holes in the d^8 configuration occupy different orbitals, with the energies $(U - 3J_{\text{H}})$ and $(U - J_{\text{H}})$, as well as two other (intraorbital) singlet states with the energies $(U - J_{\text{H}})$ and $(U + J_{\text{H}})$ [77]. Let us note that a double occupancy of either e_g orbital (with energy U), considered in the context of the intraorbital Coulomb interaction (15) is *not* an eigenstate of the local Hamiltonian (13).

In a general case the interorbital interactions are identical for all $3d$ orbitals,

$$U = A + 4B + 3C, \quad (15)$$

where $\{A, B, C\}$ are the Racah parameters [15]. In contrast to the intraorbital ones (15), the interorbital interactions are anisotropic — Coulomb $U_{\alpha\beta}$ and exchange $J_{\alpha\beta}$ elements replace then U' and J_{H} in Eq. (13), and satisfy a constraint similar to Eq. (14) which guarantees the invariance of interactions in the orbital space [78],

$$U = U_{\alpha\beta} + 2J_{\alpha\beta}, \quad (16)$$

for each pair of interacting orbitals $\{\alpha\beta\}$. Additional symmetries follow for each e_g and t_{2g} representation separately, and Hund's exchange depends on the orbital states of the pair of interacting electrons. For a pair of e_g electrons this interaction is somewhat stronger,

$$J_{\text{H}}^e = 4B + C, \quad (17)$$

than the one between two t_{2g} electrons,

$$J_{\text{H}}^t = 3B + C. \quad (18)$$

Thus the parameter J_{H} used in Eq. (13) and below refers

to the above values and depends on whether a system with e_g or t_{2g} orbital degrees of freedom is considered. More details about the structure of local Coulomb interactions which finally depends on a single parameter,

$$\eta = \frac{J_H}{U}, \quad (19)$$

may be found in Ref. [78].

While the experimental values of the Racah parameters $\{B, C\}$ are known with rather high accuracy from the atomic spectra given in Ref. [79] for several transition metal ions, the values of U (or A) are known in general only with much lower accuracy. Unfortunately, the mechanism of screening which leads to the values of $U \approx 5\text{--}10$ eV, reduced from the respective atomic values, is difficult to implement in the theory. Hence, the value of U is frequently used as a parameter, unless it can be derived from the experimental data, as for instance from the optical excitations, see below.

The above structure of the electron–electron interactions (13) determines the excitation energies ε_n due to charge transitions $d_i^m d_j^m \rightleftharpoons d_i^{m+1} d_j^{m-1}$, which enter the superexchange in the respective denominators of various contributions $\propto 4t^2/\varepsilon_n$. Examples of such spectra are presented in Ref. [30]. As a rule, the high-spin states have the lowest energy ($U - 3J_H$) independently of the electron number m in the electronic configuration d^m under consideration, while the energies of low-spin states depend on m , and may even contain fractions of J_H due to the anisotropy of $J_{\alpha\beta}$ Hund's elements, see Eqs. (17) and (18), as found for instance in the case of LaMnO₃ [80].

The spin-orbital superexchange is the effective low-energy Hamiltonian which involves products of spin and orbital operators. The spin interactions are described by spin scalar products $\mathbf{S}_i \cdot \mathbf{S}_j$ on each bond $\langle ij \rangle$ connecting two nearest neighbor transition metal ions and obey the SU(2) symmetry, while the orbital operators $\{\boldsymbol{\tau}_i, \boldsymbol{\tau}_j\}$, with $\boldsymbol{\tau}_i = \{\tau_i^+, \tau_i^-, \tau_i^z\}$, obey only much lower symmetry (at most cubic for a cubic lattice) and appear either as a scalar product $\boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j$, or only as products of certain components. For instance, an Ising term $\tau_i^z \tau_j^z$ resembles the interactions in the 2D compass model (11). In general the spin-orbital superexchange is of the form [30],

$$\mathcal{H}_J = J \sum_{\langle ij \rangle \parallel \gamma} \left\{ \hat{\mathcal{J}}_{ij}^{(\gamma)} (\mathbf{S}_i \cdot \mathbf{S}_j + S^2) + \hat{\mathcal{K}}_{ij}^{(\gamma)} \right\}, \quad (20)$$

with the constant J defined in Eq. (10). The orbital operators $\hat{\mathcal{J}}_{ij}^{(\gamma)}$ and $\hat{\mathcal{K}}_{ij}^{(\gamma)}$ depend on the direction $\gamma = a, b, c$ in the cubic lattice and involve the active orbitals on each bond $\langle ij \rangle$ (either e_g or t_{2g}) along direction γ — they participate in $d_i^m d_j^m \rightleftharpoons d_i^{m+1} d_j^{m-1}$ virtual excitations, and thus these interactions have the symmetry of the lattice (*i.e.* cubic symmetry in the perovskites). As an example we introduce here the superexchange between V^{3+} ions in the d^2 configuration with $S = 1$ spins [81], as realized in RVO₃ perovskites considered below in Sect. 5, and controlled by the orbital operators

$$\hat{\mathcal{J}}_{ij}^{(\gamma)} = \frac{1}{2} \left[(1 + 2\eta r_1) \left(\boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j + \frac{1}{4} n_i n_j \right) - \eta r_3 \left(\boldsymbol{\tau}_i \times \boldsymbol{\tau}_j + \frac{1}{4} n_i n_j \right) - \frac{1}{2} \eta r_1 (n_i + n_j) \right]^{(\gamma)}, \quad (21)$$

$$\hat{\mathcal{K}}_{ij}^{(\gamma)} = \left[\eta r_1 \left(\boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j + \frac{1}{4} n_i n_j \right) + \eta r_3 (\boldsymbol{\tau}_i \times \boldsymbol{\tau}_j + \frac{1}{4} n_i n_j) - \frac{1}{4} (1 + \eta r_1) (n_i + n_j) \right]^{(\gamma)}. \quad (22)$$

They arise from the $d_i^2 d_j^2 \rightleftharpoons d_i^3 d_j^1$ charge excitations, leading either to high-spin or to low-spin d_i^3 configurations, so Hund's exchange in the multiplet structure of V^{2+} ions enters via the coefficients $r_1 \equiv 1/(1 - 3\eta)$ and $r_3 \equiv 1/(1 + 2\eta)$ (the low-spin excitations occur also at energy U , so the corresponding coefficient is $r_2 \equiv 1$). Equations (21) and (22) are general and refer to two active orbital flavors along the cubic axis γ . The leading orbital interactions are proportional to the scalar products $(\boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j)^{(\gamma)}$ of orbital operators on the bonds as both orbitals are active and may generate charge excitations, but the structure of local Coulomb interactions (13) is responsible for additional terms,

$$(\boldsymbol{\tau}_i \times \boldsymbol{\tau}_j)^{(c)} = \frac{1}{2} (\tau_i^+ \tau_j^+ + \tau_i^- \tau_j^-) + \tau_i^z \tau_j^z, \quad (23)$$

which violate the conservation of the orbital quantum numbers. The operator $n_i^{(\gamma)}$ stands for the number of active electrons at site i along the bond $\langle ij \rangle$, for instance for a bond along the c axis this number is $n_i^{(c)} \equiv n_{ia} + n_{ib}$ (this notation for the t_{2g} orbitals was introduced in Eq. (3)).

The superexchange model (20) consists typically of several terms which originate from different charge excitations. This feature made it possible to relate the averages of these different excitations to the spectral weights in the optical spectroscopy [82], and serves now as a standard theoretical tool to explain the observed anisotropy and temperature dependence of the spectral weights in the optical excitations [30]. In a correlated insulator the electrons are almost localized and the only kinetic energy which is left [83] is associated with the same virtual charge excitations that contribute also to the superexchange (20). Therefore, we may define the individual kinetic energy contributions $K_n^{(\gamma)}$, which refer to different energy regimes in the optical transitions and can be determined from the superexchange using the Hellman–Feynman theorem [84],

$$K_n^{(\gamma)} = -2 \left\langle H_n^{(\gamma)}(ij) \right\rangle. \quad (24)$$

For convenience, we define the energy contribution $K_n^{(\gamma)}$ for the Hubbard subband n as a positive quantity.

The magnetic properties of the transition metal oxides with active orbital degrees of freedom are usually discussed in terms of magnetic exchange constants which determine both the type of the magnetic order in the ground

state (at $T = 0$) and the magnetic excitations (magnons observed in the neutron scattering experiments). The exchange constants are usually found for a bond $\langle ij \rangle$ along each nonequivalent axis γ by averaging over the orbital operators in Eq. (20):

$$J_{ij} = \left\langle \hat{\mathcal{J}}_{ij}^{(\gamma)} \right\rangle, \quad (25)$$

which leads to an anisotropic spin exchange model Hamiltonian adequate for anisotropic magnetic phases, such as for instance A -AF phase realized in LaMnO_3 , or C -AF phase realized in LaVO_3 ,

$$H_S = J_{ab} \sum_{\langle ij \rangle_{ab}} \mathbf{S}_i \cdot \mathbf{S}_j + J_c \sum_{\langle ij \rangle_c} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (26)$$

This procedure assumes implicitly that spin and orbital operators can be separated from each other and ignores the possibility of quantum entanglement [85] and of composite spin-orbital excitations introduced in Refs. [77, 86]. It turns out that such excitations play a prominent role in destabilizing the classical AF long-range order in the d^9 spin-orbital model [28], and have observable consequences in the perovskite vanadates, see Sect. 5.

In some cases, however, the spin and orbital degrees of freedom may be disentangled and the obtained theoretical results explain well the experimental findings. One of the best examples is LaMnO_3 , where the exchange constants $\{J_{ab}, J_c\}$ deduced from the neutron scattering [87] can be explained by the superexchange model assuming a classical ansatz for the ground state with AO order,

$$|\Phi_0\rangle = \prod_{i \in A} |\theta_A\rangle_i \prod_{j \in B} |\theta_B\rangle_j, \quad (27)$$

with the orbital states, $|\theta_A\rangle_i$ and $|\theta_B\rangle_j$, characterized by the opposite angles ($\theta_A = -\theta_B$) on two sublattices A and B in the ab planes, and repeated in the subsequent planes along the c axis. The AO order is stable below the orbital transition temperature $T_{\text{OO}} \approx 760$ K [88], which is rather high compared with the Néel temperature $T_N \approx 140$ K — therefore one may consider the AO order between the sublattices ($i \in A, j \in B$),

$$\begin{aligned} |\theta_A\rangle_i &= \cos\left(\frac{\theta}{2}\right) |z\rangle_i + \sin\left(\frac{\theta}{2}\right) |x\rangle_i, \\ |\theta_B\rangle_j &= \cos\left(\frac{\theta}{2}\right) |z\rangle_j - \sin\left(\frac{\theta}{2}\right) |x\rangle_j, \end{aligned} \quad (28)$$

as frozen in the temperature range $T < 300$ K relevant for the magnetic excitations. Here we used the simplified notation for the e_g orbital basis introduced in Eq. (2). Using the well motivated parameter set, the experimental values of the exchange constants in LaMnO_3 are reproduced by the angle $\theta \approx 94^\circ$, but it has been shown that somewhat higher values of θ would also be consistent with a model including explicitly charge transfer superexchange terms [30]. In any case, the occupied orbitals in LaMnO_3 are closer to symmetric/antisymmetric combinations of $\{|z\rangle, |x\rangle\}$ than to the directional $(3x^2 - r^2)/(3y^2 - r^2)$ orbitals, as suggested in the early literature on the subject.

The experimental proof that the spin and orbital op-

erators may be *disentangled* in LaMnO_3 is provided by the optical spectroscopy, which shows rather distinct anisotropy of the low-energy spectral weights between the polarization in ab planes on the one hand and along the c axis on the other [89]. It is quite remarkable that the temperature dependence of these spectral weights may be very well explained by the spin-orbital superexchange model of Ref. [80], using the same parameters as those used to calculate the exchange constants, in the relevant temperature range $0 < T < 300$ K [89]. It follows alone from the temperature variation of spin correlation functions for a bond $\langle ij \rangle$ within the ab planes and along the c axis,

$$s_{ab} = \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle^{(ab)}, \quad s_c = \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle^{(c)}, \quad (29)$$

while the AO order remains unchanged, as explained in Ref. [30].

In spite of the disentangled spin and orbital dynamics in the RMnO_3 perovskites, where $R = \text{Lu}, \dots, \text{La}$ stands for a rare earth atom, several their properties are not yet fully understood. One of them is the nature of the insulating state which comes partly due to JT interactions [90–92] and partly due to the orbital superexchange interactions [80]. Another puzzling feature is the phase diagram of the RMnO_3 family of compounds, which exhibits a phase transition from the A -AF to a rather peculiar E -AF phase with decreasing size of R ions [88].

5. Fingerprints of spin-orbital entanglement in the RVO_3 perovskites

5.1. Spin-orbital entanglement

The coupling between spin and orbital operators in the spin-orbital superexchange may be quite strong in some cases — the experimental data show that the RVO_3 perovskites provide an excellent example of such a situation, see below. Although the C -AF phase observed in the entire family of the RVO_3 compounds [93, 94], where $R = \text{Lu}, \dots, \text{La}$ stands for a rare earth atom, satisfies to some extent the Goodenough–Kanamori rules [75], with FM order along the c axis coexisting with AO order of active a and b orbitals (3). However, the AO order is very weak here and the orbital fluctuations play a very important role [81]. This situation is opposite to the frozen AO order in LaMnO_3 , which can explain both the observed magnetic exchange constants and the distribution of the optical spectral weights. In LaVO_3 the FM exchange interaction is enhanced far beyond the usual mechanism following from the splitting between the high-spin and low-spin states due to finite Hund’s exchange J_H . Evidence of orbital fluctuations in the RVO_3 perovskites was also found in pressure experiments, which demonstrate a distinct competition between the C -AF and G -AF spin order, accompanied by the complementary G -AO and C -AO order of $\{a, b\}$ orbitals [94].

To understand better the essence of entangled spin-orbital states, we present first the results of the model calculation with four-site chains along the c axis, described by the spin-orbital superexchange models as derived for titanates and vanadates. These calculations

served to identify spin-orbital entangled states for increasing multiplet splitting $\propto \eta$ [85]. A prototype model to study frustration and entanglement in coupled spin and pseudospin (orbital) systems is the one-dimensional (1D) SU(4) model [95]. This example is remarkable, as in a purely spin 1D model one expects no frustration when only nearest-neighbor interactions are present. However, both spins and pseudospins appear here on a completely symmetrical and equal footing with joint spin-pseudospin operators and compete with each other, forming a group of elementary generators in the SU(4) symmetry. Three types of elementary excitations contribute to the thermodynamic properties: spin, orbital, and joint spin-orbital ones. This is indeed confirmed by the entropy data of this model obtained from a numerical analysis [96], which increases three times faster than that of the 1D AF Heisenberg model. This also implies that the intersite correlation functions are intimately interrelated and it is impossible to separate the two subsystems. Hence, one has to treat explicitly entangled spin-pseudospin states.

As a useful tool to verify the Goodenough–Kanamori rules [75] in spin-orbital models for t_{2g} electrons with either $S = 1$ or $S = 1/2$ spins and pseudospins $\tau = 1/2$, we introduce spin and orbital correlations defined for a bond $\langle ij \rangle$,

$$S_{ij} = \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle / (2S)^2, \quad T_{ij} = \langle \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j \rangle. \quad (30)$$

When they are compared with each other, and with the composite spin-orbital correlation function defined as a difference between the exact value and the MF factorized correlations on a bond $\langle ij \rangle$ [85],

$$C_{ij} = [\langle (\mathbf{S}_i \cdot \mathbf{S}_j)(\boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j) \rangle - \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle \langle \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j \rangle] / (2S)^2, \quad (31)$$

one may conclude whether or not the spin and orbital operators are entangled. If $C_{ij} < 0$, spin and orbital operators are entangled, and joint spin-orbital fluctuations contribute even at $T = 0$, while if $C_{ij} = 0$ — the spin and orbital operators are disentangled and their MF decoupling is exact. Two spin-orbital models were investigated in Ref. [85]: (i) the titanate model for Ti^{3+} ions in d^1 ionic configuration in the RTiO_3 perovskites with $S = 1/2$ [97], and (ii) the vanadate model for V^{3+} ions in d^2 configuration in the RVO_3 perovskites with $S = 1$ [81]. For more details about the structure of the superexchange \mathcal{H}_J (20) in both models see for instance Ref. [30].

As the chain-like cluster is 1D and only two orbital $\{a, b\}$ flavors contribute in each case, one recovers the SU(4) model in the d^1 (titanate) case at $\eta = 0$, and $S_{ij} = T_{ij} = C_{ij} = -0.25$ for $N = 4$ sites [85]. This result manifestly contradicts the celebrated Goodenough–Kanamori rules [75], as both spin and orbital correlations have the same sign. By a closer inspection one finds that the ground state wave function for the four-site cluster is close to a total spin-orbital singlet, involving a linear combination of (spin singlet/orbital triplet) and (spin triplet/orbital singlet) states for each bond $\langle ij \rangle$. At fi-

nite η the SU(4) degeneracy of all intersite correlations is removed — one finds $T_{ij} < C_{ij} < S_{ij} < 0$ in the regime of spin singlet ($S = 0$) ground state, spin and orbital operators are entangled, and the Goodenough–Kanamori rule is violated again, as it states that the spin and orbital correlations should be complementary to each other. A qualitatively similar case is found in a mathematical SU(2) \otimes SU(2) model [98] (not realized in transition metal oxides), where the ground state is entangled in a broad range of parameters, including the exactly solvable case with alternating spin and orbital singlets on the bonds [99].

The vanadate d^2 model behaves in a similar way in a range of small values of η , with all three S_{ij} , T_{ij} and C_{ij} correlations being again negative. The composite spin-orbital correlations are here finite ($C_{ij} < 0$), spin and orbital variables are *entangled*, and the MF factorization of the ground state into spin and orbital part fails. Only for sufficiently large η do the spins reorient in the FM ground state, and decouple from the orbitals. In this regime, corresponding to the experimentally observed C -AF phase of LaVO_3 (and other cubic vanadates), spin-orbital entanglement ceases to exist in the ground state. However, as we will see below, it has still remarkable consequences at finite temperature, where entangled spin-orbital states again play a role.

A crucial observation concerning the applicability of the Goodenough–Kanamori rules to the quantum models of t_{2g} electrons in one dimension can be made by comparing spin exchange constants J_{ij} calculated from Eq. (25) with the actual values of intersite spin correlations S_{ij} (30). One finds that exchange interaction is negative ($J_{ij} < 0$), and formally favors FM spin orientation in the singlet phase at low values of η , but it is accompanied by AF spin correlations ($S_{ij} < 0$). This demonstrates that the ground state energy calculated in the MF theory would be *enhanced*, so the MF approach is qualitatively incorrect and cannot be used [85]. This result follows from large spin-orbital fluctuations which cause also large fluctuations of the exchange constants around the average value, measured by $\delta J = \{(\langle \hat{J}_{ij}^{(\gamma)} \rangle)^2 - J_{ij}^2\}^{1/2}$. Altogether, this result challenges the usual interpretation of the magnetic data in the spin-orbital systems with the exchange constants determined by averaging over the orbital operators, see Eq. (25). Fortunately, Hund’s exchange is large enough in transition metal oxides and this conceptual difficulty is removed, but one may expect that experimental results in the range of finite temperature will still depend on the entangled states discussed above.

5.2. Phase diagram of the RVO_3 perovskites

The phase diagram of the RVO_3 perovskites [93, 94] is qualitatively different from the one for the RMnO_3 perovskites [88] and indicates the proximity of spin and orbital energy scales. Experimental studies have shown that the C -AF order is common to the entire family of the RVO_3 vanadates, and in general the magnetic tran-

sition occurs below the orbital transition, $T_{N1} < T_{OO}$, except for LaVO_3 with $T_{N1} \approx T_{OO}$ [93, 94]. When the ionic radius r_R decreases, the Néel temperature T_{N1} also decreases, while the orbital transition temperature T_{OO} increases, passes through a maximum close to YVO_3 , and next decreases towards LuVO_3 . This nonmonotonic dependence of T_{OO} on r_R provided an experimental challenge to the theory which was addressed only recently using the spin-orbital superexchange model [100]. One finds that the C -AF order develops in LaVO_3 below $T_{N1} \approx 143$ K, and is almost immediately followed by a weak structural transition stabilizing the weak G -AO order at $T_{OO} \approx 141$ K [93, 94]. This provides a constraint on the theoretical model. Remarkably, the magnetic order parameter in the C -AF phase of LaVO_3 is strongly reduced to $\approx 1.3 \mu_B$, much below the reduction expected from quantum fluctuations in the C -AF phase (being only 6% for $S = 1$ spins [101]) — also this reduction of the measured magnetization could not be explained so far.

In order to unravel the physical mechanism responsible for the decrease of T_{OO} from YVO_3 to LuVO_3 one has to analyze in more detail the evolution of GdFeO_3 distortions with decreasing ionic radius r_R [100]. Such distortions are common for the perovskites [102], and one expects that they should increase when the ionic radius r_R decreases, as observed in the RMnO_3 perovskites [88]. In the RVO_3 family the distortions are described by two subsequent rotations of VO_6 octahedra, see Ref. [100]: (i) by an angle ϑ around the b axis, and (ii) by an angle φ around the c axis. Increasing angle ϑ causes a decrease of V–O–V bond angle along the c direction, being $\pi - 2\vartheta$, and leads to an orthorhombic lattice distortion $u = (b - a)/a$, where a and b are the lattice parameters of the $Pbnm$ structure of RVO_3 . By the analysis of the structural data for the RVO_3 perovskites [103, 104] one finds the following empirical relation between the ionic radius r_R and the angle ϑ :

$$r_R = r_0 - \alpha \sin^2 \vartheta, \quad (32)$$

where $r_0 = 1.5 \text{ \AA}$ and $\alpha = 0.95 \text{ \AA}$ are the empirical parameters. This allows one to use the angle ϑ to parametrize the dependence of the microscopic parameters of the Hamiltonian and to investigate the transition temperatures T_{OO} and T_{N1} as functions of r_R .

The spin-orbital model introduced in Ref. [100] to describe the phase diagram of RVO_3 reads

$$\begin{aligned} \mathcal{H} = & J \sum_{\langle ij \rangle \| \gamma} \left\{ (\mathbf{S}_i \cdot \mathbf{S}_j + S^2) \mathcal{J}_{ij}^{(\gamma)} + \mathcal{K}_{ij}^{(\gamma)} \right\} \\ & + E_z(\vartheta) \sum_i e^{i \mathbf{R}_i \cdot \mathbf{Q}} \tau_i^z \\ & - V_c(\vartheta) \sum_{\langle ij \rangle \| c} \tau_i^z \tau_j^z + V_{ab}(\vartheta) \sum_{\langle ij \rangle \| ab} \tau_i^z \tau_j^z \\ & - gu \sum_i \tau_i^x + \frac{1}{2} NK [u - u_0(\vartheta)]^2, \end{aligned} \quad (33)$$

where the operators $\hat{\mathcal{J}}_{ij}^{(\gamma)}$ and $\hat{\mathcal{K}}_{ij}^{(\gamma)}$ are given by Eqs. (21)

and (22). The superexchange is supplemented by the crystal field term $\propto E_z$, the orbital interactions terms $\propto V_c$ and $\propto V_{ab}$ induced by lattice distortions, and the orbital-lattice term $\propto g$ which is counteracted by the lattice elastic energy $\propto K$. All these terms are necessary in a realistic model which reproduces the behavior of the RVO_3 perovskites at finite temperature.

The crystal field splitting breaks the cubic symmetry in distorted VO_6 octahedra, as obtained in the electronic structure calculations [105] and from the point charge model [100], and the actual filling of t_{2g} orbitals is

$$n_{ic} = 1, \quad n_{ia} + n_{ib} = 1, \quad (34)$$

so the superexchange (21) and (22) in Eq. (33) is expressed by the orbital operators $\tau_i = \{\tau_i^+, \tau_i^-, \tau_i^z\}$ (and their components) which refer to two active orbital flavors $\{a, b\}$, as explained in Sect. 4. The splitting $\propto E_z$ between a (yz) and b (zx) orbitals is given by the pseudospin τ_i^z operators,

$$\tau_i^z = \frac{1}{2} (n_{ia} - n_{ib}). \quad (35)$$

Its spatial dependence is characterized by the vector $\mathbf{Q} = (\pi, \pi, 0)$ in reciprocal space — it alternates in the ab planes, but is uniform along the c axis. Thus, this splitting competes with the (weak) G -AO order supporting the observed C -AF phase at temperature $T < T_{N1}$.

In addition, the model (33) includes: (i) intersite orbital interactions $\propto V_{ab}, V_c$ (which originate from the coupling to the lattice), and (ii) orbital-lattice term $\propto g$ which induces orbital polarization $\langle \tau_i^x \rangle \neq 0$ when the lattice distortion u increases. The orbital interactions induced by the distortions of the VO_6 octahedra and by GdFeO_3 distortions of the lattice, $V_{ab} > 0$ and $V_c > 0$, also favor the C -AO order (like the crystal field $E_z > 0$). Let us note that $V_c > 0$ counteracts the orbital interactions included in the superexchange via $\hat{K}_{ij}^{(c)}$ operators (22). The last two terms in Eq. (33) describe the linear coupling $\propto g > 0$ between active $\{yz, zx\}$ orbitals and the orthorhombic lattice distortion u . The elastic energy which counteracts lattice distortion u is given by the force constant K , and N is the number of V^{3+} ions. The coupling $\propto gu$ acts as a transverse field in the pseudospin space. While the eigenstates $\frac{1}{\sqrt{2}}(|a\rangle \pm |b\rangle)$ of τ_i^x (favored by $g > 0$) cannot be realized due to the competition with all the other terms, increasing lattice distortion u (increasing angle ϑ) modifies the orbital order and intersite orbital correlations.

The crystal field splitting $E_z(\vartheta)$, orbital interactions $\{V_{ab}(\vartheta), V_c(\vartheta)\}$, and the orbital-lattice coupling $g_{\text{eff}}(\vartheta) \equiv gu$ depend on the tilting angle ϑ . In case of V_c one may argue that its dependence on the angle ϑ is weak, and a constant $V_c(\vartheta) \equiv 0.26 \text{ J}$ was chosen in Ref. [100] in order to satisfy the experimental constraint that the C -AF and G -AO order appear almost simultaneously in LaVO_3 [93]. The experimental value $T_{N1}^{\text{exp}} = 143 \text{ K}$ for LaVO_3 [93] was fairly well reproduced in the present model taking $J = 200 \text{ K}$. The functional dependence of the remaining two parameters $\{E_z(\vartheta), V_{ab}(\vartheta)\}$ on the tilting angle

ϑ was derived from the point charge model [100] using the structural data for the RVO₃ series [103, 104] — one finds

$$E_z(\vartheta) = Jv_z \sin^3 \vartheta \cos \vartheta, \quad (36)$$

$$V_{ab}(\vartheta) = Jv_{ab} \sin^3 \vartheta \cos \vartheta. \quad (37)$$

Finally, the effective coupling to the lattice distortion has to increase faster with the increasing angle ϑ in order to dominate for large values of ϑ , and the following dependence was shown [100] to give a satisfactory description of the phase diagram of the RVO₃ perovskites:

$$g_{\text{eff}}(\vartheta) = Jv_g \sin^5 \vartheta \cos \vartheta. \quad (38)$$

Altogether, magnetic and orbital correlations described by the spin-orbital model (20), and the magnetic T_{N1} and orbital T_{OO} transition temperatures depend on three parameters: $\{v_z, v_{ab}, v_g\}$.

Due to the proximity of both orbital and magnetic phase transitions in the RVO₃ perovskites, it is crucial to design the MF approach in such a way that the spin-orbital coupling is described *beyond* the factorization of spin and orbital operators. On the one hand, the correct MF treatment of the orbital and magnetic phase transitions in the RVO₃ vanadates requires the coupling between the on-site orbital, $\langle \tau_i^z \rangle_G \equiv \frac{1}{2} |\langle \tau_i^z - \tau_j^z \rangle|$, and spin order parameters in the *C*-AF phase, $\langle S_i^z \rangle_C$, as well as a composite $\langle S_i^z \tau_i^z \rangle$ order parameter, similar to that used for the RMnO₃ perovskites [80]. On the other hand, the on-site MF theory including the above coupling [106] does not suffice for the RVO₃ compounds as the orbital singlet correlations $\langle \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j \rangle$ on the bonds $\langle ij \rangle$ along the *c* axis play so crucial role in stabilizing the *C*-AF phase [81] and the orbital fluctuations are important [107]. Therefore, the minimal physically acceptable approach to the present problem is a self-consistent calculation for a bond $\langle ij \rangle$ along the *c* axis, coupled by the MF terms to its neighbors along all three cubic axes [100]. This procedure, with properly selected model parameters, was shown to be successful in reproducing the experimental phase diagram of Ref. [94]. One finds that indeed the orbital order occurs below a higher temperature than the magnetic one ($T_{OO} > T_{N1}$) in the RVO₃ perovskites to the left of LaVO₃, i.e. with smaller ionic radius, $r_R < r_{La}$.

As presented in Ref. [100], the remarkable dependence of both spin T_{N1} and orbital T_{OO} transition temperature in the RVO₃ perovskites follows from the respective changes in the orbital correlations with decreasing r_R . First, the singlet correlations are drastically suppressed from LaVO₃ towards LuVO₃. Second, the increase of orbital intersite interactions due to the JT term (37) induces gradual increase of the orbital temperature T_{OO} with decreasing r_R . Finally, while $\langle \tau_i^x \rangle \approx 0.03$ is rather weak in LaVO₃, it steadily increases along the RVO₃ perovskites when r_R decreases, and finally it becomes as important as the orbital order parameter itself, i.e. $\langle \tau_i^x \rangle \approx \langle \tau_i^z \rangle_G$. Let us note that in the entire parameter range the latter order parameter is substantially reduced from the classical value $\langle \tau^z \rangle_{G, \text{max}} = 0.5$ by singlet orbital fluctuations in the entire parameter regime, being

$\langle \tau_i^z \rangle_G \approx 0.32$ and 0.36 for LaVO₃ and LuVO₃, respectively.

It is quite remarkable that the above changes in the orbital state modify the magnetic exchange constants $\{J_{ab}, J_c\}$ along both nonequivalent cubic directions, see Eq. (25), and thus the value of T_{N1} is reduced with decreasing r_R . Let us note that the superexchange energy J does not change, so the entire effect stems from the orbital correlations [100]. This also implies that the width of the magnon band given at $T = 0$ by $W_{C\text{-AF}} = 4(J_{ab} + |J_c|)$ is reduced by a factor close to 1.8 from LaVO₃ to YVO₃, in agreement with surprisingly low magnon energies observed in the *C*-AF phase of YVO₃ [108].

Summarizing, the microscopic model (33) describes gradual changes of the orbital and magnetic correlations under the coupling to the lattice which suppresses orbital fluctuations generated by virtual charge fluctuations responsible for the spin-orbital superexchange. It provides an almost quantitative understanding of the systematic experimental trends for both orbital and magnetic transitions in the RVO₃ perovskites [100], and is able to reproduce the observed nonmonotonic variation of the orbital transition temperature T_{OO} for decreasing r_R . However, the theoretical description of the magnetic transition to the *G*-AF phase at T_{N2} , which occurs for small r_R [93], remains to be addressed by future theory. More examples of spin-orbital entanglement in the field of the perovskite vanadates are shortly discussed in the next two subsections.

5.3. Optical spectral weights for LaVO₃

As a second example of spin-orbital entanglement in the cubic vanadates at finite temperature we discuss briefly the evaluation of the optical spectral weights from the spin-orbital superexchange for LaVO₃, following Eq. (24). First we rewrite the superexchange operator $H^{(\gamma)}(ij)$ for a bond $\langle ij \rangle \parallel \gamma$, contributing to operator \mathcal{H}_J (20), as a superposition of increments arising from $d_i^z d_j^z \rightleftharpoons d_i^z d_j^x$ charge excitations to different spin and orbital states in upper Hubbard subbands labelled by n [82],

$$H^{(\gamma)}(ij) = \sum_n H_{n,ij}^{(\gamma)}. \quad (39)$$

One finds the superexchange terms $H_{n,ij}^{(c)}$ for a bond $\langle ij \rangle$ along the *c* axis [82],

$$H_{n,ij}^{(c)} = -\frac{1}{3} J r_1 (2 + \mathbf{S}_i \cdot \mathbf{S}_j) \left(\frac{1}{4} - \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j \right), \quad (40)$$

$$H_{n,ij}^{(c)} = -\frac{1}{12} J (1 - \mathbf{S}_i \cdot \mathbf{S}_j) \left(\frac{7}{4} - \tau_i^z \tau_j^z - \tau_i^x \tau_j^x + 5\tau_i^y \tau_j^y \right), \quad (41)$$

$$H_{n,ij}^{(c)} = -\frac{1}{4} J r_3 (1 - \mathbf{S}_i \cdot \mathbf{S}_j) \left(\frac{1}{4} + \tau_i^z \tau_j^z + \tau_i^x \tau_j^x - \tau_i^y \tau_j^y \right), \quad (42)$$

and $H_{n,ij}^{(ab)}$ for a bond in the ab plane,

$$H_{n,ij}^{(ab)} = -\frac{1}{6}Jr_1(2 + \mathbf{S}_i \cdot \mathbf{S}_j) \left(\frac{1}{4} - \tau_i^z \tau_j^z \right), \quad (43)$$

$$H_{n,ij}^{(ab)} = -\frac{1}{16}J(1 - \mathbf{S}_i \cdot \mathbf{S}_j) \left(\frac{19}{6} \mp \tau_i^z \mp \tau_j^z - \frac{2}{3}\tau_i^z \tau_j^z \right), \quad (44)$$

$$H_{n,ij}^{(ab)} = -\frac{1}{16}Jr_3(1 - \mathbf{S}_i \cdot \mathbf{S}_j) \left(\frac{5}{2} \mp \tau_i^z \mp \tau_j^z + 2\tau_i^z \tau_j^z \right). \quad (45)$$

When the spectral weight is evaluated following Eq. (24), it is reasonable to try first the MF approximation and to separate spin and orbital correlations from each other. The spectral weights require then knowledge of spin correlations along the c axis and within the ab planes (29), as well as the corresponding intersite correlations $\langle \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j \rangle$ and $\langle \tau_i^\alpha \tau_j^\alpha \rangle$ with $\alpha = x, y, z$. From the form of the above superexchange contributions one sees that high-spin excitations $H_{n,ij}^{(\gamma)}$ support the FM coupling while the low-spin ones, $H_{2,ij}^{(\gamma)}$ and $H_{3,ij}^{(\gamma)}$, contribute with AF couplings.

The low-energy optical spectral weight for the polarization along the c axis $K_{1,\text{exp}}^{(c)}$ decreases by a factor close to two when the temperature increases from $T \approx 0$ to $T = 300$ K [109] — this change is much larger than the one observed in LaMnO_3 [89]. However, the theory based on the MF decoupling of the spin and orbital degrees of freedom gives only a much smaller reduction of the weight close to 27%, and has no chance to explain the experiment as the maximal possible reduction of $K_1^{(c)}$ found for $s_c = 0$ in the limit of $T \rightarrow \infty$ amounts to 33% [30]. Let us note that both spin and orbital intersite correlations change in the temperature range $0 < T < 300$ K used in experiment, but this variation is clearly not sufficient to describe the experimental data.

In contrast, when a cluster method is used to determine the optical spectral weight from the high-spin superexchange term (40) by including orbital as well as joint spin-and-orbital fluctuations along the c axis, the temperature dependence resulting from the theory follows the experimental data [82]. This may be considered as a remarkable success of the theory based on the spin-orbital superexchange model derived for the RVO_3 perovskites, and the proof that spin-orbital entangled states contributes in a crucial way in the finite temperature regime. In addition, the theoretical calculation predicts that the low energy spectral weight is low along the c axis. The spectral weight in the ab planes behaves in the opposite way — it is small at low energy, and high (but not as high as the low-energy one for the c axis) at high energy. This weight distribution and its anisotropy between the c and ab directions reflect the nature of magnetic correlations, which are FM and AF in these two directions. A more precise comparison of these theory predictions for the ab polarization is not possible at present, but we expect that future experiments will also confirm them.

5.4. Peierls dimerization in YVO_3

The third and final example of the spin-orbital entanglement at finite temperature in the family of vanadate perovskites is the remarkable first order magnetic transition at $T_{N2} = 77$ K from the G -AF to the C -AF spin order with rather exotic magnetic properties, found in YVO_3 [110]. This magnetic transition is unusual and particularly surprising as the staggered moments are approximately parallel to the c axis in the G -AF phase, and reorient above T_{N2} to the ab planes in the C -AF phase, with some small alternating G -AF component along the c axis. First, while the orientations of spins in C -AF and G -AF phase are consistent with the expected anisotropy due to spin-orbit coupling [111], the observed magnetization reversal with the weak FM component remains puzzling. Second, it was also established by neutron scattering experiments [108] that the scale of magnetic excitations is considerably reduced for the C -AF phase (by a factor close to two) as compared with the exchange constants deduced from magnons measured in the G -AF phase. In addition, the magnetic order parameter in the C -AF phase of LaVO_3 is strongly reduced to $\approx 1.3 \mu_B$, which cannot be explained by rather small quantum fluctuations in the C -AF phase [101]. Finally, the C -AF phase of YVO_3 is dimerized. Until now, only this last feature found a satisfactory explanation in the theory [112, 113], see below.

We remark that the observed dimerization in the magnon dispersions may be seen as a signature of *entanglement in excited states* which becomes active at finite temperature. The microscopic reason of the anisotropy in the exchange constants

$$\mathcal{J}_{c1} \equiv \mathcal{J}_c(1 + \delta_S), \quad \mathcal{J}_{c2} \equiv \mathcal{J}_c(1 - \delta_S), \quad (46)$$

is the tendency of the orbital chain to dimerize, activated by thermal fluctuations in the FM spin chain [113] which support dimerized structure in the orbital sector. As a result one finds alternating stronger and weaker FM bonds along the c axis (46) in the dimerized C -AF phase (with $\delta_S > 0$). The observed spin waves may be explained by the following effective spin Hamiltonian for this phase (assuming again that the spin and orbital operators may be disentangled which is strictly valid only at $T = 0$):

$$\begin{aligned} \mathcal{H}_S = & \mathcal{J}_c \sum_{\langle i,i+1 \rangle \| c} [1 + (-1)^i \delta_S] \mathbf{S}_i \cdot \mathbf{S}_{i+1} \\ & + \mathcal{J}_{ab} \sum_{\langle ij \rangle \| ab} \mathbf{S}_i \cdot \mathbf{S}_j + K_z \sum_i (S_i^z)^2. \end{aligned} \quad (47)$$

Following the linear spin-wave theory the magnon dispersion is given by

$$\begin{aligned} \omega_{\pm}(\mathbf{k}) & \\ & = 2\sqrt{\left(2\mathcal{J}_{ab} + |\mathcal{J}_c| + \frac{1}{2}K_z \pm \mathcal{J}_c\eta_{\mathbf{k}}\right)^2 - (2\mathcal{J}_{ab}\gamma_{\mathbf{k}})^2}, \end{aligned} \quad (48)$$

With

$$\gamma_{\mathbf{k}} = \frac{1}{2}(\cos k_x + \cos k_y), \quad (49)$$

$$\eta_{\mathbf{k}} = (\cos^2 k_z + \delta_S^2 \sin^2 k_z)^{1/2}. \quad (50)$$

The single-ion anisotropy term $\propto K_z$ is responsible for the gap in spin excitations. Two modes measured by neutron scattering [108] are well reproduced by spin-wave energies $\omega_{\pm}(\mathbf{k})$ obtained from Eq. (48) using the experimental exchange interactions: $\mathcal{J}_{ab} = 2.6$ meV, $\mathcal{J}_c = -3.1$ meV, $\delta_S = 0.35$. We note that a somewhat different Hamiltonian with more involved interactions was introduced in Ref. [108], but the essential features seen in the experiment are well reproduced already by the present effective spin exchange model \mathcal{H}_S , see Eq. (47).

The observed dimerization in the magnon spectra in YVO₃ motivated the search for its mechanism within the spin-orbital superexchange model. Dimerization of AF spin chains coupled to phonons is well known and occurs in several systems [114]. The spin-Peierls transition discovered in CuGeO₃ [115] led to renewed interest in the dimerization instability of the AF spin chains. In the spin-orbital model for the RVO₃ perovskites a similar instability might also occur without the coupling to the lattice when Hund's exchange is sufficiently small. In particular, the ground state at $\eta = 0$ may be approximated by the dimerized chain with strong FM bonds alternating with the AF ones, if such chains are coupled by AF interactions along the a and b axes [116] (a free 1D chain would give the entangled disordered ground state as described in Sect. 5.1).

At realistic values of $\eta > 0.10$ the C -AF order with FM chains along the c axis is found in the ground state [81]. Numerical studies performed at finite temperature have shown that periodic dimerization of the magnetic exchange interaction occurs in a certain finite temperature range, while the ground state is the fully polarized and uniform FM state [111, 112]. These findings served as a motivation to investigate the mechanism of the spin-Peierls dimerization in FM spin chains. The microscopic 1D model which stands for the situation encountered in the C -AF phase of YVO₃ reads [113]:

$$H_{S\tau} = J \sum_i (\mathbf{S}_i \cdot \mathbf{S}_{i+1} + 1) \times \left(\boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_{i+1} + \frac{1}{4} - \gamma_H \right), \quad (51)$$

where γ_H stands for the contribution due to the high-spin states proportional to the Hund exchange (19) and stabilizes FM spin order. While the spin and orbital operators are disentangled in the FM ground state, one may consider a coupled FM spin chain to an orbital chain with interactions which favor the AO order, as realized in the C -AF phase. Due to their mutual interrelation the exchange interactions along the spin (orbital) chain depend on the orbital (spin) correlations, and their modulation may be described by δ_S and δ_{τ} parameters (46). They can be found from a self-consistent solution of the coupled MF equations for spin and orbital correlations, and one finds indeed dimerized spin and orbital chains in a finite range of temperature [113].

Summarizing, spin-orbital entanglement in the excited states is also responsible for the exotic magnetic properties of the C -AF phase of YVO₃. They arise from the coupling between the spin and orbital operators which triggers the dimerization of the FM interactions as a manifestation of a universal instability of FM chains at finite temperature, which occurs either by the coupling of spin to the lattice or by their coupling to purely electronic degrees of freedom [113]. This latter mechanism could play a role in many transition metal oxides with (nearly) degenerate orbital states.

6. Coexisting charge and orbital order

The first step towards understanding the doped systems with orbital degrees of freedom is the question concerning possible QP states deciding about coherent hole propagation in the orbitally ordered background. As discussed in Sect. 2, a single hole doped into the AF background as in CuO₂ planes of La₂CuO₄ may propagate through the lattice because it couples to quantum spin fluctuations and becomes dressed with a “cloud” of magnons [117]. This results in the new energy scale $\propto J$ in place of the hole hopping t , so the hopping is strongly renormalized. The QP which can propagate coherently through the AF background after the hole is doped is called a *spin polaron* [38]. A more complex situation occurs in the systems with partly filled degenerate orbitals, where a doped hole may couple not only to magnons but also couples to crystal-field excitations [14]. In addition, QP states with higher spin states may occur, as for instance a triplet QP in case of an $S = 1/2$ antiferromagnet doped by a single electron and triggered by Hund's exchange coupling in the orbitally degenerate background [118]. This motivates two questions in the theory: (i) whether orbital excitations could couple to the moving hole and generate as well a new energy scale, as the hole-magnon coupling does, and (ii) whether spin-orbital entanglement has any important consequences for the hole dynamics. Both of them were addressed in the orbital t - J model for e_g electrons [119], and in the analogous models for t_{2g} orbitals developed recently, see below.

Two situations with a hole doped into an AO ordered background were considered in the past: (i) a hole doped into an FM ab plane of LaMnO₃ which has an AO order of e_g orbitals in the ground state [120], and (ii) a hole doped into an ab plane with an AO order of t_{2g} orbitals and FM spin order [121], as realized for instance in Sr₂VO₄. In the first case it was shown that the orbitons have in general a gap and have a lower dispersion than the magnons. Therefore, the quantum effects are weak but nevertheless a hole can move by interorbital hopping processes. While the constraint of creating no double occupancies has to be obeyed along the hole hopping, the bandwidth is strongly renormalized with respect to that suggested by the LDA+ U approach [120]. Such interorbital hopping processes are absent in the t_{2g}

ordered background with alternating yz/zx orbitals in an ab plane, and due to the specific t_{2g} orbital symmetries the orbitons are dispersionless. Thus the string picture dominates the character of the t_{2g} orbital polarons [122] even more than in the case of systems with e_g orbital degrees of freedom.

An intriguing question in this context addressed only recently is whether spin quantum fluctuations can still contribute to the QP spectral properties when both types of order, spin and orbital, alternate in an ab plane, as for instance in the C -AF phase of RVO_3 perovskites. A crucial observation for the spectral properties of a hole doped into this *entangled* AF/AO ground state is a simultaneous excitation of a magnon and an orbiton when a hole moves by a single step in the lattice [123]. This dominates the behavior of the hole doped into the AF/AO state, because the orbitals confine the hole motion by forcing the hole to retrace its path which implies that the hole motion by its coupling to the quantum spin fluctuations is prohibited. Thus, *the string-like potential which acts on the hole is induced by the orbitals* although it has a joint spin-orbital character. Hence, this important feature of the orbitally induced string formation could be understood as a topological effect. This happens even if the energy of the orbital excitations is reduced to zero, i.e., when the hole moves entirely by incoherent processes in the orbital sector. Hence, the mere presence of orbitals is sufficient to obtain the (almost) classical behavior of a hole doped into the ground state with AF/AO order. This result, in connection with the fact that the mother-compound of the superconducting iron-pnictides shows a variety of spin-orbital phenomena [124], suggests that further investigation of the hole propagation in spin-orbital systems is a fascinating subject for future studies.

The properties of doped $R_{1-x}Sr_xVO_3$ systems are puzzling and it is not understood until now why (i) $La_{1-x}Sr_xVO_3$ is insulating in a broad range of doping below $x_c = 0.18$, and (ii) why the AF order survives even for $x > x_c$ when the system becomes metallic and loses the AO order in the ab planes [125]. The gradual changes of the optical conductivity under increasing doping demonstrate that the anisotropy between the ab and c direction decreases, but surprisingly is not completely lost even in the metallic regime. The differences observed in the optical conductivity and Raman scattering spectra between $La_{1-x}Sr_xVO_3$ and $Y_{1-x}Sr_xVO_3$ suggest that the orthorhombic lattice distortion plays also here a very important role and influences the hole dynamics [126]. It has been argued that the C -AF phase is more robust under hole doping [127] and survives in a broad doping range [128], but a complete understanding of doped vanadate perovskites awaits a more careful theoretical study.

Doped $R_{1-x}(Sr,Ca)_xMnO_3$ compounds are studied much longer and are better understood. The FM metallic state is induced by doping via the double exchange mechanism [7] which was also formulated for degenerate e_g orbitals [129], and the phase diagrams of the doped perovskite systems show a remarkable sequence of mag-

netic phases [130], from the A -AF phase, through the insulating and metallic FM phase, towards the C -AF phase and G -AF phase in the highly doped regime. Similar (but not the same) sequence of magnetic phases was reported in the bilayer $La_{2-2x}Sr_{1+2x}Mn_2O_7$ systems [131]. As in the $R_{1-x}Sr_xVO_3$ perovskites, also in the layered systems the orbital ordered (or liquid) state determines whether the intersite spin correlations are AF or FM, as shown for the monolayer [132] and bilayer [133] manganites using a t - J -like model which includes orbital degeneracy. These model calculations illustrate as well the complementarity of spin and orbital order expressed by the Goodenough-Kanamori rules [75]. In these systems the short-range charge order gradually develops with increasing doping in the realistic parameter regime [134]. However, more complete models including the charge transfer physics are necessary to describe the features observed in the optical spectra, as for instance in insulating $LaSrMnO_4$ [135].

Although there is no complete understanding of the phase diagram and in particular of the mechanism of the metal-insulator transition which leads to the colossal magnetoresistance, a lot of progress could be made using model Hamiltonians. It was recognized that the orbital degeneracy plays a crucial role both in the double exchange [129] and for the interactions with the lattice due to the JT effect [136], and phase diagrams which resemble the qualitative behavior of the doped manganites were obtained [137]. However, a more realistic treatment requires also electron correlations among e_g electrons which are more difficult to implement [8]. In contrast to the nondegenerate Hubbard model, the orbital Hubbard model for FM manganites does not show an instability towards the orbitally polarized FO state and one finds instead the disordered orbital liquid ground state [138]. This concept was crucial in explaining the doping dependence of the stiffness constant in the FM $La_{1-2x}Sr_xMnO_3$ manganites [139], but for a quantitative explanation both the double exchange due to correlated e_g electrons and the superexchange due to t_{2g} core spins had to be included [140]. This approach had also a remarkable success [141] in explaining the observed magnon dispersion and the doping dependence of the magnetic exchange constants in the $La_{2-2x}Sr_{1+2x}Mn_2O_7$ systems, including the observed phase transition from the FM to the A -AF structure [142].

As expected, the orbital order melts in general when the manganites are doped, but there are cases when a different type of orbital order coexisting with charge order emerges again at half doping. The famous case is the so-called (charge exchange) CE phase in half-doped ($x = 0.5$) manganites [74], where the two-sublattice charge order coexists with orbital order on the sites with the majority of e_g electron charge, and the FM zigzag chains staggered in ab planes. Although the double exchange provides some arguments justifying the stability of this complex type of order [143] which competes with the FM phase in the relevant parameter regime and wins for sufficiently large and realistic AF superexchange be-

tween the $S = (3/2)t_{2g}$ core spins [144], the problem is subtle and the range of parameters which gives the CE phase in the ground state is rather narrow. In particular, this phase is destabilized by intersite Coulomb interaction [133], while the JT distortions play an important role in stabilizing it [145]. We emphasize again that AF interactions between t_{2g} electrons are small — for this case the CE phase was found in the charge-ordered phase using a finite-temperature diagonalization technique [146]. The mechanism invoked there to stabilize the CE phase is subtle and employs the cooperative JT interaction between next-nearest Mn³⁺ neighbors mediated by the breathing mode distortion of Mn⁴⁺ octahedra and displacements of Mn⁴⁺ ions. It is worth noting that the topological phase factor in the Mn–Mn hopping [147] leading to gap formation in 1D models [143] describing the CE phase, as well as the nearest neighbor JT coupling, are not able to produce the observed zigzag FM chains for the realistic parameters [146]. Recent X-ray structural analysis of Pr_{0.5}Ca_{0.5}MnO₃ and Eu_{0.5}Ca_{1.5}MnO₄ suggest that the orbital shape and the charge disproportionation are sensitive to the dimension of Mn–O network [148], which together with the possible different role of the JT effect in both compounds poses new interesting questions in the theory.

The controversy about the nature of the charge order in this phase which arose due to signatures of the Zener polarons observed in the neutron data [149] seems to be resolved now in favor of the more conventional picture of zigzag chains and coexisting charge-and-orbital order in the CE phase. Melting of this composite order with increasing temperature is fascinating and the magnetic order disappears first, giving coexisting charge and orbital order in the intermediate temperature regime, before both melt resulting in a disordered phase [150]. This suggests that the link between (weak) charge and orbital order is particularly strong here, similar as in the magnetite below the Verwey transition [11]. Recently, charge ordered AF phase was also reported in La_{1.5}Sr_{0.5}CoO₃, and preliminary theoretical concepts in the framework of spin-orbital physics were presented [151].

Stripe phases appear also in the doped systems with active orbital degrees of freedom, but are qualitatively different from the ones observed in the cuprates, see Sect. 2. Stripe order was found in doped manganites [152] and also discovered in doped La_{2-x}Sr_xNiO₄ nickelates about the same time as in the cuprates [153]. However, in contrast to the cuprates the stripes in La_{5/3}Sr_{1/3}NiO₄ are diagonal and contain one (and not half) hole per unit cell [154]. Intriguing features seen in the spin excitation spectra of La₂NiO_{4+δ} nickelates were reported recently [155] which suggest that the inward dispersion, seen also in cuprates, has a common origin in stripe phases. Simulations performed within the LDA+*U* approach suggest that a subtle interplay between the charge and spin order and octahedral distortions is essential for the formation of an insulating state [156]. Preliminary HF calculations emphasize the importance of orbital degeneracy in the

case of nickelates for the realistic e_g hopping model [157], where one finds indeed that diagonal stripes with the observed filling (of one hole per unit cell) are more stable than other phases, in contrast to the predictions of the degenerate Hubbard model with diagonal hopping (which does not agree with experiment). It remains a challenge for the theory to develop a more complete theory of the stripe phases in the nickelates, including the electron correlations and the coupling of e_g electrons to the lattice distortions, and to understand better differences between the stripe phase in the nickelates and in the cuprates.

7. Summary and open problems

Summarizing, charge order is common in doped transition metal oxides and arises even in absence of intersite Coulomb interactions, while the kinetic energy of doped charges (holes or electron) competes with the magnetic (orbital) superexchange. Under such circumstances stripe phases realized in the cuprates, nickelates, and manganites are favored as then the two above energies are optimized simultaneously — the kinetic energy in the domain walls and the superexchange in the magnetic domains between them. When orbital degrees of freedom are also active, the charge order is accompanied by certain, usually weak, orbital order. Excellent examples of this composite type of charge-and-orbital order are the low temperature phase of Fe₃O₄, and the CE phase in the half-doped manganites.

In the perovskite lattice the orbital order is stabilized easier in the correlated insulators with orbital e_g degrees of freedom than in the ones with the t_{2g} active orbitals, as the superexchange and the JT interaction with the lattice act supporting each other in e_g systems [80], while interactions with the lattice in general compete with the superexchange in t_{2g} systems [100]. As a result, the orbital and magnetic transition occur independently from each other and at quite different temperatures in e_g systems, in contrast to the case of the RVO₃ perovskites providing an example of the proximity and interplay of the magnetic and orbital phase transition. Both these different situations were successfully described within spin-orbital superexchange models with added orbital–lattice interactions.

A qualitative difference between the orbital order in e_g and t_{2g} systems is that the orbital order is more robust in e_g case and may be usually treated by classical (MF) approaches, while t_{2g} orbitals may fluctuate easier and thus couple stronger to the spins. It is for this reason that composite spin-orbital fluctuations occur in correlated titanates and vanadates insulators. Although such fluctuations are quenched in the ground state of these systems for realistic parameters, they develop at increasing temperature due to the presence of excited states with spin-orbital entanglement. For instance, such composite spin-orbital fluctuations are responsible for the temperature dependence of the optical spectral weights in LaVO₃ [82] and trigger spin-orbital dimerization in the

C-AF phase of YVO_3 in the intermediate temperature regime [111]. Similarly interesting phenomena in orbital ordered states are also found in the perovskite ruthenates — as an example we mention here the puzzling low temperature electronic and structural behavior recently discovered in PbRuO_3 [158].

The microscopic mechanism of melting of the orbital order in doped systems is a very challenging problem in the theory and could not be understood until now. The main difficulties follow from disorder and the necessity of using Monte Carlo techniques. In this way it could be concluded that a strong competition between the FM metallic and the AF charge-ordered insulating states takes place [159]. This competition influences the transport properties and leads to short-range spin and charge correlations which evolve with time. It is intriguing to what extent this complex situation in the metallic phase influences the magnetic properties. The magnetic excitations in the metallic FM phase of several doped manganites soften at the zone boundary and may be described by the Heisenberg model with the nearest neighbor J_1 and fourth nearest neighbor J_4 exchange coupling [160]. Its microscopic origin is controversial and two different concepts were proposed to explain the experimental observations: (i) quantum fluctuations of the planar $x^2 - y^2$ orbitals associated with the *A*-AF phase [161], and (ii) the $(3z^2 - r^2)$ -type orbital fluctuations [160]. It was also shown that the ratio of J_4/J_1 changes along the $\text{A}_{1-x}\text{A}'_x\text{MnO}_3$ manganites (with *A* and *A'* being the rare-earth and alkaline rare-earth ions), while the stiffness constant is almost universal and has only very weak dependence on the chemical composition for a fixed doping x [162]. Unfortunately, both theoretical models have difficulties to explain the experimental data — an incorrect dispersion along the (111) direction follows from the first one [161], while the second one predicts a spectacular doping dependence of J_4/J_1 which is not observed. Thus, in spite of the remarkable success of the double exchange supplemented by the superexchange in the orbital liquid phase in the simplest situation [140], satisfactory theoretical explanation of the magnon dispersion in the metallic FM manganites within the microscopic model remains a challenging problem in the theory. Even more puzzling are the magnetic excitations obtained in the insulating FM phase, where several branches with a staircase-like spectrum are observed [163].

Recent studies of the phase diagram of the RMnO_3 manganites include the effect of orthorhombic distortions within theoretical models with spin superexchange and the Dzyaloshinsky–Moriya interaction responsible for the multiferroic behavior [164]. The usual approach so far is to develop an effective spin model including the spin-lattice coupling, leading to the electric polarization [165]. It seems that an explicit treatment of the orbital degrees of freedom could provide here a better understanding of the observed phenomena.

Another active direction of research in the field of transition metal oxides is the search for novel quantum

phenomena, including more examples of quantum spin-orbital entanglement. They could be found in frustrated lattices, and here we mention briefly only the triangular lattice. An interesting case and good candidate for a spin-orbital liquid might be LiNiO_2 with a triangular lattice of Ni^{3+} ions (d^7 configuration with $S = 1/2$ spin and one e_g electron) and no magnetic or orbital order down to very low temperatures. First, it was argued that a model based on symmetry arguments [166], characterized by a large number of low-lying singlets associated to dimer coverings of the triangular lattice, could explain the absence of any type of ordered phase in LiNiO_2 . Second, it was shown that excited states on oxygen ions along the 90° bonds are crucial in the superexchange [167] and they change the balance between different terms in the Hamiltonian, making the orbital interactions stronger than the spin ones [168]. In any case, interplane JT coupling seems to be too weak in LiNiO_2 to stabilize the orbital long-range order, and the microscopic reason of disorder could be alone due to strongly frustrated orbital interactions on the triangular lattice in (111) planes [168], which resemble the compass model. A completely different situation is encountered in the d^1 spin-orbital model with active three t_{2g} orbitals on the triangular lattice, as realized in NaTiO_2 , where a spin-orbital disordered liquid state is more likely [169].

As a final remark, we would like to mention recent experimental studies of Ni-based superlattices [170]. They stimulated progress in the theory which predicts that, in analogy to the gain of kinetic energy in the layered manganites [171], the correlated e_g electrons in the NiO_2 planes develop a planar $(x^2 - y^2)$ -like orbital order in $\text{LaNiO}_3/\text{LaMO}_3$ superlattices (with $M = \text{Al, Gd, Ti}$) [172]. It may be expected that future studies of the systems of reduced dimensionality will provide more unexpected properties in the near future, and could lead to developing functional materials, using both charge and orbital degrees of freedom.

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References

- [1] M. Imada, A. Fujimori, Y. Tokura, *Rev. Mod. Phys.* **70**, 1039 (1998).
- [2] V.I. Anisimov, J. Zaanen, O.K. Andersen, *Phys. Rev. B* **44**, 943 (1991); A.I. Liechtenstein, V.I. Anisimov, J. Zaanen, *Phys. Rev. B* **52**, R5467 (1995); V.I. Anisimov, F. Aryasetiawan, A.I. Liechtenstein, *J. Phys. Condens. Matter* **9**, 767 (1997).
- [3] A. Georges, G. Kotliar, W. Krauth, M.J. Rozenberg, *Rev. Mod. Phys.* **68**, 13 (1996).
- [4] K. Held, *Adv. Phys.* **56**, 829 (2007); K. Held, O.K. Andersen, M. Feldbacher, A. Yamasaki, Y.-F. Yang, *J. Phys. Condens. Matter* **20**, 064202 (2008).
- [5] W. Metzner, D. Vollhardt, *Phys. Rev. Lett.* **62**, 324 (1989).
- [6] *Superconductivity*, Vol. I, *Conventional and Unconventional Superconductors*, Vol. II, *Novel Superconductors*, Eds. K.H. Bennemann, J.B. Ketterson, Springer, Berlin 2008.
- [7] E. Dagotto, T. Hotta, A. Moreo, *Phys. Rep.* **344**, 1 (2001); Y. Tokura, *Rep. Prog. Phys.* **69**, 797 (2006).
- [8] A. Weisse, H. Fehske, *New J. Phys.* **6**, 158 (2004).
- [9] E. Dagotto, *New J. Phys.* **7**, 67 (2005).
- [10] E.J.W. Verwey, *Nature (London)* **144**, 327 (1939).
- [11] P. Piekarczyk, K. Parlinski, A.M. Oleś, *Phys. Rev. Lett.* **97**, 156402 (2006); *Phys. Rev. B* **76**, 165124 (2007).
- [12] P. Piekarczyk, A.M. Oleś, K. Parlinski, *Acta Phys. Pol. A* **118**, 307 (2010).
- [13] I.V. Solovyev, *Phys. Rev. B* **69**, 134403 (2004); *J. Phys. Condens. Matter* **20**, 293201 (2008).
- [14] J. Zaanen, A.M. Oleś, *Phys. Rev. B* **48**, 7197 (1993).
- [15] J.S. Griffith, *The Theory of Transition Metal Ions*, Cambridge University Press, Cambridge 1971.
- [16] P. Korbel, J. Spalek, W. Wójcik, M. Acquarone, *Phys. Rev. B* **52**, R2213 (1995); J. Spalek, E.M. Görllich, A. Rycerz, R. Zahorbeński, *J. Phys. Condens. Matter* **19**, 255212 (2007).
- [17] A.M. Oleś, F. Pfirsch, P. Fulde, M.C. Böhm, *J. Chem. Phys.* **85**, 5183 (1986); *Z. Phys. B* **66**, 359 (1987).
- [18] J. Zaanen, G.A. Sawatzky, J.W. Allen, *Phys. Rev. Lett.* **55**, 418 (1985).
- [19] A.M. Oleś, J. Zaanen, P. Fulde, *Physica B&C* **148**, 260 (1987).
- [20] A.M. Oleś, W. Grzelka, *Phys. Rev. B* **44**, 9531 (1991).
- [21] K. Wohlfeld, A.M. Oleś, G.A. Sawatzky, *Phys. Rev. B* **75**, 180501 (2007).
- [22] J.B. Grant, A.K. McMahan, *Phys. Rev. B* **46**, 8440 (1992).
- [23] J. Hubbard, *Phys. Rev. B* **148**, 260 (1963).
- [24] L.F. Feiner, J.H. Jefferson, R. Raimondi, *Phys. Rev. B* **51**, 12797 (1995); **53**, 8751 (1996); R. Raimondi, J.H. Jefferson, L.F. Feiner, *Phys. Rev. B* **53**, 8774 (1996).
- [25] J.-H. Park, L.H. Tjeng, A. Tanaka, J.W. Allen, P. Metcalf, J.M. Honig, F.M.F. de Groot, G.A. Sawatzky, *Phys. Rev. B* **61**, 11506 (2000); L. Baldassarre, A. Perucchi, D. Nicoletti, A. Toschi, G. Sangiovanni, K. Held, M. Capone, M. Ortolani, L. Malavasi, M. Marsi, P. Metcalf, P. Postorino, S. Lupi, *Phys. Rev. B* **77**, 113107 (2008).
- [26] K. Held, G. Keller, V. Eyert, D. Vollhardt, V.I. Anisimov, *Phys. Rev. Lett.* **86**, 5345 (2001); S. Di Matteo, N.B. Perkins, C.R. Natoli, *Phys. Rev. B* **65**, 054413 (2002); N.B. Perkins, S. Di Matteo, C.R. Natoli, *Phys. Rev. B* **80**, 165106 (2009).
- [27] F. Rodolakis, P. Hansmann, J.-F. Rueff, A. Toschi, M.W. Haverkort, G. Sangiovanni, A. Tanaka, T. Saha-Dasgupta, O.K. Andersen, K. Held, M. Sikora, I. Alliot, J.-P. Itié, F. Baudalet, P. Wzietek, P. Metcalf, M. Marsi, *Phys. Rev. Lett.* **104**, 047401 (2010).
- [28] L.F. Feiner, A.M. Oleś, J. Zaanen, *Phys. Rev. Lett.* **78**, 2799 (1997).
- [29] D.I. Khomskii, M.V. Mostovoy, *J. Phys. A* **36**, 9197 (2003); Z. Nussinov, M. Biskup, L. Chayes, J. van der Brink, *Europhys. Lett.* **67**, 990 (2004).
- [30] A.M. Oleś, G. Khaliullin, P. Horsch, L.F. Feiner, *Phys. Rev. B* **72**, 214431 (2005).
- [31] F.C. Zhang, T.M. Rice, *Phys. Rev. B* **37**, 3759 (1988).
- [32] E. Arrigoni, M. Aichhorn, M. Daghofer, W. Hanke, *New J. Phys.* **11**, 055066 (2009).
- [33] K.A. Chao, J. Spalek, A.M. Oleś, *J. Phys. C* **10**, L271 (1977); *Phys. Rev. B* **18**, 3453 (1978).
- [34] J. Zaanen, A.M. Oleś, *Phys. Rev. B* **37**, 9423 (1988).
- [35] M.A. Kastner, R.J. Birgeneau, G. Shirane, Y. Endoh, *Rev. Mod. Phys.* **70**, 897 (1998).
- [36] S.A. Trugman, *Phys. Rev. B* **37**, 1597 (1988).
- [37] C.L. Kane, P.A. Lee, N. Read, *Phys. Rev. B* **39**, 6880 (1989).
- [38] G. Martínez, P. Horsch, *Phys. Rev. B* **44**, 317 (1991).
- [39] A. Damascelli, Z. Hussain, Z.-X. Shen, *Rev. Mod. Phys.* **75**, 473 (2003).
- [40] B.O. Wells, Z.-X. Shen, A. Matsuura, D.M. King, M.A. Kastner, M. Greven, R.J. Birgeneau, *Phys. Rev. Lett.* **74**, 964 (1995).
- [41] J. Bała, A.M. Oleś, J. Zaanen, *Phys. Rev. B* **52**, 4597 (1995).
- [42] S.A. Kivelson, I.P. Bindloss, E. Fradkin, V. Oganessian, J.M. Tranquada, A. Kapitulnik, C. Howald, *Rev. Mod. Phys.* **75**, 1201 (2003); M. Raczkowski, R. Frésard, A.M. Oleś, *Low Temp. Phys.* **32**, 305 (2006); M. Vojta, *Adv. Phys.* **58**, 699 (2009); P. Wróbel, A.M. Oleś, *Phys. Rev. Lett.* **104**, 206401 (2010).
- [43] J. Zaanen, O. Gunnarsson, *Phys. Rev. B* **40**, 7391 (1989); D. Poilblanc, T.M. Rice, *Phys. Rev. B* **39**, 9749 (1989); M. Kato, K. Machida, H. Nakanishi, M. Fujita, *J. Phys. Soc. Jpn.* **59**, 1047 (1990).
- [44] J.M. Tranquada, B.J. Sternlieb, J.D. Axe, Y. Nakamura, S. Uchida, *Nature (London)* **375**, 561 (1995); J.M. Tranquada, J.D. Axe, N. Ichikawa, Y. Nakamura, S. Uchida, B. Nachumi, *Phys. Rev. B* **54**, 7489 (1996).
- [45] A.M. Oleś, *Acta Phys. Pol. B* **31**, 2963 (2000).

- [46] J. Zaanen, A.M. Oleś, *Ann. Phys. (Leipzig)* **5**, 224 (1996).
- [47] D. Góra, K. Rościszewski, A.M. Oleś, *Phys. Rev. B* **60**, 7429 (1999).
- [48] M. Fleck, A.I. Lichtenstein, E. Pavarini, A.M. Oleś, *Phys. Rev. Lett.* **84**, 4962 (2000).
- [49] M. Fleck, A.I. Lichtenstein, A.M. Oleś, *Phys. Rev. B* **64**, 134528 (2001).
- [50] M. Raczkowski, R. Frésard, A.M. Oleś, *Phys. Rev. B* **73**, 174525 (2006).
- [51] K. Yamada, C.H. Lee, K. Kurahashi, J. Wada, S. Wakimoto, S. Ueki, H. Kimura, Y. Endoh, S. Hosoya, G. Shirane, R.J. Birgeneau, M. Greven, M.A. Kastner, Y.J. Kim, *Phys. Rev. B* **57**, 6165 (1998).
- [52] A. Ino, C. Kim, M. Nakamura, T. Yosida, T. Mizokawa, Z.X. Shen, A. Fujimori, T. Kakeshita, H. Eisaki, S. Uchida, *Phys. Rev. B* **62**, 4137 (2000).
- [53] Z.-X. Shen, W.E. Spicer, D.M. King, D.S. Dessau, B.O. Wells, *Science* **267**, 343 (1995); A. Ino, C. Kim, T. Mizokawa, Z.-X. Shen, A. Fujimori, M. Takaba, K. Tamasaku, H. Eisaki, S. Uchida, *J. Phys. Soc. Jpn.* **68**, 1496 (1999).
- [54] Y. Kohsaka, C. Taylor, K. Fujita, A. Schmidt, C. Lupien, T. Hanaguri, M. Azuma, M. Takano, H. Eisaki, H. Takagi, S. Uchida, J.C. Davis, *Science* **315**, 1380 (2007); J. Zaanen, *Science* **315**, 1372 (2007).
- [55] M. Raczkowski, M. Capello, D. Poilblanc, R. Frésard, A.M. Oleś, *Phys. Rev. B* **76**, 140505 (2007).
- [56] M. Capello, M. Raczkowski, D. Poilblanc, *Phys. Rev. B* **77**, 224502 (2008); M. Raczkowski, D. Poilblanc, *Phys. Rev. Lett.* **103**, 027001 (2009).
- [57] K.I. Kugel, D.I. Khomskii, *Usp. Fiz. Nauk* **136**, 621 (1982).
- [58] C. Castellani, C.R. Natoli, J. Ranninger, *Phys. Rev. B* **18**, 4945 (1978); **18**, 4967 (1978); **18**, 5001 (1978).
- [59] Y. Tokura, N. Nagaosa, *Science* **288**, 462 (2000); G. Khaliullin, *Prog. Theor. Phys. Suppl.* **160**, 155 (2005); A.M. Oleś, *Acta Phys. Pol. A* **115**, 36 (2009).
- [60] *Frustrated Spin Systems*, Ed. H.T. Diep, World Sci., Singapore 2004; P. Fazekas, *Lectures on Electron Correlation and Magnetism*, World Sci., Singapore 1999.
- [61] B. Normand, *Contemporary Phys.* **50**, 533 (2009).
- [62] L. Longa, A.M. Oleś, *J. Phys. A* **13**, 1031 (1980).
- [63] J. van der Brink, P. Horsch, F. Mack, A.M. Oleś, *Phys. Rev. B* **59**, 6795 (1999); J. van den Brink, *New J. Phys.* **6**, 201 (2004).
- [64] J. Dorier, F. Becca, F. Mila, *Phys. Rev. B* **72**, 024448 (2005).
- [65] S. Wenzel, W. Janke, *Phys. Rev. B* **78**, 064402 (2008).
- [66] R. Orús, A.C. Doherty, G. Vidal, *Phys. Rev. Lett.* **102**, 077203 (2009).
- [67] L. Cincio, J. Dziarmaga, A.M. Oleś, arXiv:1001.5457 (2010).
- [68] W. Brzezicki, J. Dziarmaga, A.M. Oleś, *Phys. Rev. B* **75**, 134415 (2007); W. Brzezicki, A.M. Oleś, *Acta Phys. Pol. A* **115**, 162 (2009).
- [69] J.H.H. Perk, H.W. Campel, G.R.W. Quispel, F.W. Nijhoff, *Physica A* **123**, 1 (1984).
- [70] W. Brzezicki, A.M. Oleś, *Phys. Rev. B* **80**, 014405 (2009).
- [71] B. Douçot, M.V. Feigel'baum, L.B. Ioffe, A.S. Ioselovich, *Phys. Rev. B* **71**, 024505 (2005); Z. Nussinov, E. Fradkin, *Phys. Rev. B* **71**, 195120 (2005).
- [72] G. Jackeli, G. Khaliullin, *Phys. Rev. Lett.* **102**, 017205 (2009).
- [73] A. Kitaev, *Ann. Phys. (New York)* **321**, 2 (2006).
- [74] J.B. Goodenough, *Phys. Rev.* **100**, 564 (1955).
- [75] J. Kanamori, *J. Phys. Chem. Solids* **10**, 87 (1959); J.B. Goodenough, *Magnetism and the Chemical Bond*, Interscience, Wiley, New York 1963.
- [76] A.M. Oleś, *Phys. Rev. B* **28**, 327 (1983).
- [77] A.M. Oleś, L.F. Feiner, J. Zaanen, *Phys. Rev. B* **61**, 6257 (2000).
- [78] A.M. Oleś, G. Stollhoff, *Phys. Rev. B* **29**, 314 (1984).
- [79] J. Zaanen, G.A. Sawatzky, *J. Solid State Chem.* **88**, 8 (1990).
- [80] L.F. Feiner, A.M. Oleś, *Phys. Rev. B* **59**, 3295 (1999).
- [81] G. Khaliullin, P. Horsch, A.M. Oleś, *Phys. Rev. Lett.* **86**, 3879 (2001); A.M. Oleś, P. Horsch, G. Khaliullin, *Phys. Rev. B* **75**, 184434 (2007); A.M. Oleś, P. Horsch, *Properties and Applications of Thermoelectric Materials — The Search for New Materials for Thermoelectric Devices*, Eds. V. Zlatic, A.C. Hewson, *NATO Science for Peace and Security Series B: Physics and Biophysics*, Springer, New York 2009, p. 299.
- [82] G. Khaliullin, P. Horsch, A.M. Oleś, *Phys. Rev. B* **70**, 195103 (2004).
- [83] M. Aichhorn, P. Horsch, W. von der Linden, M. Cuoco, *Phys. Rev. B* **65**, 201101 (2002).
- [84] D. Baeriswyl, J. Carmelo, A. Luther, *Phys. Rev. B* **33**, 7247 (1986).
- [85] A.M. Oleś, P. Horsch, L.F. Feiner, G. Khaliullin, *Phys. Rev. Lett.* **96**, 147205 (2006).
- [86] L.F. Feiner, A.M. Oleś, J. Zaanen, *J. Phys. Condens. Matter* **10**, L555 (1998).
- [87] K. Hirota, N. Kaneko, A. Nishizawa, Y. Endoh, *J. Phys. Soc. Jpn.* **65**, 3736 (1996); F. Moussa, M. Hennion, J. Rodríguez-Carvajal, H. Moudden, L. Pinsard, A. Revcolevschi, *Phys. Rev. B* **54**, 15149 (1996); G. Biotteau, M. Hennion, F. Moussa, J. Rodríguez-Carvajal, L. Pinsard, A. Revcolevschi, Y.M. Mukovskii, D. Shulyatev, *Phys. Rev. B* **64**, 104421 (2001).
- [88] J.-S. Zhou, J.B. Goodenough, *Phys. Rev. Lett.* **96**, 247202 (2006).
- [89] N.N. Kovaleva, A.V. Boris, C. Bernhard, A. Kulakov, A. Pimenov, A.M. Balbashov, G. Khaliullin, B. Keimer, *Phys. Rev. Lett.* **93**, 147204 (2004); N.N. Kovaleva, A.M. Oleś, A.M. Balbashov, A. Maljuk, D.N. Argyriou, G. Khaliullin, B. Keimer, *Phys. Rev. B* **81**, 235130 (2010).
- [90] P. Benedetti, R. Zeyher, *Phys. Rev. B* **59**, 9923 (1999).
- [91] A. Yamasaki, M. Feldbacher, Y.-F. Yang, O.K. Andersen, K. Held, *Phys. Rev. Lett.* **96**, 166401 (2006); Y.-F. Yang, K. Held, *Phys. Rev. B* **76**, 212401 (2007).

- [92] C. Ederer, C. Lin, A.J. Millis, *Phys. Rev. B* **76**, 155105 (2007).
- [93] S. Miyasaka, Y. Okimoto, M. Iwama, Y. Tokura, *Phys. Rev. B* **68**, 100406 (2003).
- [94] S. Miyasaka, J. Fujioka, M. Iwama, Y. Okimoto, Y. Tokura, *Phys. Rev. B* **73**, 224436 (2006).
- [95] Y.Q. Li, M. Ma, D.N. Shi, F.C. Zhang, *Phys. Rev. Lett.* **81**, 3527 (1998).
- [96] B. Frischmuth, F. Mila, M. Troyer, *Phys. Rev. Lett.* **82**, 835 (1999); F. Mila, B. Frischmuth, A. Deppeler, M. Troyer, *Phys. Rev. Lett.* **82**, 3697 (1999).
- [97] G. Khaliullin, S. Maekawa, *Phys. Rev. Lett.* **85**, 3950 (2000); G. Khaliullin, *Phys. Rev. B* **64**, 212405 (2001).
- [98] C. Itoi, S. Qin, I. Affleck, *Phys. Rev. B* **61**, 6747 (2000).
- [99] A.M. Oleś, P. Horsch, G. Khaliullin, *Phys. Status Solidi B* **244**, 3478 (2007).
- [100] P. Horsch, A.M. Oleś, L.F. Feiner, G. Khaliullin, *Phys. Rev. Lett.* **100**, 167205 (2008).
- [101] M. Raczkowski, A.M. Oleś, *Phys. Rev. B* **66**, 094431 (2002).
- [102] E. Pavarini, Y. Yamasaki, J. Nuss, O.K. Andersen, *New J. Phys.* **7**, 188 (2005).
- [103] M. Reehuis, C. Ulrich, P. Pattison, B. Oulad-diaf, M.C. Rheinstädter, M. Ohl, L.P. Regnault, M. Miyasaka, Y. Tokura, B. Keimer, *Phys. Rev. B* **73**, 094440 (2006).
- [104] M.H. Sage, G.R. Blake, G.J. Nieuwenhuys, T.T.M. Palstra, *Phys. Rev. Lett.* **96**, 036401 (2006); M.H. Sage, G.R. Blake, C. Marquina, T.T.M. Palstra, *Phys. Rev. B* **96**, 195102 (2007).
- [105] M. De Raychaudhury, E. Pavarini, O.K. Andersen, *Phys. Rev. Lett.* **99**, 126402 (2007).
- [106] T.N. DeSilva, A. Joshi, M. Ma, F.C. Zhang, *Phys. Rev. B* **68**, 184402 (2003).
- [107] J.-S. Zhou, J.B. Goodenough, J.-Q. Yan, Y. Ren, *Phys. Rev. Lett.* **99**, 156401 (2007).
- [108] C. Ulrich, G. Khaliullin, J. Sirker, M. Reehuis, M. Ohl, S. Miyasaka, Y. Tokura, B. Keimer, *Phys. Rev. Lett.* **91**, 257203 (2003).
- [109] S. Miyasaka, Y. Okimoto, Y. Tokura, *J. Phys. Soc. Jpn.* **71**, 2086 (2002).
- [110] Y. Ren, T.T.M. Palstra, D.I. Khomskii, E. Pellegrin, A.A. Nugroho, A.A. Menovsky, G.A. Sawatzky, *Nature* **396**, 441 (1998); Y. Ren, T.T.M. Palstra, D.I. Khomskii, A.A. Nugroho, A.A. Menovsky, G.A. Sawatzky, *Phys. Rev. B* **62**, 6577 (2000).
- [111] P. Horsch, G. Khaliullin, A.M. Oleś, *Phys. Rev. Lett.* **91**, 257203 (2003).
- [112] J. Sirker, G. Khaliullin, *Phys. Rev. B* **67**, 100408 (2003).
- [113] J. Sirker, A. Herzog, A.M. Oleś, P. Horsch, *Phys. Rev. Lett.* **101**, 157204 (2008).
- [114] D.C. Johnston, R.K. Kremer, M. Troyer, X. Wang, A. Klümper, S.L. Budko, A.F. Panchula, P.C. Canfield, *Phys. Rev. B* **61**, 9558 (2001).
- [115] M. Hase, I. Terasaki, K. Uchinokura, *Phys. Rev. Lett.* **70**, 3651 (1993).
- [116] S.-Q. Shen, X.C. Xie, F.C. Zhang, *Phys. Rev. Lett.* **88**, 027201 (2001); A.M. Oleś, P. Horsch, G. Khaliullin, *Acta Phys. Pol. B* **34**, 857 (2002).
- [117] L.N. Bulaevski, E.L. Nagaev, D.I. Khomskii, *Sov. Phys. JETP* **27**, 836 (1968).
- [118] J. Zaanen, A.M. Oleś, P. Horsch, *Phys. Rev. B* **46**, 5798 (1992).
- [119] M. Daghofer, A.M. Oleś, *Acta Phys. Pol. A* **111**, 497 (2007).
- [120] J. van den Brink, P. Horsch, A.M. Oleś, *Phys. Rev. Lett.* **85**, 5174 (2000).
- [121] M. Daghofer, K. Wohlfeld, A.M. Oleś, E. Arrigoni, P. Horsch, *Phys. Rev. Lett.* **100**, 066403 (2008); K. Wohlfeld, M. Daghofer, A.M. Oleś, P. Horsch, *Phys. Rev. B* **78**, 214423 (2008); K. Wohlfeld, A.M. Oleś, M. Daghofer, P. Horsch, *Acta Phys. Pol. A* **115**, 110 (2009).
- [122] P. Wróbel, W. Suleja, R. Eder, *Phys. Rev. B* **78**, 064501 (2008).
- [123] K. Wohlfeld, A.M. Oleś, P. Horsch, *Phys. Rev. B* **79**, 224433 (2009).
- [124] F. Krüger, S. Kumar, J. Zaanen, J. van den Brink, *Phys. Rev. B* **79**, 054504 (2009).
- [125] J. Fujioka, S. Miyasaka, Y. Tokura, *Phys. Rev. Lett.* **97**, 196401 (2006).
- [126] J. Fujioka, S. Miyasaka, Y. Tokura, *Phys. Rev. B* **77**, 144402 (2008).
- [127] S. Ishihara, *Phys. Rev. Lett.* **94**, 156408 (2005).
- [128] K. Wohlfeld, A.M. Oleś, *Phys. Status Solidi B* **243**, 142 (2006).
- [129] J. van den Brink, D. Khomskii, *Phys. Rev. Lett.* **96**, 1016 (1999).
- [130] P. Schiffer, A.P. Ramirez, W. Bao, S.-W. Cheong, *Phys. Rev. Lett.* **75**, 3336 (1995).
- [131] C.D. Ling, J.E. Millburn, J.F. Mitchell, D.N. Argyriou, J. Linton, H.N. Bordallo, *Phys. Rev. B* **62**, 15096 (2000).
- [132] M. Daghofer, A.M. Oleś, W. von der Linden, *Phys. Rev. B* **70**, 184430 (2004).
- [133] M. Daghofer, A.M. Oleś, D.M. Neuber, W. von der Linden, *Phys. Rev. B* **73**, 104451 (2006).
- [134] K. Rościszewski, A.M. Oleś, *J. Phys. Condens. Matter* **19**, 186223 (2007); **20**, 365212 (2008).
- [135] A. Gössling, M.W. Haverkort, M. Benomar, H. Wu, D. Senff, T. Möller, M. Braden, J.A. Mydosh, M. Grüninger, *Phys. Rev. B* **77**, 035109 (2008).
- [136] M. Stier, W. Nolting, *Phys. Rev. B* **75**, 144409 (2007).
- [137] M. Stier, W. Nolting, *Phys. Rev. B* **78**, 144425 (2008).
- [138] L.F. Feiner, A.M. Oleś, *Phys. Rev. B* **71**, 144422 (2005).
- [139] T.G. Perring, G. Aeppli, S.M. Hayden, S.A. Carter, J.P. Remeika, S.-W. Cheong, *Phys. Rev. Lett.* **77**, 711 (1996).
- [140] A.M. Oleś, L.F. Feiner, *Phys. Rev. B* **65**, 052414 (2002).
- [141] A.M. Oleś, L.F. Feiner, *Phys. Rev. B* **67**, 092407 (2003).

- [142] T.G. Perring, D.T. Adroja, G. Chaboussant, G. Aeppli, T. Kimura, Y. Tokura, *Phys. Rev. Lett.* **87**, 217201 (2001).
- [143] J. van den Brink, G. Khaliullin, D. Khomskii, *Phys. Rev. Lett.* **83**, 5118 (1999).
- [144] L. Brey, *Phys. Rev. B* **75**, 104423 (2007).
- [145] H. Aliaga, D. Magnoux, A. Moreo, D. Poilblanc, S. Yunoki, E. Dagotto, *Phys. Rev. B* **68**, 104405 (2003); M. Cuoco, C. Noce, A.M. Oleś, *Phys. Rev. B* **66**, 094427 (2002).
- [146] J. Bała, P. Horsch, F. Mack, *Phys. Rev. B* **69**, 094415 (2004); J. Bała, P. Horsch, *Phys. Rev. B* **72**, 012404 (2005).
- [147] T. Hotta, Y. Takada, H. Koizumi, E. Dagotto, *Phys. Rev. Lett.* **84**, 2477 (2000).
- [148] D. Okuyama, Y. Tokunaga, R. Kumai, Y. Taguchi, T. Arima, Y. Tokura, *Phys. Rev. B* **80**, 064402 (2009).
- [149] A. Daoud-Aladine, J. Rodríguez-Carvajal, L. Pinsard-Gaudart, M.T. Fernández-Díaz, A. Revcolevschi, *Phys. Rev. Lett.* **89**, 097205 (2002).
- [150] D. Senff, F. Krüger, S. Scheidl, M. Benomar, Y. Sidis, F. Demmel, M. Braden, *Phys. Rev. Lett.* **96**, 257201 (2006); D. Senff, O. Schumann, M. Benomar, M. Kriener, T. Lorenz, Y. Sidis, K. Habicht, P. Link, M. Braden, *Phys. Rev. B* **77**, 184413 (2008).
- [151] L.M. Helme, A.T. Boothroyd, R. Coldea, D. Prabhakaran, C.D. Frost, D.A. Keen, L.P. Regnault, P.G. Freeman, M. Enderle, J. Kulda, *Phys. Rev. B* **80**, 134414 (2009).
- [152] S. Mori, C.H. Chen, S.-W. Cheong, *Nature* **392**, 473 (1998); S. Dong, R. Yu, J.-M. Liu, E. Dagotto, *Phys. Rev. Lett.* **103**, 107204 (2009).
- [153] J.M. Tranquada, D.J. Buttrey, V. Sachan, J.E. Lorenzo, *Phys. Rev. Lett.* **73**, 1003 (1994); J.M. Tranquada, J.E. Lorenzo, D.J. Buttrey, V. Sachan, *Phys. Rev. B* **52**, 3581 (1995).
- [154] S. Wakimoto, H. Kimura, K. Ishii, K. Ikeuchi, T. Adachi, M. Fujita, K. Kakurai, Y. Koike, J. Mizuki, Y. Noda, K. Yamada, A.H. Said, Yu. Shvyd'ko, *Phys. Rev. Lett.* **102**, 157001 (2009).
- [155] P.G. Freeman, M. Enderle, S.M. Hayden, C.D. Frost, D.X. Yao, E.W. Carlson, D. Prabhakaran, A.T. Boothroyd, *Phys. Rev. B* **80**, 144523 (2009).
- [156] U. Schwingenschlögl, C. Schuster, R. Frésard, *Europhys. Lett.* **81**, 27002 (2008); *Ann. Phys. (Berlin)* **18**, 107 (2009).
- [157] M. Raczkowski, R. Frésard, A.M. Oleś, *Phys. Rev. B* **73**, 094429 (2006).
- [158] S.A.J. Kimber, J.A. Rodgers, H. Wu, C.A. Murray, D.N. Argyriou, A.N. Fitch, D.I. Khomskii, J.P. Attfield, *Phys. Rev. Lett.* **102**, 046409 (2009).
- [159] R. Yu, S. Dong, C. Şen, G. Alvarez, E. Dagotto, *Phys. Rev. B* **77**, 214434 (2008).
- [160] Y. Endoh, H. Hiraka, Y. Tomioka, Y. Tokura, N. Nagaosa, T. Fujiwara, *Phys. Rev. Lett.* **94**, 017206 (2005).
- [161] G. Khaliullin, R. Kilian, *Phys. Rev. B* **61**, 3494 (2000).
- [162] F. Ye, P. Dai, J.A. FernandezBaca, H. Sha, J.W. Lynn, H. Kawano-Fujiwara, Y. Tomioka, Y. Tokura, J. Zhang, *Phys. Rev. Lett.* **96**, 047206 (2006).
- [163] S. Petit, M. Hennion, F. Moussa, D. Lamago, A. Ivanov, Y.M. Mukovskii, D. Shulyatev, *Phys. Rev. Lett.* **102**, 207201 (2009).
- [164] M. Mochizuki, N. Furukawa, *Phys. Rev. B* **80**, 134416 (2009).
- [165] M. Mostovoy, *Phys. Rev. Lett.* **96**, 067601 (2006); I.A. Sergienko, E. Dagotto, *Phys. Rev. B* **73**, 094434 (2006).
- [166] F. Vernay, K. Penc, P. Fazekas, F. Mila, *Phys. Rev. B* **70**, 014428 (2004); F. Vernay, A. Ralko, F. Becca, F. Mila, *Phys. Rev. B* **74**, 054402 (2006); F. Mila, F. Vernay, A. Ralko, F. Becca, P. Fazekas, K. Penc, *J. Phys. Condens. Matter* **19**, 145201 (2007).
- [167] M.V. Mostovoy, D.I. Khomskii, *Phys. Rev. Lett.* **89**, 227203 (2002).
- [168] A.J.W. Reitsma, L.F. Feiner, A.M. Oleś, *New J. Phys.* **7**, 121 (2005).
- [169] B. Normand, A.M. Oleś, *Phys. Rev. B* **78**, 094427 (2008).
- [170] J. Chakhalian, J.W. Freeland, G. Srajer, J. Strempler, G. Khaliullin, J.C. Cezar, T. Charlton, R. Dalgliesh, C. Bernhard, G. Cristiani, H.U. Habermeier, B. Keimer, *Nat. Phys.* **2**, 244 (2006).
- [171] F. Mack, P. Horsch, *Phys. Rev. Lett.* **82**, 3160 (1999).
- [172] J. Chaloupka, G. Khaliullin, *Phys. Rev. Lett.* **100**, 016404 (2008).