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Competition of orbital, charge and spin degrees of freedom in Jahn-Teller magnets

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Jahn-Teller (JT) magnets are compounds based on Jahn-Teller 3*d*- and 4*d*-ions with the $t_{2g}^{n_1}e_g^{n_2}$ configurations in a highly symmetric surroundings and with a ground state orbital *E*-doublet which are characterized by competition of various electronic degrees of freedom and strong electron-lattice interaction. In this paper, we present a generalized model of effective charge triplets, which allows, within a unified approach and in the most general form, to take into account charge, spin, orbital and lattice degrees of freedom for so-called single-band JT-magnets such as rare-earth nickelates $RNiO_3$.

Keywords: Jahn-Teller magnets, charge triplet model, effective spin-pseudospin-orbital hamiltonian, electron-lattice interaction.

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1. Introduction

Jahn-Teller (JT) magnets include compounds based on Jahn-Teller 3*d*- and 4*d*-ions with $t_{2g}^{n_1}e_g^{n_2}$ type configurations in highly symmetric octahedral, cubic or tetrahedral environment and with ground orbital *E*-doublet [1–5]. These are compounds based on tetra complexes with the configuration d^1 (Ti^{3+}, V^{4+}, Cr^{5+}), low-spin (LS) configuration d^3 (V^{2+}, Cr^{3+}, Mn^{4+}), high-spin (HS) configuration d^6 (Fe^{2+}, Co^{3+}), octa complexes with HS configuration d^4 (Cr^{2+}, Mn^{3+}, Fe^{4+}, Ru^{4+}), LS configuration d^7 (Co^{2+}, Ni^{3+}, Pd^{3+}), as well as octa complexes with the configuration d^9 (Cu^{2+}, Ni^{1+}, Pd^{1+}, Ag^{2+}) [2–5] (see Table 1).

All JT configurations of *d*-ions include one e_g-electron or one e_g-hole over stable fully or half-filled shells. They are similar in this sense to the configurations of a large family of ions with one *ns*-electron over filled shells for example 6s-electron in Hg^+, Tl^{2+}, Pb^{3+}, Bi^{4+}. These ionic configurations are unstable with respect to the disproportionation reaction, or even non-existent (missing oxidation states [6]). For instance, bismuth in $BaBiO_3$ prefers stable valence states of Bi^{3+} and Bi^{5+} with completely filled shells instead of the nominal valence 4+. However, unlike ions with *ns*-electrons, for JT-ions we are dealing with orbital degeneracy for e_g-electrons/holes, which means that there is a possibility of competition between the Jahn-Teller effect resulting in the orbital ordering [1], and the anti-JT disproportionation effect resulting in the formation of a system of electron and hole centers of *S*-type with an orbitally non-degenerate ground state [2–5], equivalent to a system of effective composite spin-singlet or spin-triplet bosons in a non-magnetic, or a magnetic lattice (see Table 1).

The class of JT-magnets includes a large number of promising materials with competition of orbital, spin and charge degrees of freedom, which are in the focus of modern condensed matter physics such as manganites $RMnO_3$, ferrates $(Ca,Sr)FeO_3$, ruthenates RuO_2, $(Ca,Sr)RuO_3$, $(Ca,Sr)_2RuO_4$, a wide range of Fe-pnictides (FePn) and Fe-chalcogenides (FeCh), 3D nickelates $RNiO_3$, 3D cuprate $KCuF_3$, 2D cuprates (La_2CuO_4, ...) and nickelates $RNiO_2$, silver-based compounds (AgO, AgF_2), ruthenium-cuprates $RuSr_2GdCu_2O_8$... [1–5] (see Table 1). These materials have a rich range of unique properties from various types of orbital [1], spin, charge, and spin-charge ordering, unusual metallic behavior („strange, bad metal"), to metal-insulator transitions and „exotic" spin-triplet superconductivity [2–5]. A number of JT-magnets are either multiferroics ($RMnO_3$, CuO [7,8]), or are considered as promising multiferroics ($RNiO_3$ [9]).

The anti-JT disproportionation model predicts the spin-triplet superconductivity in ruthenates Sr_2RuO_4 and RuO_2, Fe-pnictides/chalcogenides FePn/FeCh, manganite $LaMnO_3$, although one or another spin-charge order is implemented in most known „candidates" ($Ca(Sr)FeO_3$, $RNiO_3$, AgO) [2–5]. In particular, the model assumes that superconducting carriers in FePn/FeCh compounds consist of e_g holes, and not of t_{2g} electrons [2–5,10], as predicted by the one-electron multi-orbital band model. The most optimal conditions for HTSC with spinless local bosons and spinless lattice can be achieved only for low-symmetry quasi-two-dimensional d^9-systems such as 2D cuprates and nickelates.

Table 1. Examples of Jahn-Teller $3d^n$- and $4d^n$-configurations and ions indicating local symmetry, the structure of the effective composite boson and the corresponding lattice formed as a result of the anti-Jahn-Teller disproportionation reaction. The last column contains examples of real JT-magnets

JT configuration JT-ions	Symm.	LS/HS	Composite boson	Lattice	Examples of compounds
$3d^1(e_g^1)$: ^2E Ti^{3+}, V^{4+}, Cr^{5+}	Tetra	–	e_g^2: $^3A_{2g}$ $s = 1$	A_{1g} $S = 0$	β-Sr_2VO_4 $(Sr,Ba)_3Cr_2O_8$
$3d^3(e_g^3)$: ^2E V^{2+}, Cr^{3+}, Mn^{4+}	Tetra	LS	$\underline{e}_g^2$: $^3A_{2g}$ $s = 1$	A_{1g} $S = 0$	$Ba_2VGe_2O_7$ (?)
$3d^4(t_{2g}^3e_g^1)$: ^5E Cr^{2+}, Mn^{3+}, Fe^{4+}	Octa	HS	e_g^2: $^3A_{2g}$ $s = 1$	A_{2g} $S = 3/2$	CrO, CrF_2 Sr_2FeO_4 $(Ca,Sr,Ba)FeO_3$ $(Ca,Sr,Ba)_3Fe_2O_7$ $RMnO_3$, $LaMn_7O_{12}$
$4d^4(t_{2g}^3e_g^1)$: ^5E Ru^{4+}	Octa	HS	e_g^2: $^3A_{2g}$ $s = 1$	A_{2g} $S = 3/2$	$(Ca,Sr)_2RuO_4$ $(Ca,Sr)RuO_3$, RuO_2 $(Ca,Sr)_3Ru_2O_7$
$3d^6(e_g^3t_{2g}^3)$: ^5E Fe^{2+}, Co^{3+}	Tetra	HS	$\underline{e}_g^2$: $^3A_{2g}$ $s = 1$	A_{1g} $S = 3/2$	FePn, FeCh, Na_5CoO_4
$3d^7(t_{2g}^6e_g^1)$: ^2E Co^{2+}, Ni^{3+}	Octa	LS	e_g^2: $^3A_{2g}$ $s = 1$	A_{1g} $S = 0$	$RNiO_3$ $(Li,Na,Ag)NiO_2$
$3d^9(t_{2g}^6e_g^3)$: ^2E Cu^{2+}, Ni^{+}	Octa	–	$\underline{e}_g^2$: $^3A_{2g}$ $s = 1$	A_{1g} $S = 0$	CuF_2, $KCuF_3$, K_2CuF_4
$4d^9(t_{2g}^6e_g^3)$: ^2E Pd^{+}, Ag^{2+}	Octa	–	$\underline{e}_g^2$: $^3A_{2g}$ $s = 1$	A_{1g} $S = 0$	AgO (Ag^1+$Ag^{3+}O_2$)
$3d^9(t_{2g}^6e_g^3)$: $^2B_{1g}$ Cu^{2+}, Ni^{+}	Octa* quadr	–	$\underline{b}_{1g}^2$: $^1A_{1g}$ $s = 0$	A_{1g} $S = 0$	HTSC cuprates CuO, $RNiO_2$
$4d^9(t_{2g}^6e_g^3)$: $^2B_{1g}$ Pd^{+}, Ag^{2+}	quadr	–	$\underline{b}_{1g}^2$: $^1A_{1g}$ $s = 0$	A_{1g} $S = 0$	AgF_2, $KAgF_3$ Cs_2AgF_4, $LaPdO_2$ (?)

Table 2. Pseudospin, spin and orbital structure of three charge centers NiO_6 in orthonikelates $RNiO_3$

d-center	Nominal	Cluster	Charge $\Sigma = 1$ pseudospin projection	Conventional spin	Orbital state
Electron (d^8)	Ni^{2+}	$[NiO_6]^{10-}$	$M_S = -1$	1	A_{2g}
Parent (d^7)	Ni^{3+}	$[NiO_6]^{9-}$	$M_S = 0$	1/2	E_g
Hole (d^6)	Ni^{4+}	$[NiO_6]^{8-}$	$M_S = +1$	0	A_{1g}

A model of charge triplets was proposed and developed in [11–20] to describe the electronic structure and phase diagrams of quasi-two-dimensional cuprates of $La_{2-x}Sr_xCuO_4$ type, within which it was possible to simulate complex phase diagrams of CuO_2-planes resulting from the competition of the fermi-metallic and antiferromagnetic dielectric states, charge ordering and spin-singlet bosonic superconductivity.

We present in this paper a generalized model of effective charge triplets, which allows taking into account in the most general way the competition of charge, spin, orbital and lattice degrees of freedom for the so-called single-band JT-magnets such as rare-earth nickelates $RNiO_3$ (R — rare earth or yttrium) [21].

2. Charge triplet model: $\Sigma = 1$ pseudospin formalism

The generalized model of effective charge triplets assumes consideration of some highly symmetric „parental“ configu-

ration of a JT-magnet of type $RNiO_3$ with ideal octahedra NiO_6, the low-energy state of which is formed by a charge triplet $[NiO_6]^{10-,9-,8-}$ (nominally $Ni^{2+,3+,4+}$) with different spin and orbital ground states (see Table 2). In accordance with Rice–Sneddon idea proposed to describe the three charge states of $Bi^{3+,4+,5+}$ in $BaBiO_3$ [22], and developed in Ref. [11–20] for HTSC cuprates, we associate three charge states of the cluster NiO_6 with three projections of pseudospin $\Sigma = 1$ and use well-known spin algebra to describe the charge degree of freedom.

First of all, it should be noted that formally the local pseudospin $\Sigma = 1$ assumes the presence of eight (three „dipole“ and five „quadrupole“) independent operators and corresponding local parameters of the charge order (in irreducible components):

$$\hat{\Sigma}_0 = \hat{\Sigma}_z; \quad \hat{\Sigma}_\pm = \mp\frac{1}{\sqrt{2}}(\hat{\Sigma}_x \pm i\hat{\Sigma}_y); \quad \hat{\Sigma}_z^2; \quad \hat{\Sigma}_\pm^2;$$

$$\hat{T}_\pm = \frac{1}{2}\{\hat{\Sigma}_z, \hat{\Sigma}_\pm\}. \tag{1}$$

Operators

$$\hat{P}_0 = (1 - \hat{\Sigma}_z^2); \quad \hat{P}_\pm = \frac{1}{2}\hat{\Sigma}_z(1 \pm \hat{\Sigma}_z) \tag{2}$$

actually are projection operators for charge states with a projection of pseudospin $M = 0, \pm 1$, respectively, and the mean values $\langle\hat{P}_0\rangle$, $\langle\hat{P}_\pm\rangle$ actually represent the local densities of the corresponding charge states.

The operators $\hat{\Sigma}_\pm$ and $\hat{T}_\pm$ change the projection of the pseudospin to ± 1. The operator $\hat{\Sigma}_\pm^2$ changes the projection of the pseudospin to ± 2, so that it can be considered as the operator of the creation/annihilation of a composite boson. The corresponding local averages $\langle\hat{\Sigma}_\pm\rangle$, $\langle\hat{T}_\pm\rangle$, $\langle\hat{\Sigma}_\pm^2\rangle$ will describe various variants of „off-diagonal“ charge order, in particular, coherent metallic and superconducting states.

Taking into account the spin and orbital states for the charge components, we should extend the local Hilbert space to the „pseudospin-orbital-spin octet“ $|1M;\Gamma\mu;Sm\rangle(|10;E_g\mu;\frac{1}{2}\nu\rangle;\ |1-1;A_{1g}0;1m\rangle;\ |1+1;A_{1g}0;00\rangle)$, where $\mu = 0;2$, $\nu = \pm\frac{1}{2}$, $m = 0;\pm 1$ ($|E_g0\rangle \propto d_{z^2}$, $|E_g2\rangle \propto d_{x^2-y^2}$) and consider JT-magnet in the general case as a system of such „octets“. This approach will allow taking into account the effects of competition of various degrees of freedom in the most general way.

3. Effective Hamiltonian of JT-magnets: „atomic“ limit

We neglect the effects of one- and two-particle charge transfer in the simplest „atomic“ limit, so that the effective Hamiltonian of the JT-magnet will have the the form as follows

$$\hat{H}_{at} = \hat{H}_{ch} + \hat{H}_{el-lat} + H_{lat} + \hat{H}_{spin}^{\text{eff}}, \tag{3}$$

where

$$\hat{H}_{ch} = \Delta\sum_i \hat{\Sigma}_{iz}^2 + \sum_{i>j} V_{ij}\hat{\Sigma}_{iz}\hat{\Sigma}_{jz} - \mu\sum_i \hat{\Sigma}_{iz} \tag{4}$$

is the effective Hamiltonian of charge interactions (local and nonlocal correlations), μ — chemical potential determined from the condition of constancy of quantity $\sum_i\langle\hat{\Sigma}_{iz}\rangle$, in particular the condition of electroneutrality. The quantity and sign of the parameter $\Delta = \frac{1}{2}U$, where U is an effective parameter of local correlations, are of fundamental importance for JT-magnet. Large positive values of U make disproportionation energetically unfavourable and stabilize the JT center, leading to local/cooperative JT ordering with orbital order (OO) and, as a rule, to the state of a magnetic insulator. Large negative values of U (negative–U model) make anti-JT disproportionation energetically advantageous, resulting in the formation of a system of electronic and hole centers with a wide range of possible phase states.

The effective Hamiltonian of the linear electron-lattice interaction includes two fundamentally important contributions for charge states with a projection of pseudospin $M = 0$, i. e. for the JT center, and $M = \pm 1$, that is, for the electron/hole centers, respectively

$$H_{el-lat} = V_E\sum_i \hat{P}_0(\hat{v}_i^E Q_i^E)\hat{P}_0 + a\sum_i(\hat{\Sigma}_{iz}^2 + \lambda\hat{\Sigma}_{iz})Q_i^{A_{1g}}, \tag{5}$$

where the first term is the Jahn-Teller contribution of interaction with the local mode of displacements Q^E ($Q^{E0} \propto d_{z^2}$, $Q^{E2} \propto d_{x^2-y^2}$), V_E — the constant of the JT interaction, and the matrices $\hat{v}^{E0}$, $\hat{v}^{E2}$ on the basis of states $|E_g0\rangle$ and $|E_g2\rangle$ coincide with the Pauli matrices $\hat{\sigma}_z$ and $\hat{\sigma}_x$, respectively [1]. The second term in (5) is interaction with the local full-symmetric (breathing) displacement mode for charge states with a projection of pseudospin $M = \pm 1$, a and λ are constants of the electron-lattice interaction. It is the interaction with the local full-symmetric mode that makes it possible to explain both the mechanism and the features of the metal-insulator transition in orthonickelates $RNiO_3$ [23]. Naturally, taking into account electron-lattice interaction requires inclusion of the elastic energy into the Hamiltonian of the JT-magnet

$$H_{lat} = \frac{1}{2}\sum_{i\Gamma v} K_\Gamma(Q_i^{\Gamma v})^2 + \ldots, \tag{6}$$

where we identified only a local contribution. Obviously, the JT stabilization energy [1]

$$E_{JT} = \frac{V_E^2}{2K_E} \tag{7}$$

is the most important energy factor in stabilizing the JT center in the lattice.

In general, the effective spin-Hamiltonian of a JT-magnet has a complex structure. Many features of the spin interactions of the JT centers are considered in the well-known

paper of Kugel and Khomskii [1]. Below we will consider the contribution to the effective spin-Hamiltonian of the $RNiO_3$ JT-magnet of the $[NiO_6]^{10-}$ (nominally Ni^{2+}) charge spin-triplet states corresponding to the $M = -1$ component of the charge pseudospin, which can be represented as follows

$$\hat{H}^{\text{eff}}_{spin} = \hat{P}_{-1}\hat{H}_{spin}\hat{P}_{-1}, \tag{8}$$

where $\hat{P}_{-1}$ is the corresponding projection operator, and spin-Hamiltonian

$$\hat{H}_{spin} = V_{md} + \sum_{i>j} J_{ij}(\hat{\mathbf{S}}_i\hat{\mathbf{S}}_j) + \sum_{i>j} j_{ij}(\hat{\mathbf{S}}_i\hat{\mathbf{S}}_j)^2 + K\sum_i(\mathbf{m}_i\hat{\mathbf{S}}_i)(\mathbf{n}_i\hat{\mathbf{S}}_i) - \sum_i(\mathbf{h}\hat{\mathbf{S}}_i) \tag{9}$$

includes typical terms, V_{md} is magnetodipole interaction, J_{ij} and j_{ij} are integrals of bilinear and biquadratic isotropic exchange, respectively, K is constant of single-ion anisotropy, and $\mathbf{m}$ and $\mathbf{n}$ are unit vectors defining in the general case two characteristic axes of second-order single-ion anisotropy, $\mathbf{h}$ — external field [3–5].

In general, the effective Hamiltonian of the model of charge triplets (3)–(9) can serve as the basis for both quantum mechanical and classical descriptions of orthonickelate type JT-magnets using methods typical of traditional spin-magnetic systems, in particular, the theory of the effective field [16,17].

4. Conclusion

We proposed a generalized model of effective charge triplets to describe the electronic structure of single-band JT-magnets of the type of rare earth nickelates $RNiO_3$ in which the NiO sublattice is considered as a system of „pseudospin-orbital-spin octets“. The effective Hamiltonian of the model can serve as the basis for both quantum mechanical and classical descriptions of low-energy states and phase diagrams of JT-magnets within the framework of a unified approach that takes into account charge, spin, orbital and lattice degrees of freedom in the most general form.

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Conflict of interest

The author declares that he has no conflict of interest.

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