Finding true Kugel-Khomskii systems

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Crystal structure and magnetic properties of substances with orbital degeneracy

K. I. Kugel' and D. I. Khomskii
P. N. Lebedev Physics Institute
(Submitted November 13, 1972)
Zh. Eksp. Teor. Fiz. 64, 1429-1439 (April 1973)

Exchange interaction in magnetic substances containing ions with orbital degeneracy is considered. It is shown that, among with spin ordering, superexchange also results in cooperative ordering of Jahn-Teller ion orbitals, which, generally speaking, occurs at a higher temperature and is accompanied by distortion of the lattice (which is a secondary effect here). Concrete studies are performed for substances with a perovskite structure (KCuF$_3$, LaMnO$_3$, MnF$_3$). The effective spin Hamiltonian is obtained for these substances and the properties of the ground state are investigated. The orbital and magnetic structures obtained in this way without taking into account interaction with the lattice are in accord with the structures observed experimentally. The approach employed also permits one to explain the strong anisotropy of the magnetic properties of these compounds and to obtain a reasonable estimate for the critical temperatures.
50 years of Kugel-Khomskii model

\[ H = - \sum_{imjm'\sigma} t_{imjm'} c_{im\sigma}^{\dagger} c_{jm'\sigma} + U \sum_{im\sigma jm'\sigma'} n_{im\sigma} n_{jm'\sigma'} \]

perturbation \( t/U \)

super-exchange Hamiltonian

\[ J \propto \frac{t^2}{U} \]

\[ H = J_{SS} S_1 \cdot S_2 + J_{OO} \tau_1 \tau_2 + J_{SO} [\tau_1 S_2 + \tau_2 S_1] \]

\( \tau \): pseudospins in orbital space

order without distortions

no static crystal-field splitting
Orbital Physics in Transition-Metal Oxides

Y. Tokura and N. Nagaosa

An electron in a solid, that is, bound to or nearly localized on the specific atomic site, has three attributes: charge, spin, and orbital. The orbital represents the shape of the electron cloud in solid. In transition-metal oxides with anisotropic-shaped d-orbital electrons, the Coulomb interaction between the electrons (strong electron correlation effect) is of importance for understanding their metal-insulator transitions and properties such as high-temperature superconductivity and colloidal magnetoresistance. The orbital degree of freedom occasionally plays an important role in these phenomena, and its correlation and/or order-disorder transition causes a variety of phenomena through strong coupling with charge, spin, and lattice dynamics. An overview is given here on this "orbital physics," which will be a key concept for the science and technology of correlated electrons.

When more than two orbitals are involved, a variety of situations can be realized, and this quantum mechanical process depends on the orbitals (4,5). In this way, the spin S and the orbital pseudospin T are coupled. In more general cases, the transfer integral \( t_{a} \) depends on the direction of the pair of the two orbitals (\( 1/2 \text{ and } 3/2 \). This gives \( S_{z} \) well as in the real sp transfer integral between Mn atoms in the crystal.

Electronic reconstruction at an interface between a Mott insulator and a band insulator

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Surface science is an important and well-established branch of materials science involving the study of changes in material...
Orbital Liquid in Three-Dimensional Mott Insulator: LaTiO₃

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(Received 5 June 2000)

We present a theory of spin and orbital states in Mott insulator LaTiO₃. The spin-orbital superexchange interaction between $d^1(t_{2g})$ ions in cubic crystal suffers from a pathological degeneracy of orbital states at the classical level. Quantum effects remove this degeneracy and result in the formation of the coherent ground state, in which the orbital moment of $t_{2g}$ level is fully quenched. We find a finite gap for orbital excitations. Such a disordered state of local degrees of freedom on unfrustrated, simple cubic lattice is highly unusual. Orbital liquid state naturally explains observed anomalies of LaTiO₃.
Superexchange Interaction in Orbitally Fluctuating $\text{RVO}_3$

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Changes in pressure and magnetic field in the orbital and magnetic ordering temperatures of $\text{RVO}_3$ perovskites are reported; they reveal a competition between two magnetic orbitally ordered phases that have opposite preferences for the $e$-orbital component in the localized $3T_{1g}$ ground state of the V$^{3+}$ ion. This competition is shown to be biased by the VO$_{6/2}$ site distortion intrinsic to the orthorhombic structure. A remarkable enhancement of $T_N$ with pressure is found where the competition leads to enhanced orbital critical fluctuations.

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TOPICAL REVIEW

Fingerprints of spin–orbital entanglement in transition metal oxides

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Optical Stabilization of Fluctuating High Temperature Ferromagnetism in YTiO$_3$

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In quantum materials, degeneracies and frustrated interactions can have a profound impact on the emergence of long-range order, often driving strong fluctuations that suppress functionally relevant electronic or magnetic phases. Engineering the atomic structure in the bulk or at heterointerfaces has been an important research strategy to lift these degeneracies, but these equilibrium methods are limited by thermodynamic, elastic, and chemical constraints. Here, we show that all-optical, mode-selective manipulation of the crystal lattice can be used to enhance and stabilize high-temperature ferromagnetism in YTiO$_3$, a material that exhibits only partial orbital polarization, an unsaturated low-temperature magnetic moment, and a suppressed Curie temperature, $T_c = 27$ K.
50 years of Kugel-Khomskii model

Crystal structure and magnetic properties of substances with orbital degeneracy

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Exchange interaction in magnetic substances containing ions with orbital degeneracy is considered. It is shown that, among with spin ordering, superexchange also results in cooperative ordering of Jahn-Teller ion orbitals, which, generally speaking, occurs at a higher temperature and is accompanied by distortion of the lattice (which is a secondary effect here). Concrete studies are performed for substances with a perovskite structure (KCuF₃, LaMnO₃, MnF₃). The effective spin Hamiltonian is obtained for these substances and the properties of the ground state are investigated. The orbital and magnetic structures obtained in this way without taking into account interaction with the lattice are in accord with the structures observed experimentally. The approach employed also permits one to explain the strong anisotropy of the magnetic properties of these compounds and to obtain a reasonable estimate for the critical temperatures.
where is the evidence?

co-operative Jahn-Teller distortion

partially field $e_g$ levels

$KCuF_3$

$t_{2g}^6e_g^3$

The Normal Mode
$Q_2 (Q_2 > 0)$

$Q_2$ mode
the hallmark of orbital order

co-operative Jahn-Teller distortion

partially field $e_g$ levels
Jahn-Teller: splitting generates order

Crystal Distortion in Magnetic Compounds

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The crystal distortion which arises from the Jahn-Teller effect is discussed in several examples. In the case of compounds containing Cu$^{2+}$ or Mn$^{3+}$ at octahedral sites, the lowest orbital level of these ions is doubly degenerate in the undistorted structure, and there is no spin-orbit coupling in this level. It is shown that, introducing a fictitious spin to specify the degenerate orbital states, we can discuss the problem by analogy with the magnetic problems. The “ferromagnetic” and “antiferromagnetic” distortions are discussed in detail. The transition from the distorted to the undistorted structure is of the first kind for the former and of the second kind for the latter. Higher approximations are discussed briefly. In compounds like FeO, CoO, and CuCrO$_4$, the lowest orbital level is triply degenerate, and the spin-orbit coupling is present in this level. In this case the distortion is dependent on the magnitude of the spin-orbit coupling relative to the strength of the Jahn-Teller effect term. The distortion at absolute zero temperature and its temperature dependence are discussed.

static crystal-field splitting

\[ H = -g\sqrt{C}(\tau_z Q_3 + \tau_x Q_2) \]

\( \tau : \) pseudospins in orbital space

\[ E_0 + \Delta/2 \quad \Delta \quad E_0 - \Delta/2 \quad \theta \]

\[ |\theta\rangle = \sin \frac{\theta}{2} |3z^2 - 1\rangle + \cos \frac{\theta}{2} |x^2 - y^2\rangle \]

The Normal Mode
\[ Q_2 (Q_2 > 0) \]
a chicken-and-egg problem

Jahn-Teller

Kugel-Khomskii

how to disentangle the two?
The situation changes drastically if we allow for orbital polarization. Because $U$ exceeds the bandwidth, the orbital sector is already strongly polarized (as are the spins) before the lattice is allowed to react. Overlooking some unimportant details concerning the coherence of the intermediate states, the well-known rule that electronic MFT in strong coupling maps onto the classical "spin" problem holds also in this case. In other words, we find the quadrupolar orbital-ferromagnetic spin phase to be most stable (for the same reasons as Kugel and Khomskii$^{6}$). Obviously the cubic lattice is unstable in the presence of this orbital order parameter. In fact, despite large-scale changes in the electronic system the deformation is modest, indicating a rather weak electron-phonon coupling.
KCuF$_3$

$T_N \sim 40 \, K \ll T_{OO} \sim 1400 \, K$?
orbital-order transition at $T_{O0}$ in LaMnO$_3$

$T_{O0} \sim 800$ K

Resonant X-Ray Scattering from Orbital Ordering in LaMnO$_3$


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something not quite right

$KCuF_3$

$T_N \approx 40\ K \ll T_{OO} \approx 1400\ K$?

$LaMnO_3$

$T_N \approx 140\ K \ll T_{OO} \approx 800\ K$?
50 years of Kugel and Khomskii model

\[ H = -\sum_{imjm'} t_{imjm'} c_{im\sigma}^\dagger c_{jm'\sigma} + U \sum_{im\sigma jm'\sigma'} n_{im\sigma} n_{jm'\sigma'} \]

super-exchange Hamiltonian

perturbation \( t/U \) \[ J \propto \frac{t^2}{U} \]

\[ H = J_{SS} S_1 \cdot S_2 + J_{OO} \tau_1 \tau_2 + J_{SO} [\tau_1 S_2 + \tau_2 S_1] \]

\( \tau \): pseudospins in orbital space

order without distortions

no static crystal-field splitting
LDA+DMFT with Wannier functions

\[
H = - \sum_{ii'} \sum_{mm'} \sum_{\sigma} t_{mm'}^{ii'} c_{im\sigma}^{\dagger} c_{i'm'\sigma} + U \sum_{im} n_{im\uparrow} n_{im\downarrow} + \frac{1}{2} \sum_{im \neq m' \sigma' \sigma} (U - 2J - J \delta_{\sigma\sigma'}) n_{im\sigma} n_{im'\sigma'} - J \sum_{m \neq m'} (c_{m\uparrow}^{\dagger} c_{m' \downarrow}^{\dagger} c_{m' \uparrow} c_{m \downarrow} + c_{m\uparrow}^{\dagger} c_{m' \downarrow}^{\dagger} c_{m' \downarrow} c_{m \uparrow})
\]

\[
G_{m,m'} = \sum_{k,n} \left[ \frac{1}{i\omega_n + \mu - H_{0k} - \Sigma(i\omega_n)} \right]_{m,m'}
\]
LDA+DMFT with Wannier functions

\[
H = - \sum_{ii'} \sum_{mm'} \sum_{\sigma} t_{mm'}^{ii'} c_{i m \sigma}^\dagger c_{i' m' \sigma} + U \sum_{im} n_{im \uparrow} n_{im \downarrow} + \frac{1}{2} \sum_{im \neq m' \sigma \sigma'} (U - 2J - J \delta_{\sigma \sigma'}) n_{im \sigma} n_{im' \sigma'} - J \sum_{m \neq m'} (c_{m \uparrow}^\dagger c_{m \downarrow}^\dagger c_{m' \uparrow} c_{m' \downarrow} + c_{m \uparrow}^\dagger c_{m \downarrow} c_{m' \uparrow}^\dagger c_{m' \downarrow})
\]

DMFT and cDMFT

quantum impurity solvers:
- general HF QMC
- general CT-INT QMC
- general CT-HYB QMC

- A. Flesch, E. Gorelov, E. Koch and E. Pavarini
the KK mechanism in $e_g^3$ KCuF$_3$

\[ p = n_1 - n_2 \]


\[ T_{KK} \ll T_{OO} > 1400 \text{ K} \]

LDA+DMFT

reminder: mean field theory overestimates $T_{KK}$
but also JT alone is not the full story

\[ \text{KCuF}_3 \]
\[ T_N \sim 40 \text{ K} \ll T_{OO} \sim 1400 \text{ K} ? \]

\[ \text{LaMnO}_3 \]
\[ T_N \sim 140 \text{ K} \ll T_{OO} \sim 800 \text{ K} ? \]
Unusual structural evolution in KCuF$_3$ at high temperatures by neutron powder diffraction


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excellent agreement with GGA+U

$U=7$ eV, $J=0.9$ eV
magnetic state does not matter for $\delta$
but para gives extremely shallow minimum

$$\delta = \frac{1}{2} \frac{l - s}{l + s}$$

(exp AF GGA+U
para GGA+U)

(same result of GGA+DMFT)
GGA+U energy curve

U=7.0 J=0.9

6E\text{tot} \ s_{\text{Cu-F}} \text{ in Å}

5 K, 300 K, 603 K, 903 K

(same result of GGA+DMFT)
effects of distortion: a simple model

\[ E_{\text{ionJT}}(\Delta) = \Gamma - \sqrt{\Gamma^2 + (g \Delta)^2} - C_{\text{Ewald}} \Delta^2 / 2 + 2Be^{-a/\rho^2\sqrt{2}}[\cosh(\Delta/\rho) - 1], \]

- change in \( e_g \) crystal-field splitting
- change in Ewald term
- Born-Mayer potential
Landau theory describes phase transitions as the competition between energy and entropy: The ordered phase has lower energy, while the disordered phase has larger entropy. When heating the system, ordering is reduced entropically until it vanishes at the critical temperature. This picture implicitly assumes that the energy difference between the ordered and disordered phases does not change with temperature. We show that for orbital ordering in the Mott insulator KCuF$_3$, this assumption fails qualitatively: entropy plays a negligible role, while thermal expansion energetically stabilizes the orbitally ordered phase to such an extent that no phase transition is observed. To understand this strong dependence on the lattice constant, we need to take into account the Born-Mayer repulsion between the ions. It is the latter, and not the Jahn-Teller elastic energy, which determines the magnitude of the distortion. This effect will be seen in all materials where the distortion expected from the Jahn-Teller mechanism is so large that the ions would touch. Our mechanism explains not only the absence of a phase transition in KCuF$_3$, but even suggests the possibility of an \textit{inverted} transition in closed-shell systems, where the ordered phase emerges only at high temperatures.
Kugel-Khomskii candidates

$K\text{CuF}_3$

$t_{2g}^6e_g^3$

$\text{LaMnO}_3$

$t_{2g}^3e_g^1$
orbital-order transition at $T_{oo}$ in $\text{LaMnO}_3$

$T_{oo} \sim 800 \text{ K}$

Resonant X-Ray Scattering from Orbital Ordering in $\text{LaMnO}_3$


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Neutron-diffraction study of the Jahn-Teller transition in stoichiometric $\text{LaMnO}_3$

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The parent compound of the giant magnetoresistance Mn-perovskite $\text{LaMnO}_3$, has been studied by thermal analysis and high-resolution neutron powder diffraction. The orthorhombic $Pbnm$ structure at room temperature is characterized by an antiferrodistorsive orbital ordering due to the Jahn-Teller effect. This ordering is evidenced by the spatial distribution of the observed Mn-O bond lengths. $\text{LaMnO}_3$ undergoes a structural phase transition at $T_N \sim 750 \text{ K}$, above which the orbital ordering disappears. There is no change in symmetry although the lattice becomes metrically cubic on the high-temperature side. The MnO$_6$ octahedra become nearly regular above $T_N$ and the thermal parameter of oxygen atoms increases significantly. The observed average cubic lattice is probably the result of dynamic spatial fluctuations of the underlying orthorhombic distortion. [S0163-1829(98)51706-7]
LaMnO$_3$ : $T_{KK} \sim 600$ K !!

$$|\theta\rangle = \sin \frac{\theta}{2} |3z^2 - 1\rangle + \cos \frac{\theta}{2} |x^2 - y^2\rangle$$

**Experiments**
- red: cDMFT 4 sites
- black: DMFT

**Super-exchange**
- non-JT crystal-field

**Figures**
- $I_0$: ideal cubic
- $R_0$: real but no JT
- $R_{6}$, $R_{11}$
- $R_{800K}$, $R_{2.4}$
Orbital Correlations in the Pseudocubic $O$ and Rhombohedral $R$ Phases of LaMnO$_3$

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The local and intermediate structure of stoichiometric LaMnO$_3$ has been studied in the pseudocubic and rhombohedral phases at high temperatures (300–1150 K). Neutron powder diffraction data were collected and a combined Rietveld and high real space resolution atomic pair distribution function analysis was carried out. The nature of the Jahn-Teller (JT) transition around 750 K is confirmed to be orbital order to disorder. In the high-temperature orthorhombic ($O$) and rhombohedral ($R$) phases, the MnO$_6$ octahedra are still fully distorted locally. More importantly, the intermediate structure suggests the presence of local ordered clusters of diameter $\sim$16 Å ($\sim$4 MnO$_6$ octahedra) implying strong nearest-neighbor JT antiferrodistortive coupling. These clusters persist well above the JT transition temperature even into the high-temperature $R$ phase.

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$T_{OO} \sim 800 \, K$

$T_{JT} > 1150 \, K$
Unusual Evolution of the Magnetic Interactions versus Structural Distortions in RMnO$_3$ Perovskites

J.-S. Zhou and J. B. Goodenough

Uniaxial pressure experimental phase diagram of RMnO$_3$ perovskites. The diagram shows the phase transitions and structural distortions as a function of temperature and pressure. The JT transition is indicated by a blue line, and the IMT (Insulator-Metal Transition) by a green line. The perovskites are orthorhombic at low pressures, but the structure transforms into a double distortions (DD) phase at higher pressures. The JT active directions are marked by blue arrows, and the samples are denoted by symbols.
KK critical temperatures

$T_{KK}$ decreases with IR

$T_{00}$ in experiments

$T_{KK}$ from orbital polarization

$T_{KK}$ from total energy


Kugel-Khomskii candidates

e_g systems

KCuF$_3$

$\text{KCrF}_3$

LaMnO$_3$

ReMnO$_3$

$t_{2g}^6e_g^3$

$t_{2g}^3e_g^1$
perhaps we looked in the wrong place..

t$_{2g}$ titanates at low temperature?

larger orbital degeneracy, smaller electron-lattice coupling, smaller crystal-field coupling
Orbital Liquid in Three-Dimensional Mott Insulator: LaTiO$_3$

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(Received 5 June 2000)

We present a theory of spin and orbital states in Mott insulator LaTiO$_3$. The spin-orbital superexchange interaction between $d^1(t_{2g})$ ions in cubic crystal suffers from a pathological degeneracy of orbital states at the classical level. Quantum effects remove this degeneracy and result in the formation of the coherent ground state, in which the orbital moment of $t_{2g}$ level is fully quenched. We find a finite gap for orbital excitations. Such a disordered state of local degrees of freedom on unfrustrated, simple cubic lattice is highly unusual. Orbital liquid state naturally explains observed anomalies of LaTiO$_3$.

$d^1$ electronic configuration
Coulomb-enhanced crystal field

Mott Transition and Suppression of Orbital Fluctuations in Orthorhombic 3d¹ Perovskites

E. Pavarini, S. Biermann, A. Poteryaev, A. I. Lichtenstein, A. Georges, and O. K. Andersen

LaTiO₃

YTiO₃

t₂g¹

LDA+DMFT 770 K

Δ=200-300 meV
but what about low T, right above $T_N$?
change of orbitals at low T?

$\psi_{KK}$

$\Delta \varepsilon_{CF} \gg T_{KK}$

$\psi_{CF}$

$\Delta \varepsilon_{CF} < T_{KK}$

KK

CF

$\Delta \varepsilon_{CF} \ll T_{KK}$

$\psi^*$

Orbital

$T_{KK}$

$T_N$

$T_{KK}$

$T$

$\psi$ = occupied orbital
Origin of orbital ordering in YTiO$_3$ and LaTiO$_3$

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The origin of orbital order in correlated transition-metal compounds is strongly debated. For the paradigmatic $e_g$ systems KCuF$_3$ and LaMnO$_3$, it has been shown that the electronic Kugel’-Khomskii mechanism alone is not sufficient to drive the orbital-ordering transition up to the high temperatures at which it is experimentally observed. In the case of $t_{2g}$ compounds, however, the role played by the superexchange interaction remains unclear. Here we investigate this question for two representative systems, the 3$d$ $t_{2g}$ Mott insulators LaTiO$_3$ and YTiO$_3$. We show that the Kugel’-Khomskii superexchange transition temperature $T_{KK}$ is unexpectedly large, comparable to the value for the $e_g^3$ fluoride KCuF$_3$. By deriving the general form of the orbital superexchange Hamiltonian for the $t_{2g}$ configuration, we show that the GdFeO$_3$-type distortion plays a key part in enhancing $T_{KK}$ to about 300 K. Still, orbital ordering above 300 K can be ascribed only to the presence of a static crystal-field splitting.
General Super Exchange Hamiltonians

General superexchange Hamiltonians for magnetic and orbital physics in $e_g$ and $t_{2g}$ systems

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Material-specific super-exchange Hamiltonians are the key to studying spin and orbital physics in strongly correlated materials. Recently, via an irreducible-tensor operator representation, we derived the orbital superexchange Hamiltonian for $t_{2g}^1$ perovskites and successfully used it, in combination with many-body approaches, to explain orbital physics in these systems. Here, we generalize our method to $e_g^n$ and $t_{2g}^n$ systems at arbitrary integer filling $n$, including both spin and orbital interactions. The approach is suitable for numerical implementations based on \textit{ab initio} hopping parameters and realistic screened Coulomb interactions and allows for a systematic exploration of superexchange energy surfaces in a realistic context.

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II. FORMALISM

The superexchange Hamiltonian has the form:

\[ \hat{H}_{\text{SE}} = \frac{1}{2} \sum_{ij} \hat{H}_{ij}^{ij}, \]  

(1)

where \( i \) and \( j \) are neighboring sites coupled via hopping integrals. This Hamiltonian acts in the subspace of states with \( |n_i, n_j\rangle \), where \( n_i \) and \( n_j \) are the site occupations with the constraint \( n_i + n_j = N = 2n \), where \( n \) is the number of electrons per site. From strong-coupling second-order perturbation theory, Eq. (1) can be written as

\[ \hat{H}_{\text{SE}} = -\hat{H}_T (\hat{H}_U - E_0)^{-1} \hat{H}_T, \]

so that

\[ \hat{H}_{\text{SE}}^{ij} = -\hat{H}_T (\hat{P}_i + \hat{P}_j) \hat{H}_T. \]

Here, \( \hat{P}_j \) is an operator which projects, with an energy denominator, to atomic excited states of type \( |n_i + 1, n_j - 1\rangle \), and \( \hat{H}_T \) is the hopping part of the Hubbard Hamiltonian from which the superexchange interaction is derived, while \( \hat{H}_U \) is the electron-electron repulsion.

Let us start from the well-known case of magnetic exchange for the single-band Hubbard model:

\[ \hat{H} = -\sum_{\sigma} \sum_{i,j} t_{ij}^{\sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}, \]

(2)

where \( \hat{n}_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma} \), \( t_{ij}^{\sigma} \) is the hopping integral and \( U \) the screened Coulomb parameter. Since the atomic limit of the half-filled Hubbard Hamiltonian has only spin degrees of freedom, one can write the associated exchange Hamiltonian in an irreducible tensor basis as

\[ \hat{H}_{\text{SE}}^{ij} = \sum_{qq'} \sum_{vv'} \xi_{qq'}^{ij} D_{qq'}^{ij} \xi_{vv'}^{ij}, \]

(3)

where \( q = 0, 1 \) is the rank of the operators and \( v \) the associated components. For \( q = 0 \), the only component is \( v = s \), while for \( q = 1 \), we have instead \( v = x, y, z \) in the real harmonics representation. For convenience, we normalize the tensors such that

\[ \sum_{\alpha} \langle 0 | c_{\alpha s} \langle \hat{H}_T | c_{\alpha s} | 0 \rangle = 1. \]

(4)

With this convention, the irreducible tensors are

\[ \xi_{0s}^{0s} = \frac{1}{\sqrt{2}} \sum_{\alpha} c_{\alpha s} c_{\alpha s}, \]

(5)

\[ \xi_{s}^{s} = \frac{1}{\sqrt{2}} \sum_{\alpha s} c_{\alpha s}^\dagger [\hat{\sigma}_v | \alpha s \rangle \langle \alpha s | \hat{\sigma}_v^t], \]

(6)

where \( \hat{\sigma}_v \) is the \( v = x, y, z \) Pauli matrix. At half-filling \( (n_i = n_j = 1) \), we define the projectors as

\[ \hat{P}_i = \sum_{\alpha, \mu \nu} |\alpha_\mu\rangle \langle \alpha\nu | \hat{\sigma}_\mu \langle \alpha\mu | \hat{\sigma}_\nu | |\alpha\nu\rangle \]

(7)

where \( |\alpha\pm\rangle \) are atomic (site \( i \)) multiplets with \( n_i \pm 1 \) electrons, quantum number \( \alpha\pm \) and energy \( E_{\alpha\pm} \). In the case of the single-band Hubbard model, \( |\alpha_+\rangle \) and \( |\alpha_-\rangle \) are, respectively, the doubly occupied and the vacuum state; in general, however, \( \alpha_+ \) and \( \alpha_- \) will label several excited states with different energies. Here, \( E_0 \) is the energy of the ground state with \( N = n_i + n_j = 2 \) electrons in the atomic limit, here, \( E_0 = 0 \). The tensor elements in Eq. (3) are obtained using the orthogonality properties of irreducible tensors. To this end, we multiply by a pair of irreducible operators, one for site \( i \) and one for site \( j \), and trace over all states in the atomic ground multiplet. This yields

\[ D_{0s,0s}^{ij} = -\frac{\text{Tr} \left[ \xi_{0s}^{ij} \xi_{0s} \hat{H}_T (\hat{P}_i + \hat{P}_j) \hat{H}_T \right]}{\text{Tr} \left[ (\xi_{0s}^{ij})^2 \right]} \]

\[ = -2 \frac{|t_{ij}|^2}{U}, \]

and

\[ D_{v1,v1}^{ij} = -\frac{\text{Tr} \left[ \xi_{v1,v1}^{ij} \hat{H}_T (\hat{P}_i + \hat{P}_j) \hat{H}_T \right]}{\text{Tr} \left[ (\xi_{v1,v1}^{ij})^2 \right]} \]

\[ = 2 \frac{|t_{ij}|^2}{U} \delta_{v1,v1}. \]
irreducible tensor decomposition
\[ |\theta, \phi\rangle = -|\pi - \theta, \phi \pm \pi\rangle \]

\[ = \sin \theta \cos \phi |xz\rangle + \cos \theta |xy\rangle + \sin \theta \sin \phi |yz\rangle. \]
representation of orbital

\[ |\theta, \phi\rangle = - |\pi - \theta, \phi \pm \pi\rangle \]

\[ = \sin \theta \cos \phi |xz\rangle + \cos \theta |xy\rangle + \sin \theta \sin \phi |yz\rangle. \]
titanates: $T_{KK} \sim 300$ K

$|\theta, \phi\rangle = -|\pi - \theta, \phi \pm \pi\rangle$

$= \sin \theta \cos \phi |xz\rangle + \cos \theta |xy\rangle + \sin \theta \sin \phi |yz\rangle$. (58)
Crystal structure and magnetic properties of substances with orbital degeneracy

K. I. Kugel’ and D. I. Khomskii
P. N. Lebedev Physics Institute
(Submitted November 13, 1972)
Zh. Eksp. Teor. Fiz. 64, 1429-1439 (April 1973)

Exchange interaction in magnetic substances containing ions with orbital degeneracy is considered. It is shown that, among with spin ordering, superexchange also results in cooperative ordering of Jahn-Teller ion orbitals, which, generally speaking, occurs at a higher temperature and is accompanied by distortion of the lattice (which is a secondary effect here). Concrete studies are performed for substances with a perovskite structure (KCuF₃, LaMnO₃, MnF₃). The effective spin Hamiltonian is obtained for these substances and the properties of the ground state are investigated. The orbital and magnetic structures obtained in this way without taking into account interaction with the lattice are in accord with the structures observed experimentally. The approach employed also permits one to explain the strong anisotropy of the magnetic properties of these compounds and to obtain a reasonable estimate for the critical temperatures.

— Kugel-Khomskii systems — where are they?
The irreducible tensor decomposition

\[ \hat{H}_{SE}^{ij} = \sum_{rr'} \sum_{\mu \mu'} \hat{t}^{r,\mu}_{i} D_{r\mu,r'\mu'}^{ij} \hat{t}^{r',\mu'}_{j} \]

<table>
<thead>
<tr>
<th>( r, \mu )</th>
<th>( r', \mu' )</th>
<th>( t_{ix} )</th>
<th>( t_{iy} )</th>
<th>( D'_{r',r''} \times U/2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 s</td>
<td>0 s</td>
<td>( -W_b )</td>
<td>( -V_b )</td>
<td>( (t_{b,xx}^{e} + i t_{b,yy}^{e} + t_{b,zz}^{e}) )</td>
</tr>
<tr>
<td>0 s</td>
<td>1 z</td>
<td>( -W_1 )</td>
<td>( -V_1 )</td>
<td>( t_{b,xx}^{e} )</td>
</tr>
<tr>
<td>0 s</td>
<td>2 z</td>
<td>( -W_2 )</td>
<td>( -V_2 )</td>
<td>( t_{b,xx}^{e} )</td>
</tr>
<tr>
<td>1 z</td>
<td>1 z</td>
<td>( +W_1 )</td>
<td>( +V_1 )</td>
<td>( t_{b,xx}^{e} )</td>
</tr>
<tr>
<td>1 z</td>
<td>2 z</td>
<td>( +W_2 )</td>
<td>( +V_2 )</td>
<td>( t_{b,xx}^{e} )</td>
</tr>
<tr>
<td>2 z</td>
<td>3 z</td>
<td>( +W_2 )</td>
<td>( +V_2 )</td>
<td>( t_{b,xx}^{e} )</td>
</tr>
<tr>
<td>1 x</td>
<td>1 x</td>
<td>( +W_1 )</td>
<td>( +V_1 )</td>
<td>( t_{b,xx}^{e} )</td>
</tr>
<tr>
<td>2 x</td>
<td>2 x</td>
<td>( +W_2 )</td>
<td>( +V_2 )</td>
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<td>1 y</td>
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<tr>
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<td>( +W_2 )</td>
<td>( +V_2 )</td>
<td>( t_{b,xx}^{e} )</td>
</tr>
</tbody>
</table>

Where:
- \( W_0 = f_{-3} + \frac{1}{3} f_{-1} + \frac{1}{3} f_1 = \frac{-1+\sqrt{30}}{3} \)
- \( W_1 = \frac{1}{2} f_{-3} + \frac{1}{4} f_{-1} + \frac{1}{4} f_1 = \frac{1+\sqrt{30}}{4} \)
- \( W_2 = \frac{1}{2} f_{-3} - \frac{1}{4} f_{-1} - \frac{1}{4} f_1 = \frac{1-\sqrt{30}}{4} \)
- \( W_3 = \frac{1}{2} f_{-3} - \frac{1}{2} f_{-1} + \frac{1}{2} f_1 = \frac{-1+\sqrt{30}}{3} \)

\( t_{b,xx}^{e} = \frac{1}{2} f_{-3} - \frac{1}{2} f_{-1} - \frac{1}{2} f_1 \)
Superexchange Interaction in Orbitally Fluctuating $RVO_3$

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Changes in pressure and magnetic field in the orbital and magnetic ordering temperatures of $RVO_3$ perovskites are reported; they reveal a competition between two magnetic orbitally ordered phases that have opposite preferences for the $e$-orbital component in the localized $3T_{1g}$ ground state of the $V^{3+}$ ion. This competition is shown to be biased by the VO$_{6/2}$ site distortion intrinsic to the orthorhombic structure. A remarkable enhancement of $T_N$ with pressure is found where the competition leads to enhanced orbital critical fluctuations.

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Orbital Fluctuations in the Different Phases of LaVO₃ and YVO₃

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FIG. 1 (color). Temperature-dependent structural and magnetic phases of LaVO₃ and YVO₃. The lines show LDA + DMFT (quantum Monte Carlo [21]) results for the occupations, n, of the three t₂g crystal-field orbitals, 1, 2, and 3 (Table I). Black lines: orthorhombic phases. Green and blue lines: monoclinic phases. The occupations down the temperature at which the orbital...
what about vanadates?
LaVO$_3$ — similar to cubic!
we should find magnetic fluctuations.

shortening the bond length. This extra gain of $T_N$ under pressure is turned off sharply for the phase in $1.10\text{Å} < IR < 1.19 \text{Å}$. In order to identify the possible mechanism responsible for the extra gain of $T_N$, we will elaborate the pressure effect on the structure and the structural evolution versus $IR$ for these regions of $IR$. For $IR < 1.10 \text{Å}$, the orbitals undergo $G$-type ordering at $T_{OO}$ and an orbital-flipping transition to $C$-type ordering at $T_{CG}$. In both types of orbital ordering, the long axis of the octahedra alternates direction within the (001) planes; there are changes from out-of-phase in the type-$G$ to in-phase in type-$C$ orbital order along the $c$ axis and structural symmetry from $P2_1$ to $Pbnm$ [10,14]. Therefore, an abrupt volume change of the octahedra at $T_{CG}$ cannot be explained by a simple switching from the in-phase to the out-of-phase configuration. The octahedral-site volume in the $G_{OO}$ phase larger than that in the $C_{OO}$ phase obtained from the structural studies [10] suggests a larger percentage of $e$ orbital is present in the $3T_{1g}$ ground state in the $G_{OO}$ phase. More interestingly, the intrinsic component of the site distortion, which can be well-resolved in the orbitally disordered phase and in the $G_{OO}$ phase, disappears in the $C_{OO}$ phase of smaller volume where each VO$_{6/2}$ site has one long and two equally short V-O bonds. It is clear, therefore, that the orbital-flipping transition results from a competition between a spin-orbital interaction and the structural bias. Pressure favors the $C_{OO}$ phase since it has a smaller cell volume and a smaller octahedral-site distortion, which explains the giant pressure dependence of $T_{CG}$ in Fig. 2. As for the phase with $IR > 1.19 \text{Å}$, the orbital-ordering temperature $T_i$ to the $G_{OO}$ phase drops below $T_N$ [8,15]. It is important to note

FIG. 3 (color online). Top: the $IR$ dependence of the coefficient $d\ln T_N/dP$ for the RV0$_3$. $T_N$ is determined in the ZFC measurement. The solid symbol for LaVO$_{3}$ is obtained in the FC measurement. Middle: the $IR$ dependence of bulk modulus $B_0$ and the coefficient $ds/dP$ for the RV0$_3$. Bottom: the phase diagram of transition temperatures versus $IR$ for RV0$_3$, data from Ref. [8].
yes, $T_N > T_{KK}$!
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the first clear case: \( \text{LaVO}_3 \)

X.-J. Zhang, E. Koch and E. Pavarini, under review
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Institute for Advanced Simulation, Forschungszentrum Jülich

Juelich Supercomputing Centre
thank you!